

A Mathematical Model Development for Microbial Arsenic Transformation and Transport

Mi-Sun Lim, InWook Yeo*, Kang-Kun Lee

School of Earth and Environmental Sciences, Seoul National University
**School of Earth and Environmental Sciences, Chonnam National University*
(e-mail: imis58@snu.ac.kr)

<Abstract>

Arsenic is a toxic and carcinogenic metalloid, whose sources in nature include mineral dissolution and volcanic eruption. Abandoned mines and hazardous waste disposal sites are another major source of arsenic contamination of soil and aquatic systems. To predict concentrations of the toxic inorganic arsenic in aqueous phase, the biogeochemical redox processes and transport behavior need to be studied together and be coupled in a reactive transport model. A new reaction module describing the fate and transport of inorganic arsenic species (As(III)), dissolved oxygen, nitrate, ferrous iron, sulfate, and dissolved organic carbon are developed and incorporated into the RT3D code.

key word: arsenic, microbial transformation, reactive transport, RT3D

1. Introduction

Despite its low crustal abundance (0.0001%), arsenic is widely distributed in nature and has a common association with the ores of metals like copper, lead, and gold [Oremland and Stoltz, 2003]. In Korea, toxic materials from abandoned mines, including arsenic, emerge as a major contaminant. The most intense reduction of arsenic (V) to arsenic (III) are driven by microbial degradation of buried deposits of peat or organic-rich leachate from a landfill, which results in the most severe pollution [McArthur et al., 2001]. The objectives of this study are to develop the arsenic transport model describing As(V)-reduction in the sequential organic-carbon degradation processes with multiple electron acceptors by microbes, and to assess the performance of the developed reactive transport model.

2. Conceptual Model

Arsenic is found in nature as arsenite [As(III)] or arsenate [As(V)]. As(V) is dominant in aerobic condition and is strongly adsorbed to the several common minerals, but As(III) is predominant in anaerobic environment and is more mobile and toxic than As(V). The influx of substrate organic materials promotes microbial respiration and creates the anoxic conditions. Moreover, anoxic conditions results in the reduction of iron-oxyhydroxides (FeOOH) and the release of sorbed arsenic to solution [McArthur et al., 2001]. Dissimilatory arsenate -respiring prokaryotes (DARPs) respire adsorbed As(V), resulting in the release of As(III) into the aqueous phase. In aquifers, these microbial reactions may mobilize arsenic from the solid to aqueous phase, resulting in As-contaminated ground water [Oremland and Stolz, 2003]. Since the anaerobic environment prevails in most subsurface condition, the conceptual model developed for this study focuses on the mobilization of arsenic from the solid phase into the aqueous phase in a subsurface aquifer. The process of the oxidation of the As(III) by microbes (CAOs and HAOs) was not considered because this process is limited to the vicinity of wells constructed by human activity by providing oxidants, which could be not common in the natural subsurface aquifer.

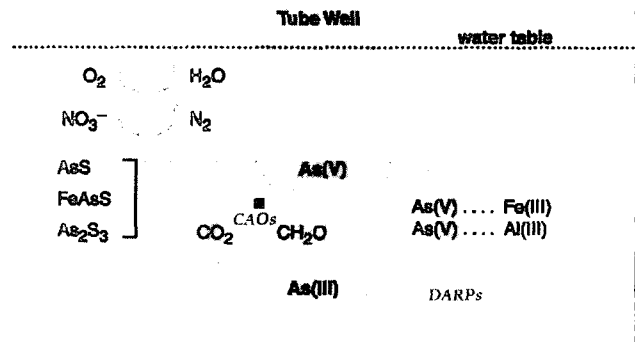


Fig. 12. A conceptual model of mobilization of arsenic from the solid phase into the aqueous phase in an aquifer. [after Oremland and Stolz, 2003]

In aquifers, these microbial reactions may mobilize arsenic from the solid to aqueous phase, resulting in As-contaminated ground water [Oremland and Stolz, 2003]. Since the anaerobic environment prevails in most subsurface condition, the conceptual model developed for this study focuses on the mobilization of arsenic from the solid phase into the aqueous phase in a subsurface aquifer. The process of the oxidation of the As(III) by microbes (CAOs and HAOs) was not considered because this process is limited to the vicinity of wells constructed by human activity by providing oxidants, which could be not common in the natural subsurface aquifer.

3. Mathematical Model

The dominant biogeochemical reactions used in the reactive transport model were the oxidation of electron donor (ED) by electron acceptor (EA). The common and assumed EAs in the subsurface aquifers are dissolved oxygen, nitrate, iron oxyhydroxides, arsenate, and sulfate. The EAs are listed in the expected sequence of use, which is established based on the Gibb's free energy of the redox reactions [Guoping et al., 1999].

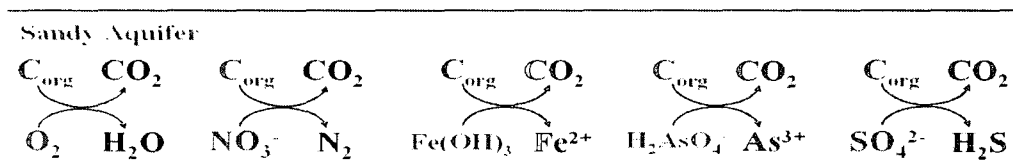


Fig. 2. Schematic view of an aquifer system showing redox reactions.

The organic carbon decay rates using five different EAs are approximated by five first-order decay terms. A Monod term is used to account for the presence (or the limitation) of various EAs, and an inhibition model is used to represent inhibition due to the presence of anyone of the earlier EAs (or the EAs' toxic effects) in the reaction chain. The kinetic model can be written as

$$\begin{aligned}
r_{C_{org},O_2} &= k_{C_{org},O_2} [C_{org}] \left[\frac{O_2}{K_{O_2} + O_2} \right] \\
r_{C_{org},NO_3^-} &= k_{C_{org},NO_3^-} [C_{org}] \left[\frac{NO_3^-}{K_{NO_3} + NO_3^-} \right] \left[\frac{k_{iO_2}}{k_{iO_2} + O_2} \right] \\
r_{C_{org},Fe^{3+}} &= k_{C_{org},Fe^{3+}} [C_{org}] \left[\frac{Fe^{3+}}{K_{Fe^{3+}} + Fe^{3+}} \right] \left[\frac{k_{iO_2}}{k_{iO_2} + O_2} \right] \left[\frac{k_{iNO_3^-}}{k_{iNO_3^-} + NO_3^-} \right] \\
r_{C_{org},As^{5+}} &= k_{C_{org},As^{5+}} [C_{org}] \left[\frac{As^{5+}}{K_{As^{5+}} + As^{5+}} \right] \left[\frac{k_{iO_2}}{k_{iO_2} + O_2} \right] \left[\frac{k_{iNO_3^-}}{k_{iNO_3^-} + NO_3^-} \right] \left[\frac{k_{iFe^{2+}}}{k_{iFe^{2+}} + Fe^{2+}} \right] \\
r_{C_{org},SO_4^{2-}} &= k_{C_{org},SO_4^{2-}} [C_{org}] \left[\frac{SO_4^{2-}}{K_{SO_4^{2-}} + SO_4^{2-}} \right] \left[\frac{k_{iO_2}}{k_{iO_2} + O_2} \right] \left[\frac{k_{iNO_3^-}}{k_{iNO_3^-} + NO_3^-} \right] \left[\frac{k_{iFe^{2+}}}{k_{iFe^{2+}} + Fe^{2+}} \right] \left[\frac{k_{iAs^{5+}}}{k_{iAs^{5+}} + As^{5+}} \right]
\end{aligned}$$

where r is the organic carbon utilization rate, k is the first order degradation rate, K is the half-saturation constant, and k_i is the inhibition constant. Since the concentration of biological available Fe^{3+} and As^{5+} are difficult to measure in the aqueous phase, these terms were replaced in the model to predict the products of these redox reactions. The concentrations of the products were limited by using two "expressed capacity" terms for iron-reduction and arsenic-reduction defined by the equations.

$$\begin{aligned}
[Fe^{3+}] &= [Fe^{2+}_{max}] - [Fe^{2+}] \\
[As^{5+}] &= [As^{3+}_{max}] - [As^{3+}]
\end{aligned}$$

The fate and transport of organic carbon and various EAs (or degradation products) in the saturated porous media can be written as:

$$\begin{aligned}
R_{C_{org}} \frac{\partial [C_{org}]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [C_{org}]}{\partial x_j} \right) - \frac{\partial (v_i [C_{org}])}{\partial x_i} + \frac{q_s}{\phi} [C_{org}]_s - r_{C_{org},O_2} - r_{C_{org},NO_3^-} - r_{C_{org},Fe^{3+}} - r_{C_{org},As^{5+}} - r_{C_{org},SO_4^{2-}} \\
R_{O_2} \frac{\partial [O_2]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [O_2]}{\partial x_j} \right) - \frac{\partial (v_i [O_2])}{\partial x_i} + \frac{q_s}{\phi} [O_2]_s - Y_{O_2/C_{org}} \cdot r_{C_{org},O_2} \\
R_{NO_3^-} \frac{\partial [NO_3^-]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [NO_3^-]}{\partial x_j} \right) - \frac{\partial (v_i [NO_3^-])}{\partial x_i} + \frac{q_s}{\phi} [NO_3^-]_s - Y_{NO_3^-/C_{org}} \cdot r_{C_{org},NO_3^-} \\
R_{Fe^{2+}} \frac{\partial [Fe^{2+}]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [Fe^{2+}]}{\partial x_j} \right) - \frac{\partial (v_i [Fe^{2+}])}{\partial x_i} + \frac{q_s}{\phi} [Fe^{2+}]_s + Y_{Fe^{2+}/C_{org}} \cdot r_{C_{org},Fe^{3+}} \\
R_{As^{3+}} \frac{\partial [As^{3+}]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [As^{3+}]}{\partial x_j} \right) - \frac{\partial (v_i [As^{3+}])}{\partial x_i} + \frac{q_s}{\phi} [As^{3+}]_s + Y_{As^{3+}/C_{org}} \cdot r_{C_{org},As^{5+}} \\
R_{SO_4^{2-}} \frac{\partial [SO_4^{2-}]}{\partial t} &= \frac{\partial}{\partial x_j} \left(D_{ij} \frac{\partial [SO_4^{2-}]}{\partial x_j} \right) - \frac{\partial (v_i [SO_4^{2-}])}{\partial x_i} + \frac{q_s}{\phi} [SO_4^{2-}]_s - Y_{SO_4^{2-}/C_{org}} \cdot r_{C_{org},SO_4^{2-}}
\end{aligned}$$

where Y is the stoichiometric yield value.

4. Nuemrial Example

The domain is a 350m×10m section of unconfined aquifer with a hydraulic gradient from the left (constant head of 100m) to the right sides (constant head of 99m) and thickness of 10m. The aquifer is assumed to be organic-rich with concentration of 100mg/L. The initial concentrations of oxygen(O^2), nitrate(NO_3^{-1}), ferrous iron(Fe^{2+}), arsenite(As^{3+}), and sulfate(SO_4^{2-}) are assumed to be 4.0mg/L, 20.0mg/L, 0.0mg/L, 0.0mg/L, and 10.0mg/L respectively. $[Fe^{2+}_{max}]$ and $[As^{3+}_{max}]$ are set at 25.0mg/L and 7.2mg/L.

Numerical experiment was run for 365 days to simulate the six reactive species. The variations of concentrations in terms of the time and distance are shown in Fig. 3(a) and (b). Fig. 3. shows the organic-carbon degradation as it is consumed by sequential multiple electron acceptors. Especially, the As(V) reduction to As(III) causes the arsenic (III) mobilization and its subsequent transport.

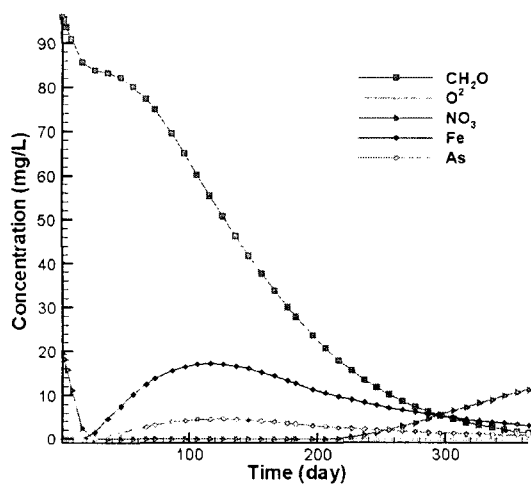


Fig. 3.(a)The variations of concentrations versus the time at 75m

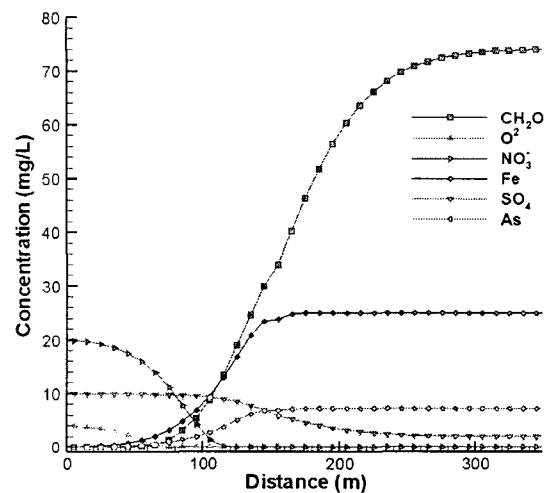


Fig. 3.(b)The variations of concentrations versus the distance at 26day

5. Conclusions

The developed arsenic transformation and transport model showed a reasonable distribution of arsenic (III). However, this run is still preliminary and is being planned to be further tested against the laboratory or field data. The model can be used to predict mobilization of arsenic and evolution of its contaminant plume in groundwaters.

Acknowledgement

This study is financially supported by the Ministry of Science and Technology through KISTEP (M1030400003-03B4200-00310), which is greatly acknowledged.

References

- Clement, T. P., 1997. RT3D-A modular computer code for simulating reactive multi-species transport in 3-dimensional groundwater aquifers, Pacific Northwest National Laboratory Report, PNNL-11720.
- Lu, G., T. P. Clement, C. Zheng, and T. H. Wiedemeier, Natural Attenuation of BTEX Compounds: Model Development and Field-Scale Application, *Ground Water*, 37(5), 707-717, 1999
- McArthur, J. M. P. Ravenscroft, S. Safiulla, and M. F. Thirlwall, Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh, *Water Resources Research*, 37(1), 109-117, 2001
- Oremland, R. S. and Stolz, J. F., The Ecology of Arsenic, *SCIENCE*, 300(9), 939-944, 2003