

Transformation and Mobilization of Arsenic in Fluvial Sediments as the Function of Sulfate to Iron Molar Ratios

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Arsenic (As) is carcinogenic and toxic to ecosystems. The understanding for its speciation, solubility, mobility and biotoxicity in environments could improve the efficiency for the remediation of As contaminations. The common inorganic As species are arsenite (AsO_3^{3-} [As(III)]) and arsenate (AsO_4^{3-} [As(V)]), and As(III) is more toxic than As(V). Previous studies have shown that the As speciation is closely related to the Fe and S in environments. In this study, we aimed to investigate the effect of sulfate/iron molar ratios ($\text{SO}_4^{2-}/\text{Fe}=0, 0.3, 1, 3$) on the dissolution and transformation of As in fluvial sediments using the As K-edge X-ray absorption near-edge structure (XANES) technique. During the 30-day incubation, no significant variations in pH and Eh were found among four SO_4^{2-} -Fe treatments. However, the value of Eh gradually decreased at the molar ratio of $\text{SO}_4^{2-}/\text{Fe}=3$ during the early incubation periods (0-7 day) due probably to reduction of SO_4^{2-} by microorganisms in sediments. In addition, results of linear combination fitting (LCF) analyses for As K-edge XANES indicated that precipitated As(V), including $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ dominated the As inventory in solid phases for all SO_4^{2-} -Fe treatments in the initial stage of the incubation. As incubation duration and SO_4^{2-} concentration increased, the proportions of precipitated As(V) decreased to 6.7%, 11.7%, 19.5%, and 27.6% for treatments with $\text{SO}_4^{2-}/\text{Fe}$ ratio of 0, 0.3, 1, and 3. However, proportions of S-related As, including FeAsS and As_4S_4 , increased from 7.7% to 9.6%. In terms of the As dissolution, total dissolved As ranged from 0.13-0.22 mg L⁻¹ in all treatments. However, a substantial Fe dissolution was found at $\text{SO}_4^{2-}/\text{Fe} = 3$ in the reductive environments (Eh < -160 mV). Such result could be plausibly ascribed to the reduction of SO_4^{2-} to HS^- , leading to the subsequently reductive dissolution of ferric iron-containing minerals in sediments. Accordingly, FeS or FeS_2 formed via precipitation between HS^- and Fe^{2+} , which further caused the As release from ferric iron-containing minerals. Our collective results suggested significant influences of $\text{SO}_4^{2-}/\text{Fe}$ ratios on the transformation of As. A long-term monitoring of As accumulation as well as the associated environmental factors might improve the assessment for the potential risk of As in fluvial ecosystems.

Keywords - Arsenic, Sulfate/iron ratio, Speciation, XANES