Studies of interfacial reactions between arsenic and minerals and its significance to site characterization

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Abstract Natural attenuation remediation is based on the intrinsic attenuation capacities of the subsurface. Geochemistry of the subsurface controls the fate, transport, transformation, and bioavailability of contaminants. This paper demonstrates that interfacial reactions (e.g., adsorption, desorption, oxidation, or reduction) between arsenic and minerals play an important role in the natural attenuation of arsenic, and could present important pathways for arsenic cycling in the subsurface environment. Iron oxides and kaolinites were used for this experimental study. Based on the different behavior of minerals, it is suggested that some types of minerals can act as mineral indicators for site characterization. Integration of mineralogical and geochemical indicator parameters would greatly improve the quality of site characterization. The current MCL in the USA for arsenic in drinking water may soon be lowered to 5 μg/L. It is estimated that lowering the arsenic MCL would cost billions of dollars per year.

The natural attenuation could be a potential cost-effective approach for solving the problem of arsenic-contaminated groundwater.

Keywords Arsenic adsorption · Mineral indicators · Natural attenuation · Risk assessment · Subsurface remediation

Introduction

Groundwater contamination with arsenic has received increasing attention because there is a greater awareness that arsenic is the cause of skin and bladder cancers. Anthropogenic arsenic stems from various industrial wastes, including wastes from the manufacture of insecticides and pesticides, manufacture of fertilizers, mining and smelting industries, and tannery industries. Effluents from these industrial waste piles can greatly increase the concentration of arsenic in groundwater. Maximum concentration levels (MCLs) have been used as standards for drinking water. The current MCL for arsenic in drinking water in the USA is 50 μg/L. Recently, the US Environmental Protection Agency (EPA) has proposed reducing the arsenic standard from 50 to 5 μg/L. The American Water Work Association (AWWA) expects the proposed standard to cost 1.5 billion US dollars annually and 14 billion US dollars in capital costs (AWWA Regulatory Alert, 22 June 2000). Groundwater is a major source of drinking water. It is imperative to develop cost-effective technology for cleanup of groundwater with arsenic contamination.

Natural attenuation involves all processes which help to reduce the concentration and total mass of contaminants in the subsurface environment. When these processes show the capability of attaining site-specific remediation objectives in a reasonable time period compared to other alternatives, they may be selected alone or in combination with other more active remedies as the preferred remedial alternative. Therefore, site characterization plays a central role in natural attenuation, i.e., how well scientists and engineers know about the fate of contaminants in the subsurface environments. A US National Research Council natural attenuation committee rated the likelihood that natural attenuation will succeed as a remedial strategy as

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being “high”, “moderate”, or “low” for different types of contaminants. A high level means “there is good scientific understanding of the process involved, and field evidence confirms the attenuation process can protect human health and the environment.” A moderate level means that “studies confirm that the dominant attenuation process occurs, but the process is not well understood scientifically.” A low level means “scientific understanding is inadequate to judge if and when the dominant process will occur and whether it will be protective.” (Macdonald 2000).

Biological degradation, and chemical and physical immobilization, are the basis of natural attenuation. Biodegradation is an important destructive attenuation; for instance, biodegradation of fuel hydrocarbons, like benzene, toluene, ethylbenzene, and total xylene (BTEX), is greatly affected by the availability of electron acceptors. Degradation of BTEX generally proceeds until all of the contaminants biochemically accessible to the microbes are destroyed. Biodegradation of highly chlorinated solvents, like tetrachloroethene (PCE) and trichloroethene (TCE), proceeds under natural conditions via reductive dechlorination. This process requires both electron acceptors and donors (Wiedemeier and others 1998).

Non-destructive attenuation includes processes such as sorption, dispersion, precipitation, etc. Non-destructive attenuation plays a central role in the natural attenuation of inorganic contaminants, e.g., arsenic, in the subsurface. The redox conditions of the subsurface govern the fate and transport of arsenic, for example reducing conditions in alluvial aquifers, resulting in significant exposures to the natural occurrence of As(III), which is more toxic and mobile than As(V). Geochemistry of arsenic in the environment has been reviewed (Cullen and Reimer 1989; Korte and Fernando 1991). This paper demonstrates that interfacial reactions (e.g., adsorption, desorption, oxidation, or reduction) between arsenic and minerals could present an important pathway for arsenic cycling in the subsurface environment. Minerals, such as silicates, clays, and iron hydroxides, are found in all types of sediments, soils, and as suspended particles in lakes, rivers, and estuaries. They can behave differently toward the attenuation of arsenic. Occurrence of the minerals varies from place to place, or zone to zone in the subsurface, and is influenced by geochemical conditions and geological surroundings. Minerals can play important roles in controlling the fate, transformation, and transport of arsenic in the subsurface environments. Unfortunately, mineralogical studies of the subsurface have been largely neglected so far. To a certain extent, many natural attenuation processes have not yet been explicitly investigated. One reason could be because of the limited understanding of the reactions between minerals and contaminants. The objective of this experimental study was to investigate the behavior of minerals in the adsorption/desorption and oxidation/reduction of arsenic. In addition, this paper will discuss some minerals which may serve as potential indicators for natural attenuation site characterization at arsenic-contaminated sites.

Methodology

Determination of As(V) and As(III) adsorption

A batch test was conducted to investigate the adsorption of As(V) and As(III). A 50-mg sample was treated in a 50 mL crimp-cap vial with 0.03, 0.3, 0.6, 1.2, and 1.5 mM As(V) and As(III) solutions, respectively. The vials were sealed with Teflon-coated rubber-septa in a glove box. Then, the suspension was shaken for 24 h and then filtered using a membrane filter (0.1-μm pore size). The filtrates were analyzed using inductively coupled plasma – atomic emission spectrometry (ICP-AES) for total concentration of As(V) and As(III). Concentration of adsorbed As(III) or As(V) was the difference between the initial As (III) or As(V) concentration and the total equilibrium supernatant As(III) or As(V) concentration.

Desorption of As(III) and As(V)

The arsenic-treated samples were extracted with a 1-mM mixture of KH₂PO₄/K₂HPO₄ to determine the desorption of As(V) and As(III). The residual solids were suspended in a 50-mL crimp-cap vial with 1 mM solution of 50:50 KH₂PO₄/K₂HPO₄ (pH 7). The purpose of this extraction was to desorb As(III) and As(V) adsorbed on the surfaces of the mineral phases through competitive ligand exchange with H₂PO₄⁻ and HPO₄²⁻. The vials were sealed with Teflon-coated rubber-septa in a glove box. After a 48-h shaking reaction period, the suspension was filtered using a membrane filter (0.1-μm pore size). The filtrates were analyzed for arsenic speciation using ion chromatography – graphite furnace atomic absorption spectrometry (IC-GFAAS) and ion chromatography – hydride generation – atomic fluorescence spectrometry (IC-HG-AFS). The desorption of As(III) and As(V) is defined as the difference between the quantities of As(III) and As(V) adsorbed by minerals and the quantities of As(III) and As(V) extracted from As(V)- and As(III)-treated minerals. More detailed method descriptions of determining arsenic adsorption and desorption were given in a previously published paper (Lin and Puls 2000).

Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR data were collected on a computer-controlled Digilab model FTS-45 FTIR Spectrophotometer operating under Digilab Win-IR software and equipped with an MTEC Model 200 photoacoustic (PA) cell. Sample and background spectra were collected over the 4,000 to 400 cm⁻¹ range using 256 scans at a resolution of 4 cm⁻¹ in the FTIR-PAS mode (i.e., data points were recorded every 2 cm⁻¹). Spectral manipulations and band component analyses were carried out using the GRAMS/32 version 5 IR/Raman software application package written by Galactic Industries Corporation (New Hampshire).

X-ray diffraction (XRD) analysis

The XRD analysis was performed at the School of Geology and Geophysics at the University of Oklahoma. (A part of the XRD analyses was conducted at the OMNI Laboratory...