

## U(VI) sorption on montmorillonite in the presence of phosphate.

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Uranium (U) contamination of soils and groundwater is a serious environmental concern due to past mining, processing, and waste disposal activities. In oxidizing environments, U(VI) is the most stable valence state for uranium, occurring in the linear uranyl ion,  $UO_2^{2+}$ . Among the in-situ remediation strategies for oxic subsurface environments, phosphate-based treatments have generated significant interest. U(VI) has a strong affinity for phosphate, which can lead to the nucleation of low-solubility U(VI)-phosphate minerals or enhance U(VI) sorption to subsurface minerals via the formation of ternary surface complexes. In addition, U(VI)-phosphate associations are common forms of U(VI) in contaminated soils and sediments at U.S. Department of Energy (DOE) facilities, and have been observed in the Hanford 300 Area, the Oak Ridge Reservation, and the Fernald Site. However, the molecular mechanisms controlling U(VI) speciation in heterogeneous phosphate-bearing systems are currently poorly constrained, which hinders the design of efficient remediation strategies and the prediction of uranium transport in treated systems.

Previous work by coworkers in the U(VI)- $PO_4^{3-}$ -goethite ( $\alpha$ -FeOOH) system [1] has pointed towards the existence of ternary surface complexes at the goethite surface. The characterization of these species was possible thanks to the use of extended X-ray absorption fine structure (EXAFS) spectroscopy at the uranium  $L_{III}$ -edge. Following a similar approach in the present work, we investigated the effect of phosphate on U(VI) sorption on montmorillonite, a dioctahedral 2:1 clay mineral. Montmorillonite was chosen because phyllosilicate clays are a common component of the fine fraction of soils and sediments at many DOE sites. Previous work has also shown that montmorillonite is a strong sorbent for U(VI) [2,3].

In order to identify chemical divides that separate regimes where specific mechanisms (e.g. ternary surface complexation or precipitation of U(VI) phosphates) dominate, we determined U(VI) adsorption isotherms as a function of  $[PO_4^{3-}]$ , pH,  $P_{CO_2}$ , and electrolyte cation. To further characterize the nature of U(VI) speciation in these separate regimes, relevant samples were analyzed in more detail using EXAFS and XRD. Besides providing new knowledge of the U(VI)- $PO_4^{3-}$ -montmorillonite system, comparison with the previously studied goethite system will allow determinations of how sorbent structure influences uranium-phosphate reactions in heterogeneous systems, which is fundamental for potential remediation applications involving real soils and sediments.

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[2] McKinley *et al.* (1995) *Clays and Clay Minerals*, **43**, 586-598.

[3] Turner *et al.* (1996) *Geochim. Cosmochim. Acta* **60**, 3399-3414.

## Radiocarbon Analysis of Microbial DNA and PLFA from Arsenic Impacted Aquifers in Bangladesh.

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### Abstract

It is generally agreed that microbial respiration drives the release of arsenic from the sediment to water in drinking water aquifers throughout Southeast Asia. This microbial respiration requires organic carbon, and it is this source of organic carbon that is poorly constrained. It has been hypothesized that the carbon could be derived from: 1) young anthropogenic sources, 2) carbon deposited with the sediments, 3) carbon from organic rich peat lenses, or 4) older petroleum byproducts. However, no method is currently available to directly determine the source of organic carbon. In order to better constrain the source of organic carbon we developed a method to determine the radiocarbon signature of microbial DNA and phospholipids fatty acids (PLFAs) from groundwater samples. The radiocarbon signatures of the DNA and PLFA will reflect the source of organic carbon utilized by heterotrophic microbes. For DNA, the method includes filtering over 2,000 liters of groundwater onto a 0.2  $\mu$ m filter followed by DNA extraction and purification. For PLFAs the method includes filtering over 1,000 liters of groundwater onto a newly developed carbon free filter. The DNA method enables us to collect, extract, and purify over 150  $\mu$ g of DNA with an absorbance at 260/280 > 1.8 and an A260/230 > 2; indicating pure DNA. The new method was utilized at Site F in the Lashkardi Village, Araihaazar, Bangladesh. The site represents an area where rapid recharge of anthropogenic carbon might occur. Results indicate that in the Holocene Aquifer the DNA is significantly older than groundwater ages and does not contain modern carbon but is younger than estimated sediment ages. We hypothesize that the carbon in the aquifer is recharged at the water table and is significantly retarded as it is transported to depth. Further utilization of this novel method should help to better constrain the carbon sources driving arsenic release in the shallow aquifers of Southeast Asia.