



## **Free energy of cadmium, copper, nickel and zinc adsorption reaction in variable charge soils**

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Soils can be contaminated by many human actions including discharge of heavy metals at the soil surface, through disposal of city wastes, sewage sludge and pesticide application, or the subsurface releases from landfills. Both, the persistency and the mobility of contaminants are largely determined by the extent of its retention by soil particles, and the evaluation of the free energy ( $\Delta G$ ) of metal adsorption is a measurement of the reaction strength. Free energy of heavy metals adsorption reaction, calculated from the thermodynamic molar relationship  $\Delta G = RT (\log \text{metal in equilibrium solution} - \log \text{metal added})$ , was studied in surface and subsurface samples to an alfisol [Rhodic Kandiudalf (RK)] and to a highly weathered oxisols [Anionic "Rhodic" Acrudox (AR); Anionic "Xanthic" Acrudox (AX)] of the State of São Paulo, Brazil. As the pH and the ionic strength are important environmental factors influencing the solution chemistry of heavy metals in variable charge systems, adsorption envelopes were elaborated by reacting the soil samples with individual aqueous solutions of 0.01, 0.1 and 1.0 mol L<sup>-1</sup> Ca(NO<sub>3</sub>)<sub>2</sub> containing nitrate salts of the adsorptive heavy metal (Cd, Cu, Ni and Zn) at the initial concentration of 5 mg L<sup>-1</sup>, with an increasing pH value from 3.0 to 8.0. The negative values of  $\Delta G$  confirm the feasibility of the process and the spontaneous nature of metals ions adsorption. Independently of the sampling depth, metals adsorption and the free energy of the reaction increased with the pH increasing. The alfisol showed higher  $\Delta G$  values than the oxisols, mainly in surface horizons. At a same pH, Cu showed the highest  $\Delta G$  values, indicating higher affinity than other metals. Additionally, the highest  $\Delta G$  values for Cu adsorption were reached at a smaller pH value than Cd, Ni and Zn, indicating that Cu retention can preferentially occurs. In general, surface horizons show higher  $\Delta G$  values, probably

due to the effect of organic matter. However, subsurface samples exhibited high  $\Delta G$  values for Cu adsorption, probably due to formation of inner-sphere complex with the iron oxides surfaces. Commonly, the relative affinity of a soil for a metal cation increases with the tendency of the cation to form inner-sphere surface complexes. This tendency was confirmed when the free energy for Cu adsorption was not affected by the ionic strength. Free energy values for Cd, Ni and Zn adsorption decreased as the ionic strength increased, because of the weak electrostatic bonding mechanisms involved in the formation of outer-sphere complex between these metal ions and the soil adsorbents.