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Geochemistry of arsenic-rich shallow groundwaters in Cambodia

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We report here details of the occurrence in Cambodia of arsenic-rich (> 100 µg/l) groundwaters similar to those causing massive health impacts in Bengal and elsewhere. Particular attention has been paid to the aqueous phase speciation of arsenic and the relationships between compositional parameters that may inform models of the origin of these hazardously high arsenic concentrations.

Sampling of shallow (< 60 m) Quaternary alluvial aquifers in central and southern Cambodia was undertaken over the period July 2002 to November 2003 using standard water sampling and preservation methods. Speciation of arsenic was determined by IC-ICP-MS. Preservation of speciation during storage was checked by determination of As(III) and As(V) separated in the field using SPE cartridges.

Groundwater arsenic concentrations of up to 800 µg/l were found. The most significant "hot spots" were found SE of Phnom Penh in Kandal Province and are clustered close to the present-day courses of the Mekong and Bassac Rivers.

The groundwaters are mostly circumneutral, Ca-Mg-(Na)-HCO_3 dominated waters with low SO_4 & Cl. The As-rich groundwaters were further characterised by low Eh, high Fe and sometimes high Mn and NH_4, and as such, they are very similar to arsenic-rich groundwaters found in similar environments in the Ganges-Brahmaputra-Meghna Delta. Aqueous arsenic was almost exclusively inorganic, with As(III) generally predominating. Measured As(III)/As(V) ratios were broadly comparable to the equilibrium ratios calculated from *in situ* Eh and pH.

The inverse relationship between As and SO_4 and the lack of high As in very shallow groundwaters suggests that pyrite oxidation is unlikely to be the major mechanism of arsenic release from Cambodian aquifer sediments. Similarly no significant correlation of As with PO_4 was determined, lending no support to theories of competitive desorption.

Instead, the association of high As with low Eh and high Fe provides circumstantial evidence that, as in Bengal, microbially mediated dissolution of As-bearing hydrated ferric oxides may have been the dominant mechanism of release of sedimentary arsenic. Such a model is supported by our XAS studies of Cambodian aquifer sediments as well as by microbiological investigations ongoing in our laboratory.

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The arsenic problem during Aquifer Storage and Recovery (ASR)

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Aquifer storage and recovery (ASR) is the process of artificially recharging and storing excess water in a confined aquifer, then recovering that water at a time of need. Some concerns exist regarding widespread utilization of ASR in Florida due in part to the discovery that some recovered water samples from the upper Floridan Aquifer System (Suwannee Limestone) in southwestern Florida contain more than 100 µg/L arsenic, while the injected water is virtually arsenic free.

Our study shows that Suwannee Limestone ground water in the region is virtually arsenic-free (<0.5 µg/L) and oxygen depleted. The average arsenic concentration for 306 samples of the aquifer matrix is 3.5 ppm, which is higher than the global average for limestone of 2.6 ppm. Maximum arsenic concentrations for limestone samples range up to 54.1 ppm. Our combined geochemical, lithologic and mineralogical study of the Suwannee Limestone shows that: (1) The arsenic in the Suwannee limestone is primarily concentrated in trace minerals, particularly framboidal pyrite. (2) Framboidal pyrite contains arsenic at concentrations in excess of 1000 ppm, (3) Other trace minerals and organic material contain arsenic in much lower amounts when compared to framboidal pyrite. (4) Framboidal pyrite is ubiquitous throughout the Suwannee Limestone, but is most abundant in high porosity zones. (5) Previously suggested iron oxyhydroxide minerals are apparently not an important source of arsenic.

The breakdown of pyrite and mobilization of arsenic during ASR could be caused by a change in redox. In most Florida ASR operations, water rich in dissolved oxygen (DO) is introduced into the storage zone, as a result of prior ozone treatment. Thus, the injection of oxygen-depleted water could be an alternative to mitigate potential arsenic mobilization.

With respect to the world-wide operation of aquifer storage and recovery (ASR) facilities that intend to store water in low-DO limestone aquifer systems, it is important to carry out a detailed mineralogical/chemical investigation of the aquifer matrix prior to construction and operation. If arsenic-rich pyrite is present, the injection of oxygen-rich water will most likely cause a release of arsenic.