Imaging geochemical heterogeneities using inverse reactive transport modeling: An example relevant for characterizing arsenic mobilization and distribution

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ABSTRACT

The spatial distribution of reactive minerals in the subsurface is often a primary factor controlling the fate and transport of contaminants in groundwater systems. However, direct measurement and estimation of heterogeneously distributed minerals are often costly and difficult to obtain. While previous studies have shown the utility of using hydrologic measurements combined with inverse modeling techniques for tomography of physical properties including hydraulic conductivity, these methods have seldom been used to image reactive geochemical heterogeneities. In this study, we focus on As-bearing reactive minerals as aquifer contaminants. We use synthetic applications to demonstrate the ability of inverse modeling techniques combined with mechanistic reactive transport models to image reactive mineral lenses in the subsurface and quantify estimation error using indirect, commonly measured groundwater parameters. Specifically, we simulate the mobilization of arsenic via kinetic oxidative dissolution of As-bearing pyrite due to dissolved oxygen in the ambient groundwater, which is an important mechanism for arsenic release in groundwater both under natural conditions and engineering applications such as managed aquifer recharge and recovery operations. The modeling investigation is carried out at various scales and considers different flow-through domains including (i) a 1D lab-scale column (80 cm), (ii) a 2D lab-scale setup (60 cm × 30 cm) and (iii) a 2D field-scale domain (20 m × 4 m). In these setups, synthetic dissolved oxygen data and forward reactive transport simulations are used to image the spatial distribution of As-bearing pyrite using the Principal Component Geostatistical Approach (PCGA) for inverse modeling.

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1. Introduction

Accurate identification of physical and geochemical aquifer properties controlling groundwater contaminant behavior is critical for reliable contaminant plume prediction, remediation design and operation, and effective management of groundwater resources. Spatially distributed physical and geochemical heterogeneities control solute transport in groundwater; thus, they are of pivotal importance for understanding the fate of contaminants in the subsurface. Over the last few decades, numerous studies have focused on identifying spatially distributed physical properties of aquifers including hydraulic conductivity, porosity, and specific storage. Examples of widely used characterization techniques include pressure-based methods, such

as hydraulic tomography [1–4], and geophysical-based methods including electrical resistivity tomography [5,6] and ground penetrating radar [7,8]. The pressure-based methods use pressure measurements, which are directly sensitive and mechanistically linked to the physical parameters of interest through the groundwater flow equation, to infer the spatial parameters, i.e., hydraulic conductivity fields. The geophysical-based methods can be used to map lithologic heterogeneities in regions that are difficult to install bore wells and implemented jointly with pressure-based methods. These techniques have been applied to successfully estimate or "image" the physical heterogeneity of the subsurface in field cases (e.g., [1]). Here, and throughout this manuscript, the term "imaging" is used to describe the estimation of the spatial distribution of an aquifer property of interest.

The spatial distribution of biogeochemical properties exerts a key control on contaminant transport. For instance, the heterogeneous distribution of organic matter in aquifer systems is necessary for understanding the sorption of both organic compounds [9–12] and inorganic contaminants, including arsenic [13–19]. Similarly, the

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location of reactive mineral phases can control the fate of metals and metalloids [20–22], mineral precipitation/dissolution rates [23], and bioclogging [24] in porous media. Therefore, to quantitatively understand contaminant transport and to implement successful groundwater management strategies, it is important to characterize the spatial distribution of geochemical properties. However, only a limited number of studies have been conducted to infer spatially heterogeneous geochemical fields, likely due to (1) the limited amount of sparse measurements available at the field scale, (2) the challenge in formulating quantitative descriptions of controlling geochemical processes in the framework of groundwater flow and reactive transport models, and (3) the complexity and computational burden associated with multi-species reactive transport modeling-based inversions. Recent works overcome the former by applying geophysical-based methods to estimate the spatial distribution of reactive elements and mineral phases [25–31] as well as reactive facies [32,33]. While these methods have been successfully applied to field settings with promising results, these approaches still require collecting a large amount of geochemical data to develop a site-specific petrophysical relationship (from geophysical to hydro-geochemical properties) or correlation while the true relationship may not be unique or one-to-one [34]. In this study, we propose an effective geochemical imaging method using reactive transport based inverse modeling as well as the information content of sparse groundwater chemistry data perturbed by the controlling geochemical processes. We demonstrate the capability of the proposed method to image spatially distributed geochemical properties of several synthetic domains using sparse aqueous concentration data. We focus on geochemical environments relevant to the mobilization of arsenic via mineral dissolution in aquifer systems. In the last few decades, numerous studies have focused on understanding geochemical controls of As mobilization. While these studies have greatly contributed to developing a geochemical framework for As reactivity in the environment, arsenic contamination of groundwater remains problematic in aquifers throughout the world. Research efforts can be enhanced by developing inexpensive and efficient methods for quantifying As distribution in aquifer sediments.

Arsenic is a toxic metalloid and a naturally occurring contaminant that poses a significant threat to groundwater quality. The release of native As from sediments into surrounding pore water can be attributed to shifts in water chemistry via four principal mechanisms: (1) ion-displacement, (2) shifts in pH to alkaline values exceeding 8.5, (3) reduction of arsenate to the more labile arsenite and (4) dissolution of arsenic-bearing minerals [35–37]. The spatial distribution of As-bearing heterogeneities is a controlling factor in all the above-mentioned processes. Here, we focus on mechanism (4) which is relevant in natural and managed aquifers with fluctuating redox environments [38–46]. Specifically, we are interested in imaging As-bearing sulfidic minerals such as arsenopyrite and arsenian pyrite which can be a source of dissolved As in groundwater, particularly in shifting redox environments including injection of oxidizing recharge water into previously anoxic aquifers as part of aquifer storage and recovery operations [47–50].

The outline of the paper is as follows: in Section 2, we present the proposed methodology for forward and inverse modeling. The forward reactive transport model describes the mobilization of As via kinetic oxidative dissolution of As-bearing pyrite due to dissolved oxygen (DO) in the ambient groundwater. The inverse model is based on the computationally-efficient Principal Component Geostatistical Approach (PCGA) [3,51]. Considering increasing complexity and accounting for the scale-dependent spatial distribution of As-bearing minerals (Fig. 1), the modeling investigation was carried out at multiple scales and considered different flow-through domains including (i) a 1D lab-scale column (80 cm), (ii) a 2D lab-scale setup (60 cm × 30 cm) and (iii) a 2D field-scale cross section (20 m × 4 m). In Section 3, we illustrate the results obtained using DO observations at selected locations, and forward and inverse modeling to produce the best estimate of the spatial distribution of As-bearing pyrite. We also analyzed the estimation uncertainty and performance of the PCGA-based inverse method. Concluding remarks are provided in Section 4.

2. Methods

The Principal Component Geostatistical Approach (PCGA) is a fast Jacobian-free geostatistical inversion approach that uses the leading principal components of the prior information to save computational costs. In this study, we propose the application of this method with reactive transport simulations of arsenic release. We used a forward reactive transport model including equilibrium and
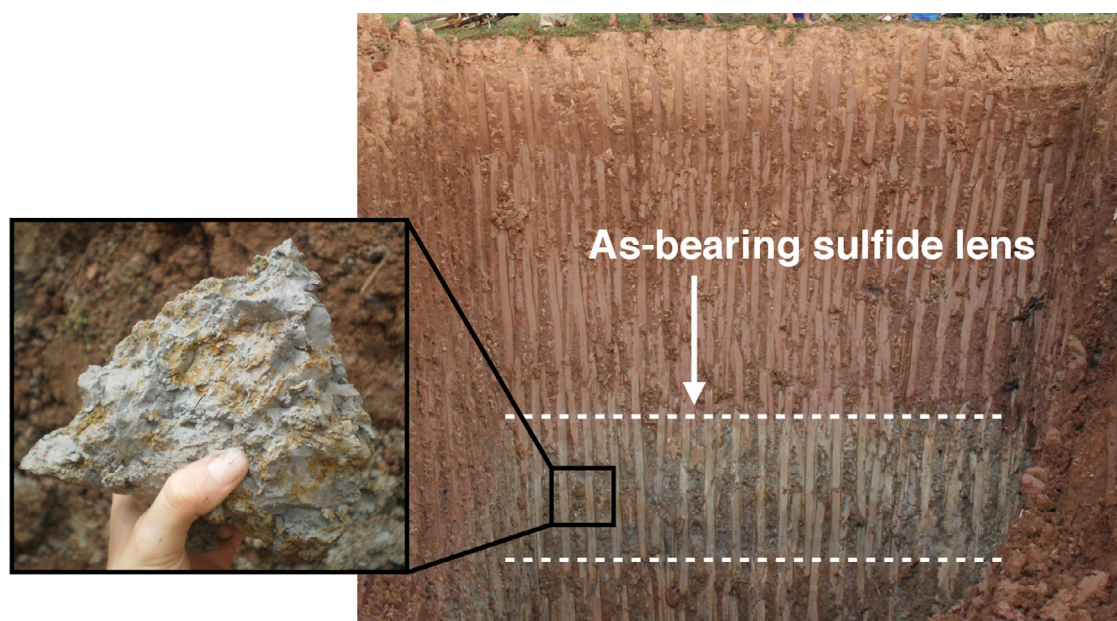

Fig. 1. Spatial distribution of arsenic-bearing sulfidic minerals (grey in color) at a 6 m depth (right) in sediments of the upper Mekong Delta, Cambodia. The distribution of sulfidic minerals has scale-dependencies as seen by the centimeter-variation within the sediments (left).