Trace metals and soil solids: effects of soil heterogeneity on Zn mobility

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Abstract

Trace metal contamination in soils is a global problem, often causing plant and microbial toxicity and leading to diminished crop production or decreased land cover and subsequent land degradation. In soils, the majority of trace metal contaminants such as Zn are associated with solid phase materials. This can be through cation exchange sites, surface adsorption and/or mineral (co-) precipitation. The specific forms or speciation of metals in soils determines both their bioavailability to plants and microorganisms and their mobility within and out of soils.

In this experiment, we used five contaminated field soils with a variety of sources and Zn:Cd ratios. Bulk soil Zn concentrations ranged from 112 mg/kg up to 26,237 mg/kg with Cd:Zn ratios between 0.05 and 0.003. Each soil was separated using sodium polytungstate, a variable density liquid, into fractions with density less than 1.6 g/mL (light fraction), between 1.6 g/mL and 2.8 g/mL (medium fraction), and greater than 2.8 g/mL (heavy fraction). It is expected that the light fraction contains organic matter, the medium fraction contains aluminosilicate primary and secondary minerals, and the heavy fraction contains high density minerals such as Fe and Mn oxides and their coprecipitates. Each fraction was analysed using µ-XRF, µ-XRD, and µ-XANES to determine the Zn solid phase forms in the natural soils.

The majority of the Zn in four of the five soils resided in the light fraction, though the smelting contaminated soil contained roughly equal light and heavy fraction Zn. A substantial portion of Zn was also present in the medium and heavy fractions of all soils, indicating the transfer of large quantities of Zn between different fractions, regardless of the initial Zn form applied. Based on XANES analysis, the light and heavy fractions from the different soils contain Zn in different chemical environments. Elemental distributions indicated Zn co-location with Fe and/or Mn in heavy fractions, while light fractions often contained Zn co-located with Ca and K as well as Fe and occasionally Mn. µ-XRD data for all soils will also be analysed to confirm differences in mineralogy between fractions and to link with Zn chemical forms.

Soil solids retain substantial portions of toxic trace metals, maintaining the metals within the soil profile and potentially limiting leaching losses to ground and surface waters. Regardless of the initial form, large amounts of the metals are able to transfer between density fractions (e.g. organic matter associated to aluminosilicate associated), indicating that the metals can still be quite mobile among fractions, perhaps impacting their bioavailability as well as their potential for loss via leaching.

Kinetics of Ca-Na ion exchange, induced by CO_2-driven acid dissolution of carbonate minerals

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During carbon dioxide sequestration in deep geological formations, injected CO_2 will dissolve into the formation water, thus lowering the pH and promoting dissolution of carbonate minerals, e.g. calcite and dolomite. The Ca^{2+} and Mg^{2+} ions from these minerals may stay in solution until eventually reprecipitated as carbonates, but the increased concentrations might also trigger ion-exchange reactions if any clays capable of ion-exchange (e.g. smectites) are present (c.f. [1]). Our knowledge of the kinetics of such ion-exchange reactions is limited, and it is unclear how protons are involved, if at all.

To study the kinetics of the Ca-Na ion-exchange, and the role of protons in the exchange, we have constructed a vessel that allows us to react carbonate minerals and clays in a CO_2-environment at elevated temperature and pressure. pH is continuously monitored, while the concentrations of dissolved ions are determined from fluid samples withdrawn periodically.

The results from two calcite-montmorillonite experiments in different ionic media are presented in Figure 1. In both experiments, calcite dissolution occurred in days, causing rapid increase of calcium in solution. A slow decrease of calcium over the next 2 weeks is attributed to ion exchange, and analysis of the clay fraction at the end of the experiment confirmed a significant increase in Ca. The role of protons is however not clear.

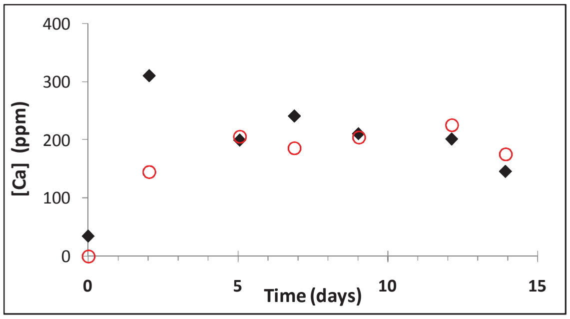

Figure 1: Measured Ca-concentration vs time, in experiments where calcite and Na-montmorillonite were reacted at 70°C and 80 bar CO_2. Filled diamonds: 0.01 M NaCl medium, open circles: 1.0 M NaCl medium.

Our results confirm that the first effect of increased acidity due to CO_2 injection will be dissolution of carbonates in host sediments, but clay minerals are likely to further modify pore water chemistry by ion exchange on the time scale of an injection cycle. This has implications for subsequent precipitation and modification of permeability.

[1] Assyag et al. (2009) *Chemical Geology* **265**, 227-235.