Determination of Surface Heterogeneity and Enthalpies of Ca-K And Pb-K Systems in Tropical Soil Using Flow Adsorption Calorimetry

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1. Introduction

Sorption reactions of Ca, Cd, and Pb dictate the extent to which these metals will be labile in the soil environment (Naidu et al., 1998). Therefore, the ability to directly monitor the energetics of sorption reactions involving these metals would provide vital information concerning the mechanisms of sorption as well as other chemical processes occurring. Flow adsorption calorimetry provides a direct and quantitative measure of the heat (enthalpy) evolved during a reaction and was used in this study to measure the energetics of reactions of Ca, Cd, and Pb occurring at the liquid/solid interface.

2. Materials and Methods

Solutions of $Ca(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ at concentrations ranging from 0 to 5 mM made up to an ionic strength of 15 mM with KNO_3 were placed in the flow stream of a flow adsorption calorimeter containing about 50 mg of an Oxisol or an Ultisol from Puerto Rico. The surface heterogeneity of the soils, in regards to the energetics of sorption, was then determined by increasing the concentration of the counterion (Ca, Cd, or Pb) in the flow stream and measuring the incremental increases in the heat of exchange. Specifically, soils were initially equilibrated with 15 mM KNO_3. Solutions containing 1 mM $Ca(NO_3)_2$ + 12 mM KNO_3 were then introduced to the flow stream and the enthalpy associated with the replacement of K by Ca was determined. After completion of the reaction, a solution containing 2 mM $Ca(NO_3)_2$ + 9 mM KNO_3 was introduced to the flow stream and the process was repeated. The concentration of Ca was incrementally increased, at the expense of K, until the final solution concentration of 5 mM $Ca(NO_3)_2$ was added to the flow stream and the system equilibrated. The process was repeated beginning with 5 mM $Ca(NO_3)_2$ and stepping the concentration of K. The same experiments were performed where Cd and Pb were added in the place of Ca.

3. Results and Discussion

The sorption of the divalent metal ions (Ca, Cd, and Pb) was endothermic when these metals replaced K from exchange sites. However, the amount of heat required to drive these reactions varied depending on the cation involved. Lead was the most energetic followed by Cd then Ca. Furthermore, our data indicated that Cd and Pb were adsorbed as inner-sphere complexes as well as at exchange sites and that the irreversible sorption of both these metals was endothermic. The chemisorption of Cd and Pb occurred at most of the concentration steps demonstrating that our soils were able to retain large quantities of these metals at high affinity sites. Contrarily, the Ca was only sorbed at exchange sites.

Our preliminary results looking at the surface heterogeneity of the soils' sorption sites, indicated that Ca competed strongly with K for exchange sites. Furthermore, we have evidence that in the Ca-K system, the energy associated with the sorption of Ca exceeds its contribution in total solution charge. For example, Ca represents 14 % of the total solution charge of the 1 mM $Ca(NO_3)_2$ + 12 mM KNO_3 solution, however, the sorption of this metal (when the above solution is placed in the flow stream) on the K-saturated Ultisol required about 27 % of the heat compared to when the 5 mM $Ca(NO_3)_2$ is placed in the flow stream.

4. Conclusions

Flow adsorption calorimetry proved its usefulness in ascertaining the heats associated with several chemical processes occurring at the solid/liquid interface. The adsorption of Ca, Cd, and Pb on K-saturated soils was endothermic with the magnitude of the endotherm varying with metal type. Furthermore, Pb and Cd (to a lesser extent) were shown to form inner-sphere surface complexes with the reaction requiring heat (endothermic process). Our results also indicated that in the Ca-K system, Ca strongly competes with K for exchange sites even when this metal is present in low concentrations relative to K (i.e. 14 % of the solution charge in the 1 mM $Ca(NO_3)_2$ + 12 mM KNO_3 solution).

References
Naidu, R., M.E. Sumner, and R.D. Harter. 1998. Sorption of heavy metals in strongly weathered soils: An overview. J. Environ. Geochem. Health 20:5-9.