

Ternary Complexation of Arsenite (As^{III}) to Organic Matter: Possible Role of Aqueous Ferrous Iron (Fe^{II})

MOHD AMIR HUSAIN AND ASHIS BISWAS

Indian Institute of Science Education and Research (IISER),
Bhopal

Presenting Author: mohd18@iiserb.ac.in

Studies have highlighted that organic matter (OM) can bind arsenite and arsenate extensively. Arsenic (As) complexation with the solid OM (e.g., in soil and sediment) decreases As mobility, while complexation with the dissolved OM (e.g., in groundwater and surface water) increases As mobility. A key mechanism of As bindings to OM has been identified as the formation of ternary complexes via ferric iron (Fe^{III}) bridging (As-Fe^{III}-OM) due to its abundance in the soil and sediment. Since the mobility of As is higher under reducing conditions, the release of As into water from soils and sediments in the form of arsenite (As^{III}) often positively correlates with the release of ferrous iron (Fe^{II}) and dissolved organic carbon (DOC). Despite the high degree of association of As^{III} with Fe^{II} and DOC in water, a study on determining the possible role of Fe^{II} in As^{III} complexation with DOC is lacking. Therefore, the present study has investigated the extent of As^{III} complexation with Suwannee River aquatic NOM (SRNOM: 2R101N) and Leonardite Humic Acid (LHA: 1S104H) (as-received and chemically-reduced) in the presence of increasing concentrations of Fe^{II}. Results showed that aqueous Fe^{II} can significantly enhance As^{III} complexation with DOC by forming As-Fe-DOC colloids (<0.20 μm to >3 kDa). The As-Fe-DOC colloids were characterized by Fe and As K-edge X-ray absorption spectroscopy (XAS). Results of the XAS analysis revealed that the speciation of Fe in colloids was predominantly Fe^{III}, suggesting that DOC used in this study, even in the chemically reduced form, could oxidize Fe^{II} to Fe^{III}. The Fe^{III}(O,OH)₆ octahedra were complexed to the oxygen-containing functional groups of the DOC (e.g., -COOH, -OH, etc.) by forming a possibly six-membered chelate ring structure. The As^{III} in colloids was bound to the DOC due to direct complexation with the oxygen-containing functional groups of the DOC and indirect complexation with the organically complexed Fe^{III}(O,OH)₆ octahedra via corner- (²C) and edge-sharing (¹E). Therefore, the possible role of As-Fe-DOC colloids in the As mobilization and transport should be considered for the system rich in As^{III}, Fe^{II}, and DOC.