

Solid-phase arsenic speciation in aquifer sediments: A micro-X-ray absorption spectroscopy approach for quantifying trace-level speciation

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Abstract

Arsenic (As) is a geogenic contaminant affecting groundwater in geologically diverse systems globally. Arsenic release from aquifer sediments to groundwater is favored when biogeochemical conditions, especially oxidation-reduction (redox) potential, in aquifers fluctuate. The specific objective of this research is to identify the solid-phase sources and geochemical mechanisms of release of As in aquifers of the Des Moines Lobe glacial advance. The overarching concept is that conditions present at the aquifer-aquitard interfaces promote a suite of geochemical reactions leading to mineral alteration and release of As to groundwater. A microprobe X-ray absorption spectroscopy (μ XAS) approach is developed and applied to rotosonic drill core samples to identify the solid-phase speciation of As in aquifer, aquitard, and aquifer-aquitard interface sediments. This approach addresses the low solid-phase As concentrations, as well as the fine-scale physical and chemical heterogeneity of the sediments. The spectroscopy data are analyzed using novel cosine-distance and correlation-distance hierarchical clustering for Fe 1s and As 1s μ XAS datasets. The solid-phase Fe and As speciation is then interpreted using sediment and well-water chemical data to propose solid-phase As reservoirs and release mechanisms. The results confirm that in two of the three locations studied, the glacial sediment forming the aquitard is the source of As to the aquifer sediments. The results are consistent with three different As release mechanisms: (1) desorption from Fe (oxyhydr)oxides, (2) reductive dissolution of Fe (oxyhydr)oxides, and (3) oxidative dissolution of Fe sulfides. The findings confirm that glacial sediments at the interface between aquifer and aquitard are geochemically active zones for As. The diversity of As release mechanisms is consistent with the geographic heterogeneity observed in the distribution of elevated-As wells.

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1. INTRODUCTION

Arsenic (As) is a naturally-occurring (geogenic) contaminant affecting groundwater in geologically diverse systems

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in Asia, Europe, Africa, and North and South America. In many cases, As contamination is localized within specific aquifer sediments due to a confluence of hydrological, geochemical, and biological conditions (Stuckey et al., 2015). Despite the localized aspect of As contamination of groundwater, the conditions needed to produce contamination are found in many locations worldwide (Smedley and Kinniburgh, 2002).

Arsenic in aquifer sediments is often associated with iron (Fe) and sulfur (S) minerals, primarily (oxyhydr)oxides and sulfides of Fe. Arsenic-bearing Fe sulfides, such as arsenopyrite, FeAsS, or As-rich pyrite FeS_{2-x}As_x, are minerals that are favored under chemically reducing conditions (Schreiber and Rimstidt, 2013). Under chemically oxidizing conditions As is associated with Fe(oxyhydr)oxides, such as goethite (α -FeOOH), through sorption and co-precipitation reactions. From the perspective of As removal from and release to groundwater, these mineral types represent oxidation-reduction (redox) end-members. Each is a solid-phase reservoir with strong potential for As release when (bio)geochemical conditions, especially redox, in aquifers change. A good understanding of As speciation in the solid phase is necessary to identify the processes liberating As to waters (Kocar et al., 2008; Haque et al., 2008; Quicksall et al., 2008; Saalfeld and Bostick, 2009).

The hydrogeochemical gradients found at interfaces between different sediment types, for example aquifer and aquitard sediments, are thought to create active biogeochemical reaction zones (McMahon, 2001). For As in glacial aquifers, this principle has been demonstrated through a statistical comparison of As concentrations in 1000s of wells on a regional-scale with screened intervals with varying proximity to an aquitard. Wells that were screened near the aquitard were more likely to have elevated well-water As concentrations than wells with screens farther from the aquitard (Erickson and Barnes, 2005a). These findings generated the first tractable explanation for the geographic distribution of elevated As in wells completed in confined glacial aquifers: the aquifer-aquitard contact zone is a hot-spot for As mobilization from the solid-phase to the aqueous-phase (Erickson and Barnes, 2005b).

The objective of the present research is to identify the solid-phase sources of As in the complex glacial aquifer system of the Des Moines Lobe glacial advance, and use that information to explain the geographic distribution of As-affected wells within this aquifer system. Our hypothesis is that the aquifer-aquitard contact zones are locations of oxidative (e.g. As-bearing pyrite) or reductive (e.g. As-sorbed ferrihydrite) alteration of minerals that release of As to groundwater. Three specific As release mechanisms are relevant for glacial aquifers and aquitards: desorption, reductive dissolution of Fe(III)(oxyhydr)oxides, and oxidative dissolution of sulfide minerals (Harvey and Beckie, 2005) (Electronic Annex, EA Appendix 1: As release mechanisms).

In this contribution we use an As 1s and Fe 1s (K-edge) microprobe X-ray absorption spectroscopy (XAS) approach to identify the solid-phase speciation of As in aquifer sediments collected from an As-affected region of the Des Moines Lobe glacial advance. We describe and

quantify differences in As speciation among: (1) aquifer sediments, (2) mid-aquitard sediments, and (3) aquitard sediments at the aquifer-aquitard contact. Our analytical approach follows a quantitative track and a descriptive track. For the quantitative track, we use sediment chemistry and a novel As speciation mapping approach to measure the total As concentration as well as relative abundance of four As species types:

- (1) mineral-bound arsenate — As(V),
- (2) mineral-bound arsenite — As(III),
- (3) As(III)-sulfide — orpiment-type sulfide in which As is the metal bound to reduced S, and
- (4) As(-I) sulfide — arsenopyrite and arsenian-pyrite type sulfides, in which As substitutes for sulfur in the disulfide and is bound to both Fe and S.

For the descriptive track, we use linear combination fitting and hierarchical clustering of X-ray absorption near-edge structure (XANES) spectra to describe As and Fe speciation in detail at discrete points in each sample. The spectroscopic data are interpreted in the context of existing databases of well water chemistry.

2. MATERIALS AND METHODS

2.1. Regional setting

Samples for analysis were collected from rotary-sonic cores of glacial deposits within the footprint of the Des Moines Lobe Glacial advance in west-central Minnesota, USA (Fig. 1) (Welch et al., 2000). This region is a nexus of drinking-water wells that exceed the U.S. EPA maximum contaminant level (MCL) As > 10 $\mu\text{g L}^{-1}$. The upper aquifers are glacial materials deposited by different ice-streams within the Des Moines Lobe. These fast-moving glaciers were similar to those active in Antarctica today and originated from an ice dome in what is now central Canada at the end of the last glaciation (Patterson, 1998; Jennings, 2006). The ice-streams had different points of origin and traveled different paths and therefore entrained and deposited diverse geologic materials (Slatt and Eyles, 1981). The geographic extent of the sediments is controlled by bedrock and pre-Des Moines-lobe glacial deposit topographic highs to the east and west. Des Moines Lobe ice-stream sediments are underlain by older aquifer sediments from previous glacial periods (Harris et al., 1999; Patterson et al., 1999; Harris and Berg, 2006) that are constrained by the same bedrock topography (Wright, 1972). Because Des Moines Lobe deposits are widespread and complex, identification of these glacial deposits as a probable source of As to well water leaves a wide range of possible geologic sources of As. No single formation has been identified as the source of arsenic to well waters.

Glacial aquifers typically form in glacial-outwash sediments composed of sands and gravels deposited by fast-moving glacial meltwater (Fig. 2) (Prothero and Schwab, 1996), but may also form in sandy lake sediment. The sediments confining these aquifers are glacial tills composed of poorly sorted sediments in a matrix of finely-ground clay-

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