Potential bioavailability of mercury in humus-coated clay minerals

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ABSTRACT

It is well-known that both clay and organic matter in soils play a key role in mercury biogeochemistry, while their combined effect is less studied. In this study, kaolinite, vermiculite, and montmorillonite were coated or not with humus, and spiked with inorganic mercury (IHg) or methylmercury (MeHg). The potential bioavailability of mercury to plants or deposit-feeders was assessed by $CaCl_2$ or bovine serum albumin (BSA) extraction. For uncoated clay, IHg or MeHg extraction was generally lower in montmorillonite, due to its greater number of functional groups. Humus coating increased partitioning of IHg (0.5%–13.7%) and MeHg (0.8%–52.9%) in clay, because clay-sorbed humus provided more strong binding sites for mercury. Furthermore, humus coating led to a decrease in IHg (3.0%–59.8% for $CaCl_2$ and 2.1%–5.0% for BSA) and MeHg (8.9%–74.6% for $CaCl_2$ and 0.5%–8.2% for BSA) extraction, due to strong binding between mercury and clay-sorbed humus. Among various humus-coated clay particles, mercury extraction by $CaCl_2$ (mainly through cation exchange) was lowest in humus-coated vermiculite, explained by the strong binding between humus and vermiculite. The inhibitory effect of humus on mercury bioavailability was also evidenced by the negative relationship between mercury extraction by $CaCl_2$ and mercury in the organo-complexed fraction. In contrast, extraction of mercury by BSA (principally through complexation) was lowest in humus-coated montmorillonite. This was because BSA itself could be extensively sorbed onto montmorillonite. Results suggested that humus-coated clay could substantially decrease the potential bioavailability of mercury in soils, which should be considered when assessing risk in mercury-contaminated soils.

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Introduction

It is well known that soil composition can significantly affect mercury (Hg) biogeochemistry in soils (Chen et al., 2012; Dai et al., 2013; Gagnon and Fisher, 1997). Among the soil components, clay can bind large amounts of Hg, partly because of its relatively high surface area (Abollino et al., 2008; Brigatti et al., 2005; Cruz-Guzmán et al., 2006; Lothenbach et al., 1998; Sdiri et al., 2014; Zhong and Wang, 2008a). It has been reported that clay minerals are important in regulating metal–solid interactions (Kongchum et al., 2011) and play a role in Hg biogeochemistry (Zhong and Wang, 2008b). Meanwhile, soil organic matter has high affinity for Hg (Yu et al., 2006; Zhong and Wang, 2006a), and thus could strongly affect partitioning and bioavailability of Hg in soils.

Montmorillonite and vermiculite are both 2:1 clay minerals with large surface area and high cation exchange capacity (do Nascimento and Masini, 2014). Kaolinite is a 1:1 layer mineral

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with small cation exchange capacity and restricted surface area (Bernaus et al., 2005). Differences in characteristics could possibly lead to large differences in binding capacity and affinity toward Hg in various clay minerals. Furthermore, differences in surface area may also affect sorption of organic matter on clay and could greatly influence Hg binding in soils. Hence, it would be interesting to compare Hg binding and bioavailability in different clay and organic-coated clay minerals. Such research could greatly improve the understanding of Hg biogeochemistry in soils.

In the present study, three of the most common clay minerals, kaolinite, vermiculite and montmorillonite, were coated or not with humus. Partitioning, geochemical fractionation (quantified by a sequential extraction method), and potential bioavailability (assessed by a chemical extraction method) of both inorganic mercury (IHg) and methylmercury (MeHg) were then quantified. The main objective was to explore the effects of various organic-coated clay minerals on sorption and potential bioavailability of Hg in soils.

1. Materials and methods

1.1. Chemicals and containers

Kaolinite, montmorillonite, humic acid (HA) and fulvic acid (FA) were purchased from Sigma-Aldrich, USA. Vermiculite was purchased from Lingshou DingWang Company, China. All clay particles were sieved through a 75 μm mesh before use. Mercury chloride ($HgCl_2$) and methylmercury chloride (CH_3ClHg) were obtained from Sigma-Aldrich (USA) and Brooks Rand (USA), respectively. Calcium chloride ($CaCl_2$) and bovine serum albumin (BSA), used for Hg extraction, were purchased from Sigma-Aldrich, USA. Trace metal grade nitric acid (HNO_3) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent (China) and Nanjing Chemical Reagent (China), respectively. Potassium hydroxide (KOH) was from Chinasun Specialty Products (China). Methanol (CH_3OH) and $NaBet_4$, used for MeHg digestion and determination, were from TEDIA (USA) and Brooks Rand Lab (USA), respectively. All chemicals were of analytical reagent grade or higher. Background Hg levels in all chemicals were tested and found to be extremely low.

Polypropylene centrifuge tubes (Corning, USA) were used in this study, e.g., for organic coating, chemical extraction, sample digestion and dilution. Diluted nitric acid solution (2%) was used to rinse the tubes, and Hg in the rinsing solution was below the detection limit. These tubes were thus considered relatively Hg free. Adsorption of IHg or MeHg on the tubes was also tested and found to be extremely low.

1.2. Humus coating and Hg spiking

A total of 6 treatments (each with 3 replicates) were applied in this study: kaolinite; vermiculite; montmorillonite; humus-coated kaolinite; humus-coated vermiculite; and humus-coated montmorillonite. To prepare humus-coated clay particles, kaolinite, vermiculite, or montmorillonite was mixed with humus solutions (mixtures of 10 g/L HA and 10 g/L FA) in a centrifuge tube at a ratio of 0.1 g/1 mL, respectively. The mixtures were incubated in an incubator shaker at 25°C and 300 r/min.

After one month incubation, the mixtures were centrifuged at 3000 r/min for 30 min and washed twice by ultrapure water to remove unbound organic matter. Both uncoated and coated clay particles were then placed into centrifuge tubes and spiked with IHg or MeHg solutions to achieve a spiking concentration of 5 μg IHg/g or 0.05 μg MeHg/g. Background total mercury (IHg and MeHg) levels in clay particles (vermiculite: 10.75 ng/g, kaolinite: 12.06 ng/g, montmorillonite: 5.60 ng/g) were less than 1% of spiked IHg concentrations (5 μg/g), and could thus be ignored. Background MeHg levels in clay were below the detection limit. The spiked particles in capped centrifuge tubes were incubated for 3 days in an incubator shaker at 25°C and 300 r/min. Afterwards, the mixtures were centrifuged at 3000 r/min for 30 min and washed once by ultrapure water to remove any unbound Hg. Methylation of Hg should be negligible within the incubation period (i.e., 3 days) according to our preliminary experiment. Subsequently, the Hg-spiked particles were evaluated for THg or MeHg concentrations (details below) and used for chemical extraction or sequential extraction.

1.3. Extraction of Hg from Hg-spiked particles

Mercury extraction by $CaCl_2$ (1.47 g/L or 0.01 mol/L, 0.1 g soil/1 mL extractant, Gupta and Sinha, 2007) or BSA (10 g/L, 0.1 g soil/0.3 mL extractant, Zhong and Wang, 2006a) was used to assess potential bioavailability of soil-bound Hg to plants (Gupta and Sinha, 2007; Jing et al., 2008) or deposit-feeders (Lawrence et al., 1999; Voparil and Mayer, 2004; Zhong and Wang, 2006a) respectively. Hg-spiked particles were mixed with either $CaCl_2$ or BSA solution in capped polypropylene centrifuge tubes and shaken at 300 r/min in an incubator shaker at 25°C for 2 hr ($CaCl_2$, Gupta and Sinha, 2007) or 4 hr (BSA, Zhong and Wang, 2006a,b). Three replicates were performed for each treatment. After that, the mixtures were centrifuged at 3000 r/min for 30 min and the supernatants were filtered through 0.45 μm membrane filters. Concentrations of THg or MeHg in the filtrates and in the remaining particles were then measured (details below). Concentrations of IHg were calculated by subtracting the MeHg concentrations from the measured THg concentrations. The mercury (IHg or MeHg) extraction rate (%, by $CaCl_2$ or BSA), quantifying the potential bioavailability of Hg in particles, was calculated as: 100 × Hg in filtrate / (Hg in filtrate + Hg remained in particle after extraction). The recoveries of mercury extraction, i.e., 100 × (Hg in filtrate + Hg remained in particle after extraction) / Hg in particle before extraction, were 96.7%–101.5%.

1.4. Quantification of Hg geochemical fractionation in particles

To quantify Hg association with various biogeochemically relevant pools in Hg-spiked particles, the commonly used five-step sequential chemical extraction method (designed specifically for Hg, Bloom et al., 2003) was used. The five geochemical fractions were operationally defined as water soluble (WATF, e.g., $HgCl_2$, extracted by deionized water), stomach acid soluble (STOF, e.g., HgO and $HgSO_4$, extracted by 0.01 mol/L HCl + 0.10 mol/L CH_3COOH), organo-complexed (ORGF, e.g., Hg-organic matter, MeHg and Hg_2Cl_2, extracted by 1 mol/L KOH), strongly complexed (STRF, e.g., Hg bound up in