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Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modeling

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ABSTRACT

This study assesses the role of competing ions in the mobilization of arsenic (As) by surface complexation modeling of the temporal variability of As in groundwater. The potential use of two different surface complexation models (SCMs), developed for ferrihydrite and goethite, has been explored to account for the temporal variation of As(III) and As(V) concentration, monitored in shallow groundwater of Bengal Basin over a period of 20 months. The SCM for ferrihydrite appears as the better predictor of the observed variation in both As(III) and As(V) concentrations in the study sites. It is estimated that among the competing ions, PO_4^{3-} is the major competitor of As(III) and As(V) adsorption onto Fe oxyhydroxide, and the competition ability decreases in the order $PO_4^{3-} \gg Fe(II) > H_4SiO_4 = HCO_3^-$. It is further revealed that a small change in pH can also have a significant effect on the mobility of As(III) and As(V) in the aquifers. A decrease in pH increases the concentration of As(III), whereas it decreases the As(V) concentration and vice versa. The present study suggests that the reductive dissolution of Fe oxyhydroxide alone cannot explain the observed high As concentration in groundwater of the Bengal Basin. This study supports the view that the reductive dissolution of Fe oxyhydroxide followed by competitive sorption reactions with the aquifer sediment is the processes responsible for As enrichment in groundwater.

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1. Introduction

During the last decades, the occurrence of arsenic (As) in drinking water has become a major environmental concern in many regions of the world, even in the countries of North America and Europe (Nriagu et al., 2007). Nevertheless, the problem is most severe in Bangladesh and West Bengal (jointly represents Bengal Basin), where its extent has been termed as the largest mass poisoning in human history (Smith et al., 2000).

Currently, the reductive dissolution of Fe oxyhydroxide, coupled to the microbially mediated oxidation of organic matter is the most widely accepted mechanism of As release in groundwater of the Bengal Basin (Berg et al., 2008; Bhattacharya et al., 1997; Harvey et al., 2002; Islam et al., 2004; McArthur et al., 2004; Mukherjee et al., 2008; Nath et al., 2008; Nickson et al., 1998; Polya and Charlet, 2009). Meanwhile, some studies have revealed that once As is released into groundwater, its mobility is primarily regulated by the extent of re-sorption onto the residual Fe oxyhydroxide present in the aquifer materials through formation of either inner-sphere or outer-sphere complexes (Wang and Mulligan, 2008), until adsorption sites become saturated or solid sorbents are completely dissolved (Pedersen et al., 2006; von Brömssen et al., 2008; Welch et al., 2000). In this context, competing ions such as phosphate (PO_4^{3-}), bicarbonate (HCO_3^-) and silicic acid (H_4SiO_4) might play a significant role in the mobilization of As by competing for similar adsorption sites of Fe oxyhydroxide (Sracek et al., 2004; Stollenwerk, 2003; von Brömssen et al., 2008). Nevertheless, despite its importance there is controversy regarding the relative roles of these components for As mobilization. For example, it is reported that PO_4^{3-} has a very strong affinity for adsorption sites on Fe oxyhydroxide and is a potential competitor for As adsorption in the natural environment (Acharyya et al., 1999; Dixit and Hering, 2003; Gao and Mucci, 2001; Jain and Loeppert, 2000; Manning and Goldberg, 1996). For the aquifers of Bangladesh, van Geen et al. (2008) have also found strong positive correlation between level of PO_4^{3-} exchangeable As in aquifer sediment and dissolved As concentration in groundwater, which led them to emphasize the role of adsorptive equilibria in the As mobilization. Meanwhile, Kim et al. (2000), Appelo et al. (2002), and Anawar et al. (2004) have claimed that the high concentration of HCO_3^- in groundwater may be responsible for the mobilization of As in Bengal Basin aquifers; however, this is not experimentally supported by Meng et al. (2000), Radu et al. (2005) and Stachowicz et al. (2007). Sometimes the adsorption of H_4SiO_4 has also been considered as a competitor of As adsorption onto Fe oxyhydroxide (Meng et al., 2000; Swedlund and Webster, 1999). Based on batch experiments involving multi-sorbate ions, Meng et al. (2002) have shown that although PO_4^{3-}, HCO_3^- and H_4SiO_4 can compete with As(III) adsorption onto Fe oxyhydroxide, their effect on As(V) adsorption is very small even at high concentration and suggested that the high mobility of As in Bengal Basin aquifers is due to their combined effect. Recently, by similar experiment and subsequent modeling, Stollenwerk et al. (2007) and Stachowicz et al. (2008) again have concluded that PO_4^{3-} is the major competitor for As adsorption and in the presence of significant PO_4^{3-} the competition of HCO_3^- becomes negligible. However, these contradictory conclusions are made mostly based on laboratory adsorption studies. Because of the complexity in simulation of the competitive adsorption equilibria (Stachowicz et al., 2008), so far only a very few studies (for e.g. Jessen et al., 2012; Postma et al., 2007; Swartz et al., 2004), have attempted to simulate the natural groundwater condition to assess the role of competing ions in the As mobilization.

The objective of the present study is to fill up the gap in existing knowledge with the assessment of relative roles of different competing ions in the As mobilization by means of surface complexation modeling of the naturally occurring As enriched groundwater in the aquifer of Bengal Basin. A total of 10 piezometers have been monitored for aqueous As and other important hydrogeochemical parameters including different competing ions, over a period of 20 months. Such monitoring has provided the opportunity to assess the role of different competitive adsorption equilibria in the As mobilization processes by testing the hypothesis that temporal variation of As in groundwater of Bengal Basin is governed by the variation in concentration of competing ions. Two different surface complexation models (SCMs) have been used to test this hypothesis. The relative roles of different competing ions in the As mobilization is assessed by testing the sensitivity of the modeled aqueous As concentration towards changes in the concentration of specific competing ion.

2. Materials and methods

2.1. *Piezometers installation, groundwater sampling and laboratory analysis*

Based on a survey at Chakdaha Block of Nadia District, West Bengal, two sites at the village of Sahispur (Site 1; 23°04′15.5″N, 088°36′33.5″E) and Chakudanga (Site 2; 23°04′58″N, 088°38′13″E), where the concentration of As in groundwater was high and relatively low respectively, were selected for piezometers installation (Biswas et al., 2011). At each site over an area of 25 m^2, five piezometers (well A, B, C, D and E) were installed with different screening positions (Site 1 – A: 12–21 m, B: 22–25 m, C: 26–29 m, D: 30–33 m and E: 34–37 m; Site – 2: A: 12–21 m, B: 24–27 m, C: 30–33 m, D: 36–39 m and E: 42–45 m) to collect multi depth groundwater samples (see Appendix for the picture of piezometer nests) (Biswas et al., 2011). Continuous sediment cores were collected during drilling of deepest piezometer (well E) at each site, using a split-spoon core barrel fitted to a PVC tube of 0.65 m length. Sediment samples were preserved in the field by flushing with N_2, followed by rubber capping at both end of the barrel.

The piezometers were sampled in 15 days intervals over a period of 20 months (December 2008–July 2010). The regular sampling interval at both sites was interrupted once, in the month December 2009, when pumping and in-situ bio-stimulation experiments were conducted at site 1 and 2 respectively (details of the experiments and results have been presented in Neidhardt et al. (2013a) and Neidhardt et al., (2014). The sampling was resumed again from January 2010. Groundwater was sampled for the analysis of major anions,