

## Surface complexation modeling of the sorption of Zn(II) by montmorillonite

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### Abstract

Adsorption of Zn(II) to montmorillonite samples K<sup>+</sup>-Wyoming (SWy-K), Ca<sup>2+</sup>-Texas (STx-Ca) and K<sup>+</sup>-Texas (STx-K) was studied at 25 °C in the presence of 10 mM KNO<sub>3</sub> for SWy-K and STx-K or 3.3 mM Ca(NO<sub>3</sub>)<sub>2</sub> for STx-Ca. X-ray diffraction measurements showed no change in the interlayer spacing of the montmorillonite samples on adsorption of zinc. Data from adsorption edges, adsorption isotherms, and potentiometric titrations were fitted by an extended constant capacitance surface complexation model (ECCM) which included two dominant sorption reactions: cation exchange at permanent negatively charged sites on the siloxane faces including interlayer regions of montmorillonite, and inner-sphere surface complex formation at variable-charge surface hydroxyl groups on the edges. At pH values above 9 the fit of the model to the data was less satisfactory, most probably because of surface precipitation. Generally the best fit parameters of the ECCM for the three samples agreed well. The exception was the concentration of permanent-charge sites, which was about four times greater for the Wyoming sample.

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### 1. Introduction

The abundance and availability of metal ions determines the fate of many cropping systems. Since the availability, mobility, and transport of micro nutrients in soil systems depend on adsorption–desorption reactions, it is important that we understand these surface processes. Because of their abundance in soil systems, and their high specific surface area and exchange capacity, clay minerals such as montmorillonite play a significant role in determining the availability and transport of metal species in soils and sediments.

Adsorption of metal ions onto clay minerals appears to involve two distinct mechanisms [1–5]: (i) an ion exchange reaction at permanent-charge sites, and (ii) formation of complexes with the surface hydroxyl groups. For

example, in a study of Cu(II) adsorption onto montmorillonite from a solution with 0.10 M Ca(ClO<sub>4</sub>)<sub>2</sub> as background electrolyte, Stadler and Schindler [5] suggested that in the range 3 < pH < 5 Cu sorbs in the interlayer of montmorillonite through ion exchange, while at pH > 5 the Cu forms surface complexes with aluminol groups at the edges of the crystals.

Cation exchange has been found to be an important sorption mechanism for many clay minerals [1–13], with a number of studies suggesting that exchange sites are responsible for cation uptake at low pH. This assertion is based on the following experimental evidence: (i) cations are sorbed by clays at lower pH than by the oxides of Fe, Al and Si, (ii) the uptake of metal ions at these low pH values is strongly influenced by ionic strength, and (iii) sorption does not involve significant displacement of protons, a feature of metal ion uptake by oxides. Cation exchange sites for swelling clays such as montmorillonite exist not only on external faces, but also within the interlayer regions. In some instances intercalation

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