



Quantitative analysis of radiocesium retention onto birnessite and todorokite

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ABSTRACT

Although the Cs adsorption onto soil minerals has been widely studied, the structural factor of Mn oxides affecting the adsorption behavior of trace amounts of Cs is unclear. In order to elucidate the adsorption mechanisms of radioactive Cs at trace levels and the role of Mn oxides on Cs migration in the terrestrial environment, the Cs adsorption onto birnessite and todorokite was investigated for a wide range of concentrations (1×10^{-10} mol/L to 0.1 mol/L) and an ion-exchange model was used to interpret the adsorption data. Although birnessite showed a higher Cs adsorption capacity than todorokite, most of the Cs adsorbed onto birnessite was desorbed by ion exchange. Two types of adsorption sites were observed for todorokite. Despite low density, the selectivity coefficient was much higher for the T_1 site ($\log_{Na}^{Cs} K_{sel} = 4.2$) than for the T_2 site ($\log_{Na}^{Cs} K_{sel} = -0.6$). Sequential extraction was carried out at Cs concentrations of 1×10^{-9} mol/L and 1×10^{-3} mol/L. At lower concentrations, approximately 34% of the adsorbed Cs was residual in the todorokite after the sequential extraction; this value was much higher than the results for the Cs-adsorbed birnessite as well as the Cs-adsorbed todorokite at higher concentrations. The present results indicate that the structural factors of Mn oxides significantly affect the retention capacity of radioactive Cs. Aside from phyllosilicate minerals, todorokite also contributes to the fixation of radioactive Cs in soils.

1. Introduction

As an important fission product of uranium fuels and a major component of high-level nuclear waste, radioactive cesium has been released into soils and groundwater over the past decades by nuclear accidents and from nuclear weapons testing. Recently, concerns about ^{137}Cs and ^{134}Cs have increased after the Fukushima Daiichi nuclear power plant accident in Eastern Japan because Cs was one of the primary radionuclides released into the air and the water due to leakage.

The migration-retention behavior of Cs in Fukushima soils, sediments, rivers, and aerosols has been studied using different techniques. At a micro scale, the distribution of Cs is not uniform due to the preservation of the heterogeneity in soil- and river-suspended particles (Tanaka et al., 2013). Cs adsorption onto soil components has been widely studied (Benedicto et al., 2014; Bradbury and Baeyens, 2000; Fan et al., 2014; Missana et al., 2014; Qin et al., 2012; Rani and Sasidhar, 2012); most studies have focused on phyllosilicate minerals and the characteristics of Cs adsorption on non-phyllosilicate minerals

are not fully understood. Kozai et al. (2012) have examined the chemical states of radioactive Cs in Fukushima soils and found that some fraction of Cs was irreversibly associated with the soils even though mica was not present. Following these results, Ohnuki and Kozai (2013) analyzed the adsorption and desorption behaviors of radioactive cesium onto a wide range of natural minerals include kaolinite, halloysite, chlorite, montmorillonite, mordenite, and Mn oxide. The authors found that the distribution coefficient (K_d) for some minerals was quite different at low Cs concentrations compared to high Cs concentrations. Minerals other than mica may also contribute to the fixation of radioactive Cs in Fukushima soils.

Mn oxides represent one of the most reactive phases in soil and have profound influences on the biogeochemical cycling of trace metals (Manceau et al., 1992; O'Reilly and Hochella, 2003; Villalobos et al., 2004; Yin et al., 2013; Yu et al., 2012). The high reactivity of Mn oxides can be attributed to several factors including (1) Mn oxide phases generally occur in the soil as micrometer-sized particles. The ratio of reactive surface area to volume is extremely high (Murray, 1975); (2)

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Mn oxides in soils can occur in a variety of structures (such as birnessite and todorokite). The structural architectures of these minerals are especially amenable to solid-state diffusion. Unlike phyllosilicate minerals, Mn oxides can be readily mobilized by changes in environmental conditions such as alternation of wetting and drying, farming practices, and similar conditions. Thus, metals associated with Mn oxides are not permanently immobilized and may be released upon decomposition of the Mn oxide under reduced conditions.

Much effort has been devoted to the investigation of the adsorption behavior of Cs on birnessite. The structural unit of birnessite consists of an edge-sharing MnO_6 octahedron. The tetravalent Mn is usually replaced by a trivalent Mn or a vacant site. These replacements in the Mn oxide layer lead to an excess of negative charge and cations are located at the interlayer to compensate for this negative charge. Birnessite exhibits excellent cation-exchange properties (Dyer et al., 2000). Cs adsorption on birnessite takes place with a release of interlayer cations (e.g. K^+ , Na^+) into the aqueous phase and the adsorption equilibrium is always reached within hours (Singh and Tandon, 1977). Birnessite exhibited a Cs adsorption capacity of 1×10^{-3} – 4.6×10^{-3} mol/g (Chitrakar et al., 2011, 2013; Sasaki et al., 2014), which is higher than smectite (ca. 1×10^{-3} mol/g, Missana et al., 2014) and illite (0.2×10^{-3} – 0.9×10^{-3} mol/g) (Benedicto et al., 2014; Bradbury and Baeyens, 2000).

Todorokite is a tunnel-type mineral commonly observed in terrestrial and ocean-floor environments. It consists of triple chains of edge-sharing MnO_6 octahedra that share corners to form 3×3 tunnels. It is believed that todorokite is transformed from phyllosmanganate during oxic sediment diagenesis and under low-temperature hydrothermal conditions. This assertion is supported by experimental results that have shown that todorokite could be synthesized by either a high-pressure hydrothermal treatment (Ching et al., 1999; Feng et al., 1995; Feng et al., 1998; Giovanoli et al., 1975; Golden et al., 1987; Luo et al., 1999; Liu et al., 2005; Malinger et al., 2004; Shen et al., 1993; Tian et al., 1997; Vilenko et al., 1998) or a refluxing process at atmospheric pressure (Cui et al., 2006; Cui et al., 2008; Cui et al., 2009; Feng et al., 2004) by using birnessite as the precursor. The adsorptive capacity of Cs for todorokite is much lower than for birnessite and ranges from 0.2×10^{-3} to 1×10^{-3} mol/g according to previous reports (Chitrakar et al., 2014; Feng et al., 1995). The calculated K_d of alkali ions on todorokite follow the sequence of $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, which is in agreement with the increasing order of the effective ionic radii of metal ions. Titration tests suggest that there are two types of sites for the adsorption of alkali metal ions and that Cs can be adsorbed only on the strong acidic sites (Feng et al., 1995).

At trace Cs concentrations, minerals containing adsorption sites with a high selectivity for Cs dominate the Cs fixation (Sawhney, 1972). Although Cs adsorption on birnessite and todorokite at high levels have been widely studied (Chitrakar et al., 2011, 2013, 2014; Hasany and Chaudhary, 1984; Mikhail and Misak, 1988; Om and Tandon, 1977; Sasaki et al., 2014; Singh and Tandon, 1977), Cs adsorption at trace levels using a radiotracer technique has been studied only on several hydrated Mn oxides (Hasany and Chaudhary, 1984; Mikhail and Misak, 1988; Singh and Tandon, 1977) and no experimental data are available for Cs adsorption on tunnel-type Mn oxides at trace loading ($< 1 \times 10^{-4}$ mol/L). Moreover, most of the studies have described the Cs adsorption by varying only one or several parameters (Chitrakar et al., 2011; Chitrakar et al., 2013; Chitrakar et al., 2014; Lopano et al., 2009), which is insufficient for comprehensively interpreting the Cs uptake by Mn oxides.

X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), is a nondestructive method to probe adsorbate complex mechanisms at the mineral-water interface. In our previous work, EXAFS was used to study Co, Zn, and Ce adsorption on Mn oxide (Yu et al., 2016; Yu et al., 2012; Yu et al., 2013). Recently, EXAFS was

used to probe the coordination of Cs to clay minerals at high or moderate concentrations of Cs. Bostick et al. (2002) and Qin et al. (2012) observed that Cs possesses a variable coordination environment with a Cs–O distance of 3.2–4.3 Å for various types of clay minerals and soils. Sasaki et al. (2014) found that Cs generally forms an outer-sphere complex with biogenic and synthetic birnessite. Generally, EXAFS can be used to discern the predominant sorption mechanisms at concentrations higher than 50–100 mg/kg (Bostick et al., 2002). Therefore, EXAFS may be not sensitive enough to study a system where strong binding sites constitute only a small fraction of the total amount of sorbed Cs.

An adsorption model based on Cs adsorption tests under a wide range of Cs concentrations is another effective method to estimate the site concentrations. Multisite cation exchange models were proposed to explain Cs adsorption of illite: three sites with different affinities for Cs were proposed by Brouwer et al. (1983) and Bradbury and Baeyens (2000) and two-site models were proposed by Zachara et al. (2002) and Liu et al. (2004). Missana et al. (2014) recently reported a two-site exchange model to interpret the adsorption of Cs on three homoionic smectites. An increasing amount of data have shown that multisite adsorption may also exist on Mn oxide (Feng et al., 1995; Ohnuki and Kozai, 2013). However, little research has been published on the sorption model of Cs onto Mn oxides except for the use of Langmuir- or Freundlich-like isotherms, which is insufficient for the understanding of Cs retention mechanisms. For an adequate description of Cs adsorption as well as for testing a modeling approach, a large set of experimental data is required but such large datasets are quite scarce in the literature.

Thus, the objective of the present study is to elucidate the adsorption mechanisms of Cs at trace levels and the role of manganese oxides on Cs migration in the terrestrial environment. To accomplish this, a large set of experimental adsorption data was collected under a wide range of Cs concentrations (10^{-10} mol/L to 10^{-1} mol/L) and ionic strengths (10^{-5} mol/L to 1 mol/L) to compare the adsorption behaviors of Cs on birnessite and todorokite.

2. Materials and methods

2.1. Preparation of Mn oxides

Birnessite and todorokite were prepared according to Feng et al. (2004). One-hundred and twenty-five mL of 44 g of NaOH were added to an aqueous solution of 125 mL of 14.96 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ while stirring to form pink gel precipitates of $\text{Mn}(\text{OH})_2$. Then, a solution containing 3.982 g of KMnO_4 in 250 mL of deionized water was slowly added to the above mixture under vigorous stirring to form a dark gray precipitate. The reaction mixture was stirred for another 30 min and aged at 60 °C for 12 h. The precipitate was collected on a filter with a pore size of 0.2 µm and then repeatedly washed with purified water until the pH of the filtrate reached around 7. This washed sample was named birnessite. Todorokite was prepared through a Mg^{2+} -reflux treatment using birnessite as a precursor. The prepared birnessites were dispersed in 400 mL of 0.5 mol/L MgCl_2 solutions. After gentle stirring for 12 h, the suspensions were centrifuged and the solids were washed several times with deionized water. The products were dispersed in 350 mL of deionized water and refluxed (100 °C) with stirring for 24 h at atmospheric pressure. The refluxed products were washed 3–5 times using deionized water. Both birnessite and todorokite were lyophilized using an FD-5 N freeze-drier (EYELA, Tokyo, Japan) for 24 h prior to characterization.

The cationic exchange capacity (CEC) is 2.50×10^{-3} mol/g for todorokite and 4.57×10^{-3} mol/g for birnessite. These values were obtained from the maximum Cs adsorption capacity that we observed and are consistent with previous reports (Sasaki et al., 2014; Feng et al., 1995).

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