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Thallium (Tl) sorption onto illite and smectite: Implications for Tl mobility in the environment

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Abstract

Clay minerals play a relevant role in the transport and fate of trace elements in the environment. Though illite has been referred as an important Thallium (Tl) bearing phase in soils, mechanisms and affinity of thallium for clay minerals remain poorly known. This study investigated the sorption behavior of thallium as Tl(I) onto illite and smectite, two clay minerals occurring mainly in soils and sediments. Different sorption experiments were carried out under various pH conditions and Tl concentrations, in competition with sodium and calcium at a constant ionic strength of 0.01 mol L^{-1}. Our results showed that illite displayed more affinity than smectite for thallium. With illite, the distribution coefficients (K_d in L kg^{-1}) varied between $10^{2.75 \pm 0.17}$ and $10^{4.0 \pm 0.17}$ in Na solutions versus between $10^{2.25 \pm 0.17}$ and $10^{3.0 \pm 0.17}$ in Ca solutions, depending on pH. With smectite, K_d (in L kg^{-1}) ranged between $10^{2.50 \pm 0.16}$ and $10^{3.20 \pm 0.16}$ and between $10^{1.25 \pm 0.16}$ and $10^{1.95 \pm 0.16}$ in Na and Ca solutions, respectively. Sorption behavior was described with the Multi-Site Ion Exchanger model and selectivity coefficients with respect to protons were calculated for the first time. In all cases, independently of clay mineral and background electrolyte, low capacity but highly reactive sites were dominant in thallium uptake, highlighting Tl affinity for those sites. Moreover, the exchangeable and reversible interactions between Tl^+ and clays reactive sites suggested that in changing conditions, thallium could be released in solution. The role of clay minerals in thallium environmental cycle is evident and confirmed illite to be a dominant Tl bearing phase, in some environment competing with manganese oxides. Compared to others Tl bearing mineral phases, clays are ranked as follows: MnO_2 > illite > smectite ~ ferrihydrite ≥ Al_2O_3 ~ goethite > SiO_2. Finally, over the three monovalent cations (Tl, Rb, Cs) Tl is the one less sorbed on illite independently of the background cations.

Keywords: Thallium; Smectite; Illite; Multi-Site ion Exchanger model

1. INTRODUCTION

Thallium (Tl) is a heavy metal which can be highly toxic for mammals mainly due to the similar behavior of Tl^+ compared to K^+ in biological processes (Rodríguez-Mercado and Altamirano-Lozano, 2013). It is recognized to be as toxic as lead, cadmium, mercury or arsenic (Rodríguez-Mercado and Altamirano-Lozano, 2013).

Thallium is a widely distributed trace element on earth with an average concentration of 0.49 ppm in the continental crust and 0.13 ppm in the oceanic crust (Peter and Viraraghavan, 2005). It occurs in two oxidation states, Tl(I) and Tl(III) (Vink, 1993; Kaplan and Mattigod, 1998) with Tl(I) the only species issued from the mantle to the non-altered crust (Prytulak et al., 2017). Tl(I) is the most dominant and thermodynamically stable species in the sub-surface environment (Vink, 1993; Xiong, 2009; Casiot et al., 2011). However, in some environments, Tl(III) is

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detected in various amounts (Lin and Nriagu, 1999; Peacock and Moon, 2012; Voegelin et al., 2015; Campanella et al., 2017). Thallium(I) exhibits both chalcophile and lithophile behavior (McGoldrick et al., 1979; Baker et al., 2010; Biagioni et al., 2013; Hettmann et al., 2014; Prytulak et al., 2017). It has a large ionic radius (1.50 Å, 6-fold coordination), similar to K^+, Rb^+ and Cs^+ (Shannon, 1976). Classically, Tl is assumed to substitute K^+ in biotite, K-feldspar in volcanic rocks and granitic systems (Prytulak et al., 2017).

Thallium has two main sources in sub-surface environments. The first one corresponds to the weathering of K-rich rocks (Vaněk et al., 2009) and/or S-rich minerals and more rarely Tl-rich sulfides deposit (Kaplan and Mattigod, 1998; Xiao et al., 2004; Voegelin et al., 2015) and the second one corresponds to anthropogenic sources. Contaminations result from mining of ferrous and non-ferrous sulfide ores (Lis et al., 2003; Casiot et al., 2011; Karbowska, 2016; Campanella et al., 2017), from smelting activities, coal combustion and cement production (Cheam, 2001; Lis et al., 2003; Vaněk et al., 2013; Karbowska, 2016) as well as effluents of industry which use thallium compounds (Bennett, 2017).

Nielsen et al. (2005) reported an average concentration of thallium of $3.00 \pm 2.64.10^{-11}$ mol L^{-1} for sixteen rivers worldwide. However, in highly contaminated area, in particular in acid mine drainage, concentration can reach $\sim 1.0 \cdot 10^{-6}$ mol L^{-1} (Casiot et al., 2011). In non-anthropogenic impacted soils formed from Tl-bearing bedrocks, Tl contents are widespread, varying from around 1.5 ppm (Vaněk et al., 2009) to 6000 ppm (Voegelin et al., 2015). Those ranges largely depend on the geological background. Conversely, in anthropogenically impacted soils without Tl-bearing bedrocks, Tl concentrations range between 5 ppm and 124 ppm (Lis et al., 2003; Xiao et al., 2004; Vaněk et al., 2013).

The dominant aqueous species of thallium (I) is Tl^+ (Vink, 1993; Kaplan and Mattigod, 1998; Xiong, 2007; Casiot et al., 2011). Indeed, thallium (I) makes few complexes with anions, such as sulfate, carbonate and phosphate (Kaplan and Mattigod, 1998; Casiot et al., 2011), except with Cl^- in seawater (Kaplan and Mattigod, 1998). Therefore, Tl remains mostly as a free and bioavailable ion in solution (Vink, 1993; Jacobson et al., 2005a; Casiot et al., 2011; Voegelin et al., 2015). However, in the particulate and colloidal fractions in waters, in sediments or in soils, thallium interacts with various phases. Thallium has strong affinity for manganese oxides (Bidoglio et al., 1993; Jacobson et al., 2005a; Liu et al., 2011; Peacock and Moon, 2012; Voegelin et al., 2015) and Mn(IV)-oxides, such as birnessite, are known to oxidize Tl(I) in Tl (III) (Peacock and Moon, 2012; Voegelin et al., 2015). Iron oxy-hydroxides (Liu et al., 2011; Casiot et al., 2011; Coup and Swedlund, 2015) have medium/low affinity for thallium. They are mostly known to weakly sorb Tl(I) (Liu et al., 2011; Casiot et al., 2011; Coup and Swedlund, 2015) although iron reduction with UV might oxidize Tl (I) and stabilize the resulting Tl(III) (Karlsson et al., 2006). Shaw (1952) and Prytulak et al. (2017) stipulate that Tl^+ might substitute K^+ in secondary minerals during their formation processes, due to its lithophile behavior and a similar ionic radius. Besides, Jacobson et al. (2005a) and Voegelin et al. (2015) highlighted the role of Tl uptake by clay minerals in soils. Nevertheless, it was pointed out that processes and affinity of thallium for clays remain poorly known and further studies are needed (Voegelin et al., 2015). As for other trace elements, chemical adsorption on clay minerals is recognized to play a relevant role on their mobility in the environment. Consequently, in this study we have chosen to examine thallium sorption onto two major clay minerals, illite and smectite, present in soils and river sediments. The purpose has been, (1) to assess the clay mineral exchange properties that drive the Tl uptake on those surfaces and, (2) to evidence the affinity of Tl for these minerals. In order to be close to environmental conditions, Ca and Na were chosen as competing cations towards thallium for batch experiments. Then, sorption and its reversibility were tested over a large pH range and Tl concentrations. A thermodynamic multi-site ion exchange model is used to interpret the experimental data, and (3) to discuss the relative role played by clay minerals in thallium environmental cycle in the sub-surface environment.

2. EXPERIMENTAL

2.1. Thallium species and isotopes in batch solutions

As mentioned in introduction, Tl(I) dominates thallium speciation in the environment (Vink, 1993; Kaplan and Mattigod, 1998). Fig. 1 shows Tl speciation in aqueous systems containing 10 mM $CaCl_2$ (Fig. 1A and B) or 10 mM NaCl (Fig. 1C and D), similar conditions to our batch experiments. At low pH and high Eh, Tl^{3+} is stable under aqueous $TlCl_3$ (in NaCl) or $TlCl_4^-$ (in $CaCl_2$). At high pH, Tl^+ is hydrolyzed (TlOH) as is Tl^{3+} at higher Eh values forming $TlOH_3$ and $TlOH_4^-$ aqueous complexes (Fig. 1). Thallium concentrations seem to have no effect on its speciation in those cases (Fig. 1A, B, C and D). During experiments (pH 3–11), redox potentials (Eh in V) were measured with a Pt electrode (Metrohm) on random samples. Average value (at T = 20.1 °C) was 195.7 ± 4.3 mV (n = 3). This condition placed in Tl diagrams (Fig. 1) confirms that Tl(I) would be the only stable form of thallium during batch experiments. Moreover, Tl species distribution in these specific condition (Eh, pH and Tl concentrations), reveals that Tl^+ represents more than 95% of Tl(I) species in our experiments (SI, Fig. S1).

Radioactive and stable Tl solutions were used in this study. Tl occurs in the environment only with two stable isotopes, ^{203}Tl (29.5%) and ^{205}Tl (70.5%) (Rehkämper and Nielsen, 2004). The radioisotope ^{204}Tl, used here as radiotracer, does not exist naturally but only after neutron activation of stable thallium. Its half-life is 3.78 years. Therefore, a ^{204}Tl solution of 4.90 MBq in 1 M HCl (Eckert & Ziegler®, source # 1876-98, 07/01/16; initial Tl concentration of $2.80 \cdot 10^{-7}$ mol L^{-1}) was used. Two daughter solutions were made with 1 mL of parent solution diluted in 10 mL of ultrapure water (milli Q 18.2 MΩ cm^{-2}, Millipore®). They were composed of ~0.1 M HCl (dilution fac-