

## Mn(II) and Cd(II) sorption to synthetic montmorillonite

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Redox variable environments such as riparian floodplain soils, wetlands, and rice paddies are of great importance in the mobilization of trace elements from terrestrial environments into aquatic systems. Elevated dissolved concentrations of trace elements in terrestrial and aquatic systems are of concern since they can cause detrimental effects on the biosphere due to toxic responses in plants (e.g. Mn, Zn, Cu) as well as in animals and humans (e.g. Cd, Pb). Both natural sources (e.g., presence of trace metal-enriched minerals) and anthropogenic sources (e.g., agriculture, industrial and mining activities) can lead to local enrichments of trace elements in the environment. During periods of water-saturation, high concentrations of dissolved  $\text{Mn}^{2+}$  are observed in redox variable environments as a result of the reductive dissolution of Mn(IV,III)-(oxyhydr)oxides. Consequently, the high concentrations of  $\text{Mn}^{2+}$  are expected to compete with trace elements cations (e.g.  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ) for adsorption to mineral surfaces and therefore influence their fate in the environment. Herein, the mobility and the bioavailability of trace elements in soils is mainly controlled by surface adsorption to soil solids including clay minerals, oxides of iron, manganese and aluminium, as well as natural organic matter. Clay minerals are widespread in soils and are among the most important sorbents for trace elements due to their large specific surface area, negative surface charge and reactive surface hydroxyl groups.

To date, it is not well known how and to which extent the sorption of  $\text{Mn}^{2+}$  to clay minerals surfaces influences the retention of other trace elements under reducing conditions. To investigate this, we first performed single metal sorption experiments under anoxic conditions ( $\text{O}_2 < 0.1$  ppm) using a synthetic iron-free montmorillonite (Syn-1) to elucidate the sorption of  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  at the clay mineral-water interface as function of pH (4-10), total metal concentration (0.001-1 mM) and  $\text{CaCl}_2$  background electrolyte concentration (0.1-30 mM).

The sorption of  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  to Syn-1 as function of the dissolved metal concentration (sorption isotherm) and pH (sorption edge) are shown in Figure 1. An increase of  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  sorption was observed with increasing metal concentration in solution (1a, c) and pH (1b, d) due to proton-metal cation competition for binding sites. In the sorption isotherm data (1a, c), a sorption maximum was not observed for either cation indicating that the sorption sites had not been saturated with respect to  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$ , respectively. This also applies to the data on pH-dependent sorption (1b, d) considering the chosen total metal concentrations. However, noted that the amount  $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$  sorbed at pH 7.8

and 7.4 respectively, clearly exceed the CEC of Syn-1 ( $\sim 0.07$  mol/kg), indicating an additional sorption mechanism through surface complexation. The pronounced effect of Ca on Mn and Cd sorption at  $\text{pH} \leq 5.5$  and the virtual absence of a pH-dependence at  $\text{pH}$  below 5 and  $[\text{Ca}] \geq 1$  mM indicate the binding to permanently negatively charged surfaces sites dominated the sorption of Mn and Cd under these conditions (Fig 1b, d). The clear influence of Ca on the pH-dependent sorption of Mn and Cd at  $\text{pH}$  6–9 (Fig 1b, d) further suggests that outer-sphere surface complexation to negatively charged edge surfaces sites of Syn-1 significantly contributed to Mn and Cd sorption at circumneutral to alkaline conditions. The absence of Ca-independence in Mn and Cd sorption data at trace levels of dissolved Mn and Cd implies that inner-sphere surface complexation to edge surface sites is marginal even at low concentrations. The quantitative similarity of Mn and Cd sorption at 0.1 mM Ca in both sorption isotherm data (Fig 1a, c) and pH-dependent data (Fig 1b, d) indicates that elevated levels of dissolved Mn, as observed in water-saturated terrestrial environments, may very effectively compete with Cd bound to clay minerals. As a consequence, increased Mn concentrations may trigger Cd release from clay surfaces and increase Cd mobility and bioavailability.

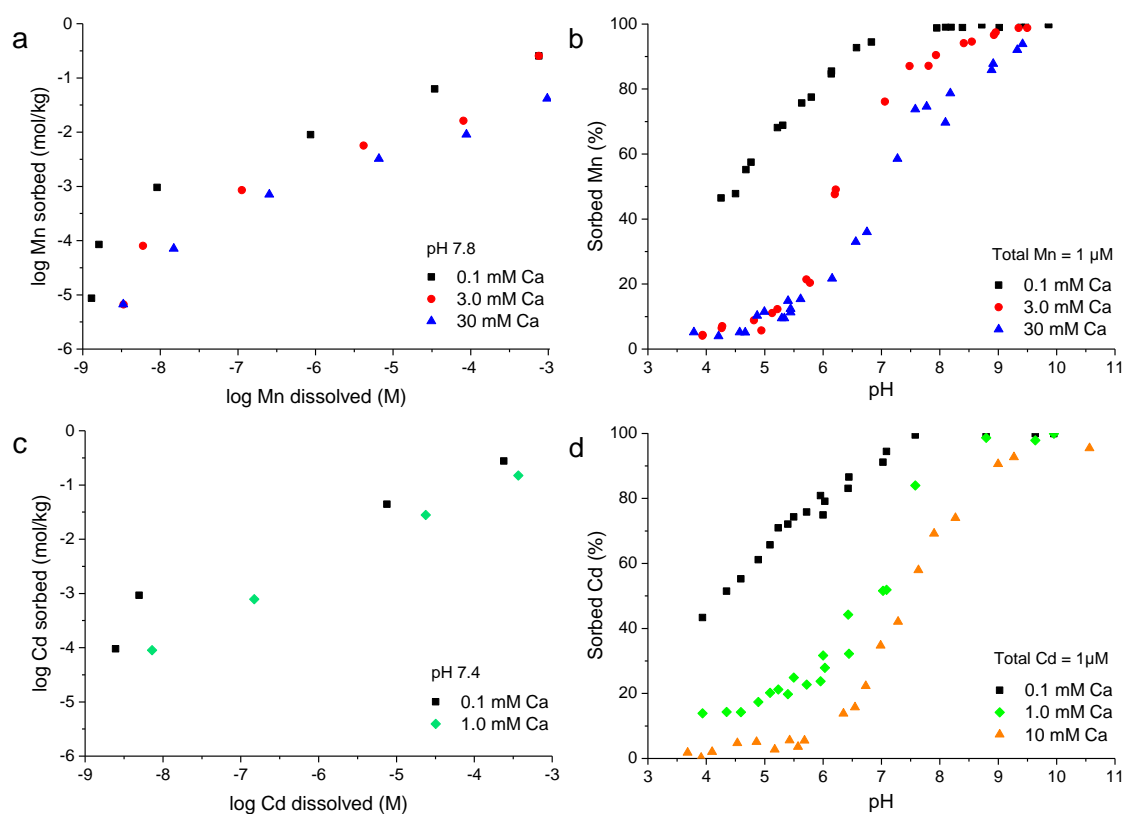


Figure 1. Sorption of  $\text{Mn}^{2+}$  (a, b) and  $\text{Cd}^{2+}$  (c, d) on Syn-1 smectite ( $\sim 1$  g/L) as function of dissolved metal concentration ( $10^{-3}$  to  $10^{-8}$  M) (a, c) and pH (b, d), at different  $\text{CaCl}_2$  concentrations. Sorption isotherms were recorded at fixed pH  $7.8 \pm 0.1$  for ( $\text{Mn}^{2+}$ ) and for pH  $7.4 \pm 0.1$  for  $\text{Cd}^{2+}$ . Total metal concentrations of 1  $\mu\text{M}$  were used to investigate pH-dependence of sorption (b, d). All samples were equilibrated for 1 day.