



## Formation and properties of inorganic Si-contaminant compounds

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Contamination of soil with inorganic contaminants such as lead (Pb), copper (Cu) and cadmium (Cd) is a major environmental issue, especially concerning food and groundwater security. Various studies demonstrate positive effects of Si regarding resilience of some crops towards these inorganic contaminants. One reason could be a complexation reaction of Si and the metal cations. However, this process has not yet been systematically investigated. Thus, our research contributes to reducing the mobility of Cd, Cu and Pb in contaminated soils and to decreasing their transfer into aquifers or plants.

The main goal of this study is to elucidate the extent and the mechanisms of the interactions between  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  and silicic acid, including the long-term kinetics, and to investigate whether the metals are bound by silicic acid. In order to understand these processes a series of precipitation experiments was performed in aqueous solution at room temperature.

Tetraethoxysilane (TEOS) as Si source and  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2$  with an initial concentration of  $10 \text{ mmol l}^{-1}$  were used for synthesis. Selectivity of Si towards the metals was tested in an equimolar solution of all three salts and TEOS. Time-dependency of particle growth was examined at sixteen different dates using dynamic light scattering (DLS) and transmission electron microscopy (TEM). The Si and metal concentration in the dialyzed aliquots were measured using microwave plasma-atomic emission spectroscopy (MP-AES). Spectroscopic analysis of the dialyzed and freeze dried solid phase, was performed using FTIR and  $^{29}\text{Si}$ -NMR spectroscopy.

DLS and TEM analyses showed that the metals had a positive effect on the polymerization reaction of silicic acid [ $\text{Cu}^{2+} > (\text{Cu}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}) > \text{Cd}^{2+} > \text{Pb}^{2+}$ ]. Initial formation of nanoparticles through homogenous nucleation was followed by particle growth. Particle growth of the control synthesis (TEOS in aqueous solution) stopped after 124 days at a size of 34 nm (Z-Average). Particles in the syntheses with the metals kept growing until the experiment was completed after 211 days reaching a final size of 260 nm for Cu-, 96 nm for Pb- and 196 nm for the Cd-variant. Final concentrations of up to  $15 \mu\text{mol l}^{-1}$  of Cu,  $10 \mu\text{mol l}^{-1}$  of Pb and  $13 \mu\text{mol l}^{-1}$  of Cd remained in the dialyzed aliquots. The Si concentrations in these aliquots increased continuously until an equilibrium was reached after 112 days at different concentrations (Cu:  $7.3 \text{ mmol l}^{-1}$ , Pb:  $6.9 \text{ mmol l}^{-1}$ , Cd:  $4.8 \text{ mmol l}^{-1}$ ). The FTIR spectra showed a shift of the Si-O stretching vibration by 10 to  $32 \text{ cm}^{-1}$  towards lower wavenumbers, which could indicate an incorporation of the metals in the polymeric network of the silicic acid. The  $^{29}\text{Si}$ -NMR relaxation experiments will show if and how Cu is incorporated. That will be the first analysis to show such structural incorporation of Cu, which might reduce the transfer of Cu into plants and aquifers.