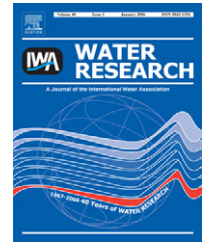


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# Mathematical model for predicting microbial reduction and transport of arsenic in groundwater systems

Mi-Sun Lim<sup>a,1</sup>, In Wook Yeo<sup>b,\*</sup>, T. Prabhakar Clement<sup>c</sup>, Yul Roh<sup>b</sup>, Kang-Kun Lee<sup>a</sup>

<sup>a</sup>School of Earth and Environmental Sciences, Seoul National University, Seoul, Korea

<sup>b</sup>Department of Earth and Environmental Sciences, Chonnam National University, Gwangju, Korea

<sup>c</sup>Department of Civil and Environmental Engineering, Auburn University, Auburn, Alabama, USA

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## ABSTRACT

A mathematical model was developed for describing the transport of arsenic, coupled with microbially-mediated biogeochemical processes. The biogeochemical characteristics of arsenic reactive transport processes were investigated in both batch and column tests, which showed that As(V) was reduced to As(III) by *Shewanella* sp., with the reduced arsenic species subsequently removed by precipitation. The breakthrough data obtained from the column experiments were used for the calibration of the arsenic reactive transport model. The reactive transport model, which only incorporated microbial reduction processes, showed a large discrepancy in predicting the observed As(III) concentration profiles, particularly later in the experiments. However, the model matched the experimental data much better with the inclusion of a term describing the precipitation process. Our results indicated that the precipitation reaction can be a major sink during microbially-mediated arsenic reactive transport. The proposed model provides a useful framework for predicting the transport of arsenic in saturated groundwater aquifers.

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## 1. Introduction

Arsenic from both anthropogenic and geologic sources is commonly found at trace levels within the subsurface, where it may exist in either the arsenopyrite (FeAsS), realgar (AsS) or orpiment (As<sub>2</sub>S<sub>3</sub>) forms (Newman et al., 1998). Arsenic is carcinogenic, and can also cause other human health effects, such as black disease and diabetes (Smedley and Kinniburgh, 2002). Understanding the mobility of arsenic in subsurface environments is important for evaluating its possible environmental and economic effects (Williams et al., 2003). The World Health Organization (WHO) suggests a maximum concentration limit (MCL) for arsenic in drinking water of 10 µg/L (WHO, 1993). This stringent standard has a significant impact on the management of arsenic contaminated sites,

since the technology for removing arsenic from groundwater may not be readily available at a local level.

Arsenic can be present in both organic and inorganic forms, and has four potential oxidation states (−3, 0, +3 and +5). In natural systems, arsenic mostly exists in inorganic forms, as oxyanions of arsenite, As(III), or as arsenate, As(V) (Adriano, 2001). In general, the inorganic forms of arsenic are more toxic than the organic forms. The inorganic forms of As(V) and As(III) have different sorption properties and toxicity levels (Anderson and Bruland, 1991; Bowell, 1994). As(III) is always more toxic than As(V) (Matschullat, 2000). Under oxidizing conditions, such as in well-mixed or oligotrophic surface waters, the predominant inorganic form of arsenic is arsenate (As(V) as H<sub>2</sub>AsO<sub>4</sub><sup>−</sup> and HAsO<sub>4</sub><sup>2−</sup>). On the other hand, under reducing conditions, such as ground water in an

\*Corresponding author. Tel.: +82 62 530 3457; fax: +82 62 530 3459.

E-mail address: [iwyeo@chonnam.ac.kr](mailto:iwyeo@chonnam.ac.kr) (I.W. Yeo).

<sup>1</sup> Current address: Korea Eco-Products Institute, Seoul, Korea.

organic-rich environment, the predominant form is arsenite (As(III) as  $\text{H}_3\text{AsO}_3^0$  and  $\text{H}_2\text{AsO}_3^-$ ) (Oremland and Stolz, 2003). As(V) can be strongly adsorbed onto the surface of several common minerals, such as ferrihydrite; whereas, As(III) adsorbs less strongly to these minerals. Therefore, in natural systems, As(III) is more mobile than As(V) (Oremland and Stolz, 2003). The distribution of arsenic species [As(III) and As(V)] in natural water is highly dependent on the redox potential (Eh) and pH values (Smedley and Kinniburgh, 2002).

Since sorption affects the mobility of arsenic in ground water systems, several controlled laboratory studies have been conducted to understand the sorption of arsenic species onto various types of soil mineral. These studies have reported that As(III) primarily sorbs onto sulfide minerals and metal oxides/oxyhydroxides (Dzombak and Morel, 1990; Huerta-Diaz and Morse, 1992). Islam et al. (2004) suggested that arsenic adsorbed onto sediment surfaces could be mobilized into groundwater by anaerobic respiration of Fe(III) reducing bacteria. In another study, Newman et al. (1997) reported that the As(V)-reducing bacterium, *D. auripigmentum*, could simultaneously reduce As(V) and  $\text{SO}_4$ , producing  $\text{H}_2\text{S}$  due to metabolic activity, which could precipitate the reduced As(III).

Previous studies on arsenic reactive transport have considered either the batch-scale equilibrium sorption or column-scale coupled adsorptive transport under abiotic conditions (Williams et al., 2003; Darland and Inskeep, 1997). None of these studies have considered the effects of the microbial reaction kinetics. Since microbial processes have a major influence on the fate of arsenic in aquifers (Newman et al., 1998), it is necessary to develop a comprehensive reactive transport model that can simultaneously describe microbially-mediated bio-chemical reactions as well as other advection–dispersion processes.

The objectives of this study were to develop and calibrate a reactive transport model that can describe the microbially-mediated reduction of As(V) to As(III) in saturated groundwater aquifers. The model was calibrated using both batch and column data. The biogeochemical kinetics was developed based on the observations from batch experiments, where a bacterial population was allowed to degrade organic matter by the consumption of arsenic as an electron acceptor. The kinetic reaction model was coded as a reaction module within the reactive transport model, RT3D (Clement, 1997; Clement et al. 1998). The results obtained from column experiments were then used to test the performance of the developed reactive transport model.

## 2. Model development

### 2.1. Conceptual model

Haque and Johannesson (2006) investigated the evolution of arsenic species along the path of groundwater flow in Florida, USA. Their study revealed that As(V) was the dominant species near the recharge area, and the concentration of As(III) progressively increased along the flow path, where the redox conditions were changed from oxic to anoxic. Further down-gradient, where the sulfide concentrations produced

due to microbially-mediated  $\text{SO}_4$  reduction were considerably high, the reduced arsenic was removed from groundwater. The field data showed that the microbial oxidation of organic matter, reductive dissolution of Fe(III) oxides/oxyhydroxides, and  $\text{SO}_4$  reduction and pyrite precipitation reactions influenced the evolution of arsenic and its speciation along the flow path. Newman et al. (1997, 1998) also indicated that microorganisms play critical roles in both the reduction and removal of As(V) from groundwater.

In our conceptual model, As(V) was assumed to be the dominant species present in natural aerobic systems. The influx of natural or anthropogenic organic substrates was assumed to promote microbial processes, which would result in the depletion of oxygen and a lowering of the redox potential. Under reducing condition, As(V)-reducing bacteria would respire adsorbed and/or dissolved As(V), with its conversion to As(III) (Oremland and Stolz, 2003; Haque and Johannesson, 2006) and subsequent removal by the precipitation process.

### 2.2. Mathematical model

#### 2.2.1. Solute transport

Solute transport equations describe both the multi-dimensional fate and transport of aqueous- and solid-phase species in saturated porous media (Clement, 1997):

$$\frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C_k) + \frac{q_s}{\phi} C_{sk} \pm r_k, \quad k = 1, 2, \dots, m, \quad (1)$$

$$\frac{\partial \tilde{C}_{im}}{\partial t} = \pm \tilde{r}_{im}, \quad im = 1, 2, \dots, (n - m), \quad (2)$$

where  $n$  is the total number of species,  $m$  the total number of aqueous-phase or mobile species,  $(n-m)$  the total number of solid-phase or immobile species,  $C_k$  the aqueous-phase concentration of the  $k$ th species (mg/L),  $\tilde{C}_{im}$  the solid-phase concentration of the  $im$ th species (mg/kg),  $D_{ij}$  the hydrodynamic dispersion coefficient ( $\text{cm}^2/\text{h}$ ),  $v_i$  the pore water velocity ( $\text{cm}/\text{h}$ ),  $q_s$  the volumetric flux of water per unit volume of the aquifer that represents the sources and sinks ( $\text{cm}^3/\text{h}/\text{cm}^3$ ),  $\phi$  the porosity,  $C_{sk}$  the concentration of source/sinks (mg/L),  $r_k$  represents all the aqueous-phase reaction rate terms (mg/L/h) that describe the mass of the species removed or produced per unit volume over time, and  $\tilde{r}_{im}$  represents all the solid-phase reaction rate terms (mg/kg/h).

The RT3D model requires the groundwater flow code, MODFLOW (A MODular three-dimensional finite-difference groundwater FLOW model), to generate a groundwater head distribution, and adopts the operator-split strategy, which allows the user to define various reaction models (Clement, 1997; Clement et al., 2000). A new kinetic model was developed, and then incorporated into the RT3D code in order to describe the fate and transport of arsenic in the subsurface environment.

#### 2.2.2. Arsenic transformation and transport

As described in the conceptual model, the arsenic transformation reaction is modeled as an oxidation–reduction process, where a carbonaceous substrate is oxidized to supply

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