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A simulation study of inorganic sulfur cycling in the water level fluctuation zone of the Three Gorges Reservoir, China and the implications for mercury methylation

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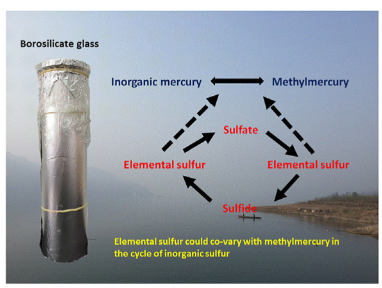
HIGHLIGHTS

- The water level fluctuation zone of the Three Gorges Reservoir is a redox rotation area.
- The accumulation of elemental sulfur appeared both in sulfate reduction and sulfide re-oxidation.
- Methylmercury content in soil/sediment is positively correlated with elemental sulfur content during the flooding period.
- Methylmercury during the flooding period may be fixed by pyrite.

GRAPHICAL ABSTRACT



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ABSTRACT

The water level fluctuation zone (WLFZ) of the Three Gorges Reservoir (TGR) in China experiences a drying and wetting rotation every year, and the water level induced redox variation may influence inorganic sulfur speciation and mercury methylation. In this work, a simulative flooding and drying experiment and a sulfate added flooding experiment were conducted to study this topic. The results showed that sulfate was reduced from the 10th d during the flooding period based on the detected sulfide in water and the increased elemental sulfur (S^0) in sediment. Sulfate reduction and sulfide re-oxidation led to the increase of S^0 contents with the maximal values of 1.86 and 0.46 mg kg^{-1} during the flooding and drying period, respectively. Methylmercury (MeHg) content in sediment displayed a rising trend (0.16–0.28 μg kg^{-1}) in the first 40 d during the flooding period, and then declined from 0.28 to 0.15 μg kg^{-1}. A positive correlation between MeHg content and S^0 content in soil ($r = 0.53$, $p < 0.05$) was found during the flooding period, and a positive but not significant correlation between the percent of MeHg in THg (%MeHg) and S^0 content ($r = 0.85$, $p = 0.08$). In sulfate added flooding simulation, MeHg content in sediment did not increase with the sulfate concentration increasing. The increased pyrite in high-sulfate treatment may fix mercury through adsorption process. This study demonstrated that

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inorganic sulfur species especially S^0 and chromium reducible sulfur (CRS) play an important role on mercury methylation in the WLFZ of the TGR.

1. Introduction

The Three Gorges Reservoir (TGR) in China, with a total storage capacity of 39.3 billion km^3, is the largest artificial reservoir in the world (Tang et al., 2016). Due to the artificial regulation, the water level of this reservoir changes seasonally from 145 m a.s.l. in summer to 175 m a.s.l. in winter every year. The 30 m's water level variation forms a large drying and wetting rotation region, named as the water level fluctuation zone (WLFZ), with a total area 306.33 km^2 (Bao et al., 2015). Like intertidal zone, paddy soil and some wetlands, the change of redox conditions in the WLFZ can alter the species of some redox-sensitive elements, *e.g.*, iron, manganese, sulfur, carbon and nitrogen, which may influence the biogeochemical processes of these multi-valent elements.

The drying and wetting rotation may change the distribution of sulfur species in the natural environment, especially in the water-body with high sulfate level. Sulfate with the concentration about 20 mg L^{-1} in the TGR originates mainly from acid deposition and agricultural non-point source pollution (Gao et al., 2016). Sulfate concentration in the TGR is higher than that of other fresh water-bodies, such as Little Rock Lake (Urban et al., 2001), New Jersey wetland (Mandernack et al., 2000), and even eutrophic Salmon Falls Creek Reservoir in USA (Gray and Hines, 2009). Sulfate reduction and sulfide re-oxidization are two important processes in sulfur cycles, which can not only balance the partition of sulfide and oxygen, but also contribute to the pH changes of soil/sediment (Jørgensen, 1977). The frequent rotation of redox conditions can accelerate the dynamic changes of sulfur speciation, which may affect the distribution of some sulfur-affinitive elements, such as mercury and iron.

The biogeochemical cycles of mercury can be influenced by sulfur speciation through several aspects. Firstly, sulfate reduction is a main driving force for biological methylation of mercury, especially in the environment of periodic variation of redox (Ullrich et al., 2001; Wang and Zhang, 2013; Ariya et al., 2015). Secondly, sulfide is a strong inorganic ligand to bind with mercury based on Lewis acid-base theory (Skyllberg, 2011), the stability constant to form HgS by Hg^{2+} and H_2S was reported as 29.4 (Skyllberg, 2011), and the formation and dissolution of mercuric sulfide (HgS) play an important role on mercury speciation in sulfidic water. Thirdly, the neutral sulfide-mercury complexes and solid nanoparticle HgS were identified as the important substances to pass through biofilm and undergo mercury methylation (Benoit et al., 1999, 2001; Zhang et al., 2012). Moreover, the formation and transformation of different iron-sulfur compounds rich in redox alternation zone, *e.g.*, mackinawite (FeS) and pyrite (FeS_2), may alter mercury speciation through adsorption, co-precipitation, oxidization and reduction, volatilization and methylation.

The risk of mercury and other heavy metals in the TGR has been concerned since 1997. Jin and Xu (1997) found that mercury in fish was mainly distributed in muscle with the contents of total mercury (THg) and methylmercury (MeHg) 17–228 and 5–174 ng g^{-1}, respectively. Afterwards, Xu (2014) found that the contents of THg and MeHg in fish muscle were 0.51–254.83 and 0.005–188.89 ng g^{-1}, respectively. Although the variations of mercury contents in fish are not significant in recent years, Li et al. (2015) reported that mercury contents in fish body showed a significant temporal trend with water-level regulation of the TGR, and followed a decreasing order of post-flooding period, pre-flooding period and flooding period. Moreover, the unique hydrologic regime of the WLFZ led to the sedimentation and enrichment of trace metals (Tang et al., 2014). As a result, biogeochemical progresses of mercury in the WLFZ of the TGR are active and diverse. So far, some studies mainly focused on the effects of vegetation growth and degradation (Zhang et al., 2014a; Liang, 2015), low-molecule-weight organic acids in root exudates (Qin et al., 2015), native bacteria (Xiang et al., 2014), sulfate (Wang et al., 2015) and soil organic matter (Zhang et al., 2014b) on the migration and transformation of mercury.

The roles of sulfur speciation on mercury methylation have been reported in reservoir sediment (Bravo et al., 2014), the sediment and porewater in estuaries (Schartup et al., 2014) and lakes (Bravo et al., 2015). However, the variations of inorganic sulfur speciation and their potential effects on mercury methylation in the WLFZ of the TGR are not clear, and have not been documented. It is necessary to understand the relationship between the cycles of inorganic sulfur and mercury methylation in redox rotation environment. In this study, the objectives were to understand the speciation changes of inorganic sulfur induced by flooding and drying rotation, and to reveal their potential influences on mercury methylation in this special area through simulation experiments.

2. Materials and method

2.1. Collection of soil and water samples

Soil samples used in the simulation experiments were collected in June 25, 2015. The sampling site next to the main stream of the Yangtze River is located at Shibao Village in Zhong County, Chongqing, China. The WLFZ in this region is free from anthropic factors, like farming and fishing activities, no factory or other sulfur and mercury emission sources around the sampling site. The altitude of the sampling site (N30°25′29.02″, E108°10′54.97″) is 165 m a.s.l. (drained for 2 months from April 23, 2015). The topsoil sample (0–10 cm) of this site was collected in plastic bags after removing the vegetation. The surface water sample was collected at the same site along the Yangtze River at 145 m a.s.l., and stored in the acid-cleaned polyethylene buckets. The environmental characteristics and the background contents of mercury and inorganic sulfur in soil and water samples are listed in Table 1.

2.2. Simulative wetting and drying experiment

The soil sample was air-dried, ground, and sieved to pass through a 2-mm sieve. The drying and wetting experiment was conducted with 250 g of homogenized soil and 1000 mL of natural river water in borosilicate glass bottle. Before use, the borosilicate glass bottles (30 cm in height and 8 cm in diameter) were immersed in 25% nitric acid (HNO_3, GR) for more than 24 h, and burned in muffle furnace at 450 °C for 30 min to remove mercury and organic matter. The flooded bottles were purged with ultra-high purity N_2 by Teflon® purging tubes for more than 30 min to remove the dissolved oxygen (DO) in water, and then were sealed by double-layer sealing film to isolate deposition and avoid re-