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Compound specific stable isotope determination of methylmercury in contaminated soil

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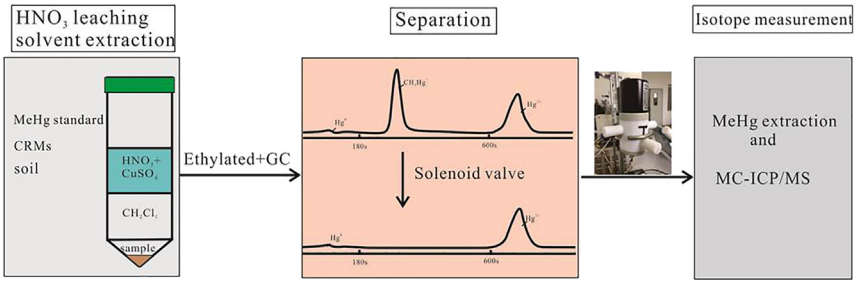
HIGHLIGHTS

- A new compound-specific method was developed for determining stable Hg isotopes in MeHg in soils and sediments.
- No significant MDF and MIF occurred during extraction processes.
- Significant differences of δ^{202}Hg values were observed between MeHg and THg in paddy soils.
- MeHg isotope analysis can be used to understand MeHg migration and transformation processes in soil–rice systems.

GRAPHICAL ABSTRACT



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ABSTRACT

Rice is one of the main sources of methylmercury (MeHg) to humans, and soil is the main source of MeHg to rice grains. Determining the Hg isotope composition in environmental samples is a good way of characterizing sources of Hg pollution and investigating environmental processes. We developed a new compound-specific method for determining stable Hg isotopes in MeHg in contaminated soil and sediment. The method involved HNO_3 leaching/solvent extraction, chemical ethylation, and separation by gas chromatography with a solenoid valve optimized to enrich MeHg. The method was optimized by using MeHg standard solution, certified reference materials and paddy soil samples. The δ^{202}Hg precision for replicate MeHg isotope analyses was 0.14‰ (2 × standard deviation, $n = 11$), and no fractionation of Hg stable isotopes was found during the separation processes. The δ^{202}Hg values for MeHg in paddy soils were −1.78‰ to −1.30‰, which were lower than the δ^{202}Hg values for total Hg (−1.32‰ to −0.44‰). The results indicated that methylation (rather than demethylation) was the dominant process in the paddy soils. The method developed in this study can help us to better understand MeHg migration and transformation processes in paddy soil-rice ecosystem.

1. Introduction

Mercury (Hg) is one of the most toxic pollutants and its ecological and toxicological effects are strongly dependent on its chemical forms (Ullrich et al., 2001). Methylmercury (MeHg), an organic Hg species, is one of the most poisonous Hg species and can bioaccumulate and biomagnify in food chains (Gilmour et al., 1992). Fish is the most important source of MeHg to humans in many regions of the world, but rice is the main source of MeHg in areas contaminated with Hg such as in southwest China where rice is the staple food supply (Feng et al., 2008; Zhang et al., 2010). Much attention has been paid to the sources of MeHg to rice grains (Qiu et al., 2008; Li et al., 2010; Li et al., 2017). MeHg concentrations and distributions in rice plants were evaluated

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throughout entire rice growth cycle and it suggested that paddy soil was the main source of MeHg to rice grains (Meng et al., 2011). MeHg in paddy soil was mainly produced by in situ methylation of Hg(II). The amount of Hg in paddy soils originated from atmospheric deposition and irrigation was negligible relative to the amount of Hg pool in the soil (Zhao et al., 2016a, 2016b). Total Hg (THg) stable isotope patterns suggested that soil and ambient air both contributed Hg to rice (Yin et al., 2013a). Results obtained from a greenhouse experiment using spiked Hg isotope approach found that MeHg was synthesized by Hg methylating microorganisms in the saturated soil and then transported to the rice grains (Strickman and Mitchell, 2016).

Paddy fields are special short-term wetlands in which both methylation and demethylation of Hg can occur (Mark et al., 2014; Zhao et al., 2016a, 2016b). The MeHg concentrations in paddy soils will be the net results of both methylation and demethylation, and MeHg production at different times will reflect the net methylation potential of the paddy soil (Zhao et al., 2016a, 2016b). Microorganisms such as sulfate-reducing bacteria, iron-reducing bacteria, and methanogens play important roles in the methylation and demethylation processes (Compeau and Bartha, 1984, 1985; Fleming et al., 2006; Gilmour et al., 1992, 2013; Oremland et al., 1991; Yu et al., 2013). The MeHg migration and transformation processes that occur in soil–rice ecosystems are still poorly understood.

Stable Hg isotope analysis techniques are useful for studying Hg sources and the processes that affect the environmental behavior of Hg (Blum et al., 2014; Yin et al., 2014). Mass-dependent fractionation (MDF, quantified as the δ^{202}Hg value) and mass-independent fractionation (MIF, quantified as the Δ^{199}Hg, Δ^{200}Hg, and Δ^{201}Hg values) commonly occur during these environmental processes, such as hydrothermal reaction, sorption/desorption, photochemical reduction, and photochemical degradation (Bergquist and Blum, 2007; Blum et al., 2014). The mechanisms of fractionation are considered as equilibrium fractionation and kinetic fractionation (Criss, 1999; Young et al., 2002). The MIF of Hg can be predicted based on the magnetic isotope effect (Buchachenko, 2001; Buchachenko et al., 2004) and the nuclear volume effect (Bigeleisen, 1996; Schauble, 2007). Laboratory experiments aimed at studying methylation and demethylation commonly use stable Hg isotopes as tracers to allow Hg isotope fractionation during the studied environmental processes. In Hg methylation experiments, sulfate-reducing bacteria in a pure culture caused MDF of stable Hg isotopes and generated MeHg with lighter Hg isotopes than Hg(II) isotope (Rodríguez-González et al., 2009; Perrot et al., 2015). Similar results have been found in abiotic methylation experiments using methylcobalamin and other methyl group donors (Jiménez-Moreno et al., 2013; Perrot et al., 2013). The MeHg remaining in the reactors became progressively heavier (increasing the δ^{202}Hg value) over time as MeHg was degraded to give volatile elemental Hg (Hg(0)), similar to what has been found during the photodecomposition of dissolved MeHg (Kritee et al., 2009; Malinovsky et al., 2010). Different Hg isotope fractionation patterns have been found during Hg methylation and demethylation of Hg, meaning that stable Hg isotope fractionation can be useful for distinguishing the effects of methylation and demethylation in paddy soils. Analyses of the stable Hg isotopes in MeHg in soil can provide data to improve our understanding of Hg methylation and demethylation of Hg in the environment.

Gas chromatography (GC) coupled with multicollector inductively coupled plasma mass spectrometry (MC-ICP/MS) was involved in measurement of compound specific Hg isotope ratios (Epov et al., 2008; Dzurko et al., 2009). But the external precision (2SD) was high as 0.56‰ for δ^{202}Hg measurement (Epov et al., 2008) and high Hg species concentration samples were needed to be digested and introduced into measurement system (Dzurko et al., 2009). An offline method was developed to measure the Hg isotope compositions of MeHg in estuarine sediments, involving distillation, ethylation, GC, and separation using a physical solenoid valve (Janssen et al., 2015). High precision and sensitivity of offline method can measure Hg isotopes in MeHg form in environmental samples such as sediments with extremely low MeHg ratio (<1%). However, Liang et al. (2004) found that unlike isolating Hg by HNO_3 leaching/solvent extraction, distillation decreases the MeHg concentration when the inorganic mercury (Hg(II)) concentration is >2 μg/g. It is therefore necessary to optimize the pretreatment method used to separate MeHg from soil samples with high THg concentrations.

In this study, we aimed to develop a new method to determine compound specific stable isotope of MeHg in contaminated soil. HNO_3 leaching/solvent extraction, chemical ethylation, and separation by gas chromatography were combined to enrich MeHg for Hg isotope analysis by MC-ICP/MS. We validated this method by experiments on MeHg standard solution and certified reference materials. The method developed in this study enables us to determine Hg isotope compositions in MeHg form in paddy soils, which can help us to better understand the mechanism of Hg methylation and demethylation and MeHg bioaccumulation in the rice grain in soil–rice systems.

2. Materials and methods

2.1. Sample collection

Samples were collected from two typical Hg-contaminated areas in Guizhou Province, southwest China. One area is in Qingzhen (N 26°34′–26°38′, E 106°28′–106°30′) polluted with Hg by emissions from a chemical plant and the other one is in Wanshan (N 27°33′, E 109°12′) polluted through Hg mining activities. Rice is an important crop in the studied areas. Surface soil samples (0–10 cm deep) were collected in each area. Each sample was double-bagged and stored at −20 °C. Later, each sample was freeze-dried, and was then grounded using a mortar and passed through a 200 mesh sieve before being analyzed for Hg contents.

2.2. THg measurements and preparation for THg isotope analysis

A 0.1 g aliquot of a soil sample was digested in a freshly prepared 3:1 (v/v) mixture of HCl and HNO_3 at 95 °C in a water bath for 45 min (Yin et al., 2013a). The THg concentration in the digest was determined by $SnCl_2$ reduction and cold-vapor atomic fluorescence spectrometry (CVAFS) (Method 1631, 2002). The effectiveness of the digestion process was verified by digesting an aliquot of European certified reference material CC580 (estuarine sediment). MeHg working standards were dissolved in 20% (v/v) HNO_3 and oxidized with 25% (w/w) BrCl. These solutions were analyzed to allow estimating the original Hg isotope composition.

The recoveries of THg concentrations in CC580 ranged from 90% to 98%, and the relative percentage differences for THg concentrations in duplicate samples were <5%. The method blank was 0.04 ng/mL. Each digest solution was diluted to give a THg concentration of 1 ng/mL before the Hg isotope composition in the solution was determined.

2.3. MeHg measurements and isotope analysis

The working MeHg standard solution (10 ng/mL, diluted from a MeHg stock solution; Brooks Rand, USA) and soil samples were dealt with HNO_3 leaching solvent extracted, and then ethylated. The solutions were then purged with the vapor passing through a trap. The trapped compounds were then released and analyzed by GC-CVAFS (Bloom, 1989; Liang et al., 2004). The MeHg separation and trapping system described by Janssen et al. (2015) was used. The GC column was designed as a helical U-tube (0.8 cm inner diameter, 90 cm length) to accumulate large amounts of MeHg. And it was filled with 15% OV-3 Chromosorb W-AW 60/80 and kept at 70 °C. The trap column was packed with 100 mg of Tenax to ensure that the derivatives were completely captured. A Teflon solenoid valve was placed between the pyrolysis system