Biogeochemical conditions governing arsenic migration in surface and subsurface environments

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Iron oxides are strong sorbents of arsenic, thereby regulating its fate and transport. As a consequence, reductive iron transformations can have pronounced influences on arsenic partitioning. In fact, the primary process by which arsenic is displaced from solids appears to be a shift from aerobic to anaerobic conditions. Nevertheless, it is presently unclear whether arsenic mobilization under anaerobic conditions results from a transformation from As(V) to As(III) or from mineralogical changes as a consequence of iron and manganese reduction. Furthermore, the specific conditions that may lead to arsenic release within anaerobic environments have yet to be fully resolved.

Here we examine desorption behaviour of arsenic from ferrihydrite-, goethite- and hematite-coated sand within aerobic and anaerobic systems under hydrodynamic conditions. It is widely believed that reductive transformation, inclusive of dissolution and recrystallization, invokes a displacement of As(III) and As(V). However, desorption and transport of As(V) is transitory whereas As(III) undergoes prolonged and pronounced desorption. Furthermore, we observe that ferrihydrite transformation limits (rather than promotes) desorption of As(III) under conditions of intense Fe(III) reduction, potentially through precipitation of a secondary arsenic-bearing ferrous-iron phase. Formation of reduced iron oxide phases through the generation of high Fe(II) concentrations (>0.8 mM) severely retards As(III) desorption. Conversely, at lower Fe(II) concentrations (<0.8 mM), ferrihydrite transformation does not appear to retard arsenite desorption—although it does not promote it either. Interestingly, we observe the greatest arsenite mobilization in the absence of Fe(II), and concomitant resulting mineralogical transformations of ferrihydrite.

In contrast to ferrihydrite, desorption of As(III) from both goethite- and hematite-coated sands is not impacted by aqueous Fe(II). Thus, long-term respiration on Fe(III) within goethite or hematite would result in arsenic release once the surface sites are sufficiently depressed to induce desorption. While As(III) desorption from hematite and goethite appears to fit the current paradigm of arsenic release under anaerobic conditions, (bio)transformation of ferrihydrite (or lepidocrocite) may in fact stabilize As(III), limiting its mobility within soils and sediments.