Heterogeneous Lead Phosphate Nucleation at Organic-Water Interfaces: Implications for Lead Immobilization

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Lead contamination is ubiquitous in soil and aquatic environments, where phosphate addition is recognized as one of the most effective methods to immobilize Pb. After phosphate addition, lead phosphate particles with extremely low solublity can form. Organic coatings on soils, which affect heterogeneous lead phosphate nucleation, can impact the effectiveness of lead immobilization.

Here, SiO_2 surfaces were coated with silanol self-assembled thin films terminated with -COOH and -OH functional groups to act as model organic coatings on soil particles. Using grazing incidence small-angle X-ray scattering (GISAXS), heterogeneous lead phosphate nucleation on coatings was measured from mixed $Pb(NO_3)_2$ and Na_2HPO_4/NaH_2PO_4. solutions at pH 7 with varied ionic strengths (IS = 0.58, 4, and 11 mM). Raman spectroscopy identified the homogeneous precipitates in solution as hydroxylpyromorphite ($Pb_5(PO_4)_3OH$). The smallest lead phosphate nuclei (4.5 ± 0.5 nm) were observed on –COOH coatings, which resulted from the highest level of lead and phosphate ion adsorption on –COOH coatings. The attraction of lead and phosphate ions, possibly lead phosphate pre-nucleation clusters (PNCs), increased the local saturation index (SI) of lead phosphate near –COOH substrates, which resulted in smallest nuclei sizes. The IS of the solution also affected the sizes of the heterogeneous precipitates on –COOH coating, with smaller nuclei (1.3 ± 0.4 nm) forming under higher IS (4 and 11 mM). This study provided new fundamental knowledge of the molecular-level interfacial processes controlling heterogeneous lead phosphate nucleation, which can help predict the fate and transport of toxic Pb in contaminated soils.