Extensive Cryptic Sulfur Cycling Affecting Arsenic Levels in Van Phuc, Vietnam

BENJAMIN C. BOSTICK^{1*}, ATHENA NGHIEM¹, MASON STAHL², CHARLES HARVEY³, A. VAN GEEN¹

¹Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY (*correspondance: <u>bostick@ldeo.columbia.edu</u>)
²Union College, Schenectedy NY

³Massachusetts Institute of Technology, Cambridge MA

Arsenic (As) groundwater contamination is extensive throughout the world and is usually associated with the microbial reductive dissolution of As-bearing iron oxides. In most cases, this iron reduction is thought to be mediated through the dissimilatory reduction of Fe by iron reducing microbes, in part because ferric iron is more abundant and more energetically favorable for use as a terminal electon acceptor than other less abundant redox active species like sulfur or manganese. Sulfur (S) concentrations are usually quite low in freshwater environments affected by As, but recent evidence suggests that S cycling is active even in environments containing abundant Fe oxides such as ferihydrite [1],. However, these processes have not been studied in sufficient detail to establish the role of S cycling in moderating Fe reduction and As concentrations in Asaffected aquifers. In this research, we examine biogeochemical and mineralogical evidence for an active cryptic sulfur cycle facilitating iron redox transformations and As partitioning in sediments in a well characterized, arsenicimpacted aquifer in Van Phuc, Vietnam.

Sediment iron mineralogies reveal a wide range of Fe mineralogies in sediments undergoing active Fe reduction, but most sediments contained at least 25% Fe(III) in Fe oxyhydroxides. These Fe minerals were transformed to Fe(II) carbonate, green rusts, and, rarely, iron sulfides. Throughout Pleistocene and Holocene aquifers, S cycling organisms were among the most abundant, while no iron reducing bacteria were found in abundances higher than 1%. In many cases, sulfide oxidizing autotrophs were abundant, even in orange sand aquifers. Given that sulfate concentratiosn are <2 mg/L in these aquifers, these organisms can only be supported by extensive S recycling. The activity of these S-cycling organisms appears to significantly alter As fate-abundant As sulfides are found in many Fe(III)-rich environments, while more reduced environments, often containing more crystalline Fe oxides, contain adsorbed As.

[1] Hansel et al. (2015), ISME Journal 9, 2400-2412