Available online at www.sciencedirect.com
ScienceDirect
Science of the Total Environment 379 (2007) 133–150
Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind
www.elsevier.com/locate/scitotenv

Arsenic attenuation by oxidized aquifer sediments in Bangladesh

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Received 11 May 2006; received in revised form 8 November 2006; accepted 20 November 2006

Abstract

Recognition of arsenic (As) contamination of shallow fluvio-deltaic aquifers in the Bengal Basin has resulted in increasing exploitation of groundwater from deeper aquifers that generally contain low concentrations of dissolved As. Pumping-induced infiltration of high-As groundwater could eventually cause As concentrations in these aquifers to increase. This study investigates the adsorption capacity for As of sediment from a low-As aquifer near Dhaka, Bangladesh. A shallow, chemically-reducing aquifer at this site extends to a depth of 50 m and has maximum As concentrations in groundwater of 900 µg/L. At depths greater than 50 m, geochemical conditions are more oxidizing and groundwater has <5 µg/L As. There is no thick layer of clay at this site to inhibit vertical transport of groundwater.

Arsenite [As(III)] is the dominant oxidation state in contaminated groundwater; however, data from laboratory batch experiments show that As(III) is oxidized to arsenate [As(V)] by manganese (Mn) minerals that are present in the oxidized sediment. Thus, the long-term viability of the deeper aquifers as a source of water supply is likely to depend on As(V) adsorption. The adsorption capacity of these sediments is a function of the oxidation state of As and the concentration of other solutes that compete for adsorption sites. Arsenite that was not oxidized did adsorb, but to a much lesser extent than As(V). Phosphate (P) caused a substantial decrease in As(V) adsorption. Increasing pH and concentrations of silica (Si) had lesser effects on As(V) adsorption. The effect of bicarbonate (HCO_3) on As(V) adsorption was negligible. Equilibrium constants for adsorption of As(V), As(III), P, Si, HCO_3, and H were determined from the experimental data and a quantitative model developed. Oxidation of As(III) was modeled with a first-order rate constant. This model was used to successfully simulate As(V) adsorption in the presence of multiple competing solutes. Results from these experiments show that oxidized sediments have a substantial but limited capacity for removal of As from groundwater.
Published by Elsevier B.V.

Keywords: Arsenic; Adsorption; Modeling; Groundwater; Bangladesh; Natural remediation

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0048-9697/$ - see front matter. Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2006.11.029

1. Introduction

Arsenic concentrations in shallow alluvial aquifers of Bangladesh and the neighboring Indian state of West Bengal often exceed the recommended drinking water standard of 10 μg/L (WHO, 1993) and the Bangladesh standard of 50 μg/L, and are a major health concern for the millions of people who rely on these aquifers for drinking water (Das et al., 1996; BGS and DPHE, 2001). Arsenic is derived from erosion of lithified sediments and crystalline rocks of the Himalayan range and adjacent regions (Uddin and Lundberg, 1998; Breit et al., 2003). Sediment is deposited on floodplains and across the lower delta where it is subjected to intense chemical weathering. Variable redox conditions and mineral dissolution/precipitation redistribute As among the solid phases (Acharyya et al., 2000; Dowling et al., 2002; Breit et al., 2003). The most widely accepted mechanism for high concentrations of As in groundwater is reduction of Fe(III) oxides and release of associated As to solution (Bhattacharya et al., 1997; Nickson et al., 1998; McArthur et al., 2001). Sulfide oxidation also has been postulated as a source of As, especially in West Bengal, India (Chakraborti et al., 2001), but this mechanism has now been largely abandoned.

Most high-As groundwater is found in wells <100 m deep, that are screened in Holocene alluvial and deltaic deposits (Ravenscroft et al., 2005; Kinniburgh et al., 2003). Aquifers associated with high-As groundwaters are typically reducing and composed of gray to black sand. Organic carbon concentrations generally range from <0.5 to 5%, although concentrations as high as 34% have been reported in layers of peat (Anawar et al., 2003; McArthur et al., 2004). Arsenite is the dominant oxidation state measured in most groundwater samples with relatively minor [As(V)] concentrations (BGS and DPHE, 2001). Arsenic in the solid phase of reduced sediments is predominantly As(III); chemical and spectroscopic evidence indicates an association between As(III) and phyllosilicate minerals (Foster et al., 2000; Breit et al., 2001; Swartz et al., 2004). Arsenic associated with diagenetic pyrite also has been reported (Stuben et al., 2003), but is not considered to be the principal sink for As in the shallow sediment (Zheng et al., 2004; Lowers et al., in press). Sediment concentrations of As are related to grain size, and generally range from about 1 mg/kg in sandy sediments to 20 mg/kg in clay layers (Tanabe et al., 2001; Harvey et al., 2002; Anawar et al., 2003; Sengupta et al., 2004).

In many areas, shallow high-As aquifers are underlain by oxidized sediments that are considered Pleistocene in age and have groundwater concentrations of As <10 μg/L (Chakraborti et al., 1999; BGS and DPHE, 2001; Harvey et al., 2002). These sediments are various shades of olive to brown in color because of Fe (III) oxide minerals. Organic carbon concentrations are <0.1% (McArthur et al., 2004; Swartz et al., 2004). Arsenic concentrations in the oxidized sediments are similar to concentrations in the reduced sediments of similar grain size, but As(V) is the dominant species, and the As(V) is associated with Fe(III) oxides (Foster et al., 2000). The preserved lateral extent and depth of this unit is variable depending on erosion and reworking of sediment but is typically within 50–100 m of the ground surface (Goodbred and Kuehl, 2000). Subaerial exposure of these sediments during the sea level low stand at the end of the Pleistocene is considered responsible for the formation of ferric oxides and loss of organic matter (Umitsu, 1993). In some areas such as the Barind Tract and Madhupur Terrace, the oxidized sediments were uplifted and are exposed at the surface (Goodbred and Kuehl, 2000).

Exploitation of these deeper oxidized aquifers in the Bengal Basin as a source of low-As water supply is increasing. New well screens are located from a few meters to more than 100 meters beneath the high-As aquifers (Yu et al., 2003; von Bromssen et al., 2005, 2006, this volume). There is a risk that excessive groundwater withdrawal could induce infiltration of high-As groundwater and contaminate the deeper aquifers (Ravenscroft et al., 2001; Harvey et al., 2002; van Geen et al., 2003). A clay aquitard, 10 m or greater in thickness, separates the high-As and low-As groundwaters in some places and could limit downward movement of contaminated groundwater (McArthur et al., 2004; Swartz et al., 2004). However, these clay layers are commonly discontinuous and reduced sandy sediments directly overlie the oxidized sediments in many areas (BGS and DPHE, 2001; Horneman et al., 2004; Swartz et al., 2004). Pumping could cause downward movement of shallow groundwater to the oxidized sands in a relatively short time (Cuthbert et al., 2002). Therefore, the capacity of oxidized sediments for As attenuation is important to the long-term viability of deeper aquifers for water supply.

Adsorption is likely to be the primary mechanism for removal of As from groundwater by oxidized sediments containing Fe(III) oxides (e.g. Stollenwerk, 2003). Adsorption efficiency depends on several factors including the concentration and oxidation state of As, the concentrations of other solutes that compete with As for adsorption sites, and the adsorption capacity of the sediment. There is evidence that oxidation of As(III) to