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Lability of adsorbed Pb(II) at metal oxide surfaces: kinetics of surface atom exchange

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The dynamics of lead (Pb) at mineral surfaces affect its mobility and bioavailability in the environment. Pb(II) forms inner- and outer-sphere complexes on mineral surfaces, and this adsorbed pool often represents a large portion of the bioavailable Pb in contaminated soils. To assess the lability of this potentially reactive adsorbed Pb(II) pool on metal oxide surfaces, we performed isotope exchange measurements at pH 5, 6, and 7. Natural isotopic abundance Pb(II) was equilibrated with rutile or goethite, and the total dissolved Pb concentration was measured after steady-state was reached. A spike containing the same total dissolved Pb concentration but enriched in ^{207}Pb was added to the reactor. The evolution of the Pb isotope ratios was then measured with time. We collected Pb L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra and zeta–potential measurements to investigate whether the kinetics of exchange could be influenced by a change in coordination environment or particle aggregation.

We find that almost all adsorbed lead is exchangeable, with up to 90% exchanged in less than 1 hour. An initially fast Pb(II) exchange (<1 hour) is followed by slower exchange that occurs on a timescale of hours to days. The fraction of exchange occurring by the faster process increases with increasing pH. The half-life of exchange by fast and slow processes decreases from ~5 hours at pH 5 to ~1 minute at pH 7. Pb L_{III}-edge EXAFS spectra indicate that similar binding mechanisms are present at all pH values and Pb(II) loadings, implying that differences in exchange rates across the pH range examined are not attributable to changes in the coordination environment. The slower exchange at pH 5 may be associated with rutile aggregation and slower diffusion into the pores of these aggregates. This finding suggests that particle aggregation and morphology may have an important control on the lability and bioavailability of adsorbed metals. The rapid exchange observed on rutile and goethite indicates that adsorbed Pb(II) may be highly bioavailable at circumneutral pH. Additionally, isotope ratios of surface-bound Pb may be transient and rapidly respond to the introduction of new Pb sources into soils or sediments.