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Modelling pH effect on competitive adsorption of Pb and Cd on soils


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Introduction

The bioavailability and fate of heavy metals in the environment are controlled by sorption reactions on the reactive surfaces of the soil. Surface complexation models (SCM) have been used as an equilibrium-based approach to describe and predict metal cation sorption reactions on a variety of soil reactive phases such as oxide and clay minerals surfaces.

We have developed a non-electrostatic SCM with a combination of surface complexation and cation exchange reactions to describe the sorption of Pb and Cd as function of pH in three soils from Central Spain differing in physical-chemical and mineralogical properties. For this purpose, based on the component additivity approach we have formulated our sorption model as an idealized soil comprised of different reactive mineral phases. Lastly, we assess the different sorption behaviour of both metals as affected by their simultaneous presence and identify possible competitive sorption processes in the soils.

Materials and Methods

Metal retention as a function of pH in three soils, classified as Plinthic Palexerult, Arenic Pachic Palexerul and Vertic Haploxerert was elucidated through an experimental procedure designed to cover several sources of variability, i.e. three soils, six pH values, and five initial metal concentrations. Experiments were done in a full factorial scheme with two repetitions for two metals, both in single- (Pb or Cd) and binary-metal (Pb + Cd) systems.

The complex heterogeneity of surface reactivity in the three different soils is reduced to four different reactive surfaces sites, including surface hydroxyl functional groups on Al and Fe oxide phases and on phyllosilicate edges, and cation exchange positions on siloxane surfaces of clays. The initial values of the adjustable model parameters (equilibrium constants for surface complexation reactions and ion exchange reactions, and surface reactive site concentration) were obtained from spectroscopic and equilibrium-based sorption studies found in the literature, as well as from geometrical estimations on the basis of SEM observations of the soil samples.

All model simulations were carried out using the computer code PHREEQC v.2 in combination with the parameter optimization program PEST.

Results and Conclusions

Common to all soil materials and initial metal concentrations, modeling results show that the Pb and Cd adsorption distributes between ionic exchanges sites at low pH values and specific sites at higher pH values. From pH 3 to 6, Pb sorbs mainly through the formation of bidentate complexes on the specific sorption sites in the three soils. The Pb distribution is related to the affinity of the specific site for Pb, which increased in the order iron oxides >> clay edges (>SOH) > aluminum oxide (>A1OH) in all of the soils. Our results confirm the greater tendency for Cd to be retained on exchange positions than Pb. In addition, Pb retention in single-metal systems on specific sites occurred at lower pH values than in the case of Cd, suggesting that adsorption of Pb involves reaction with surface hydroxyl groups at pH values where Cd interacts only with exchange sites.

Results from the binary-metal system show that the total fraction of Pb retained on specific sites is not affected strongly by the presence of Cd. However, the sorption tendency of Cd is greatly modified in the three soils when Pb is present by displacing sorbed Cd from specific sites to ionic exchange sites. This competitive sorption process leading to an increased sorption of Cd on non-specific sorption sites becomes more evident at those conditions for which Cd retention in specific sites is predicted, i.e. at high pH values and low initial metal concentration in all soils. This analysis suggests that studies of contaminant metals in real systems need to consider competition between metals for sorption sites over a range of pH and soil types in order to accurately predict contaminant mobility.