

Distributional Patterns of Arsenic Concentrations in Contaminant Plumes Offer Clues to the Source of Arsenic in Groundwater at Landfills

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*The distributional pattern of dissolved arsenic concentrations from landfill plumes can provide clues to the source of arsenic contamination. Under simple idealized conditions, arsenic concentrations along flow paths in aquifers proximal to a landfill will decrease under anthropogenic sources but potentially increase under in situ sources. This paper presents several conceptual distributional patterns of arsenic in groundwater based on the arsenic source under idealized conditions. An example of advanced subsurface mapping of dissolved arsenic with geophysical surveys, chemical monitoring, and redox fingerprinting is presented for a landfill site in New Hampshire with a complex flow pattern. Tools to assist in the mapping of arsenic in groundwater ultimately provide information on the source of contamination. Once an understanding of the arsenic contamination is achieved, appropriate remedial strategies can then be formulated. ©2013 Wiley Periodicals, Inc.**

INTRODUCTION

Arsenic concentrations in groundwater greater than the US Environmental Protection Agency's (US EPA's) maximum contaminant level (MCL) of 10 $\mu\text{g/L}$ (US EPA, 2006) can be common at landfill sites. Welch et al. (2000) state that, at some Superfund sites contaminated with volatile organic compounds, arsenic plumes appear largely derived from *in situ* aquifer materials with the occurrence of dissolved arsenic being linked to reductive dissolution or desorption processes. A primary mechanism of *in situ* arsenic sources was also identified at waste sites in New Hampshire (Delemos et al., 2006; Harte et al., 2012). However, various waste materials can contain arsenic including arsenical pesticides, cotton waste, chemical warfare agents, and pig and poultry waste from arsanilic acid feed (Welch et al., 2000). The variety of sources can complicate the understanding of the fate and transport of arsenic and, ultimately, appropriate remediation strategies.

Deciphering sources of arsenic leads to an improved selection of the appropriate remedial strategy. For example, remediation of sites with primarily anthropogenic sources might focus on a traditional strategy, such as source containment and capture of dilute plumes with pump and treat. Conversely, *in situ* sources may require an innovative

remedial strategy, such as alteration of chemical-redox processes to prevent dissolution of arsenic sorbed onto sediments or from minerals.

Many tools can help determine the source of arsenic including advanced geochemical and isotopic analysis, also called chemical forensics. Thermodynamic conditions can allow for a fundamental understanding of arsenic occurrence. Arsenic speciation can identify the predominant species and potential reactions (Stollenwerk, 2003). Isotopic analysis of carbon, nitrogen, and sulfate can provide further evidence of reaction pathways and potential sources (Böhlke, 2002). Although these aforementioned tools are beneficial in the assessment of arsenic sources, equally important pieces of evidence come from understanding the distributional pattern of arsenic in relation to the landfill or waste site, the transport pathways, and the subsurface hydrogeologic heterogeneity. This paper illustrates effects of different arsenic sources on theorized distributional patterns of dissolved arsenic concentrations in groundwater at landfill sites typical of the northeastern United States. Potential high-resolution mapping tools are also discussed and an example of advanced mapping from a landfill site in New Hampshire helps illustrate the linkage between source and dissolved arsenic transport in groundwater.

Under the idealized, homogenous aquifer example, the differences in direction and velocity of local flow paths emanating from a landfill will vary less than at other heterogeneous aquifers although shallow flow paths tend to have the greatest groundwater velocities even under homogeneous conditions.

CONCEPTUAL DISTRIBUTIONAL MODELS

Distributional patterns of dissolved arsenic from anthropogenic, mixed (anthropogenic and *in situ*), and *in situ* sources can look quite different particularly in relatively simple, homogeneous aquifers.

This is because transport processes like dilution and mixing serve to attenuate arsenic concentrations differently under these idealized source scenarios. Although determining distributional patterns in more complex, heterogeneous aquifers is far more challenging and applicable in real world field cases, it is nevertheless important to recognize traits under the idealized conditions to provide clues in the assessment of field cases.

For this paper, it is assumed that anthropogenic and *in situ* sources behave similarly under the same geochemical and redox conditions. Further, it is also assumed that reductive dissolution is the dominant *in situ* process where dissolution or desorption from oxyhydroxides or other solids is a primary source of arsenic; reductive dissolution being activated under reduced conditions. The conceptual models presented illustrate these conditions (Exhibit 1). The development of these conceptual models was based on a combination of field observations of various arsenic plumes, and fundamental principles governing the behavior of solute transport and desorption–adsorption reactions.

If the source of the arsenic is the landfill waste, an anthropogenic dominated source, the highest arsenic concentrations and the center of mass will be closest to the landfill (Exhibit 1a). Highest mass transport of arsenic will be in the center of the plume where less dilution and mixing with adjacent flow paths takes place. Under the idealized, homogenous aquifer example, the differences in direction and velocity of local flow paths emanating from a landfill will vary less than at other heterogeneous aquifers although shallow flow paths tend to have the greatest groundwater velocities even under homogeneous conditions. In this case, mixing with adjacent flow paths is the dominant attenuation process. Mixing can occur either from surficial recharge of oxygenated water in humid environments and (or) deep regional flow paths from distal (nonlandfill) locations.

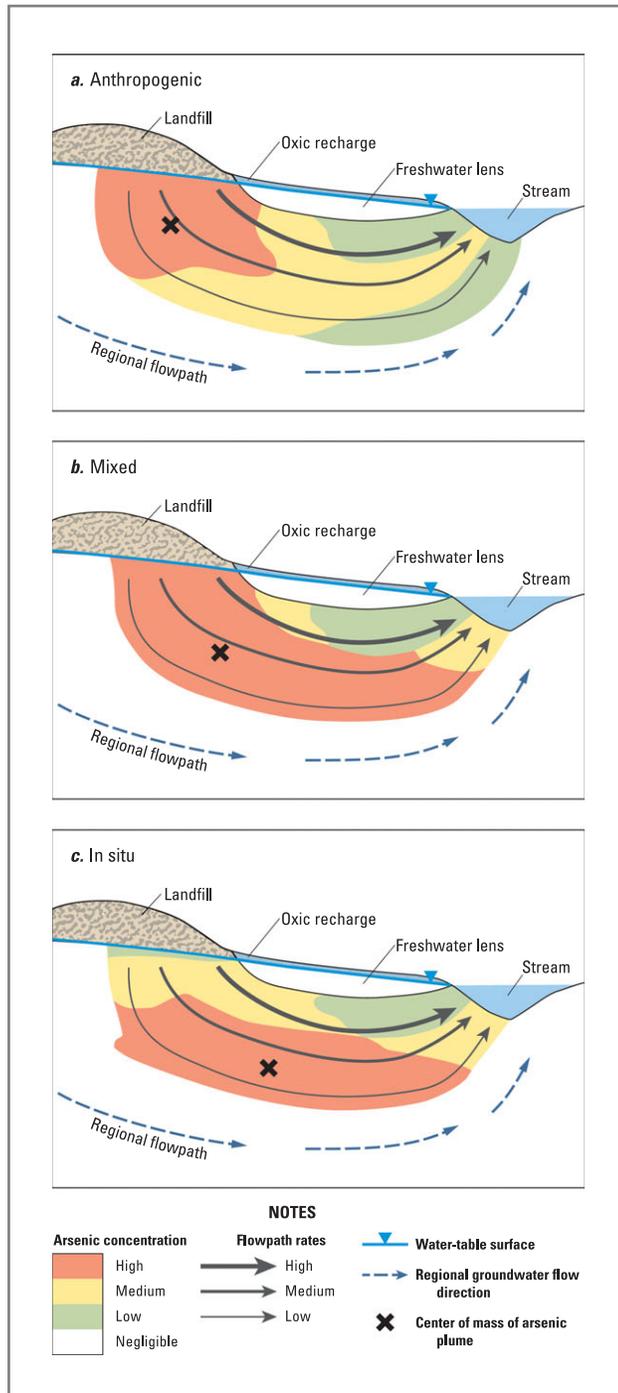


Exhibit 1. Idealized distributional patterns of dissolved arsenic concentrations in groundwater from landfills for (a) anthropogenic sources, (b) mixed, and (c) *in situ*

If the source of the arsenic is mixed (anthropogenic and *in situ*), highest arsenic concentrations and the center of mass could be further downgradient from the landfill and elevated arsenic concentrations may persist further along flow paths (Exhibit 1b) in comparison to an anthropogenic source condition. Because the *in situ* source in this example is attributed to reductive dissolution, surficial recharge of oxygenated waters will

depress arsenic concentrations in the shallow parts of the aquifer. The highest arsenic concentrations occur at intermediate and deep depths—deeper than under anthropogenic source conditions (Exhibit 1a). The reason for this is that deep flow paths tend to contain reduced groundwater conditions in which arsenic will stay in solution (Thomas, 2007).

Sources that are primarily *in situ* could have highest arsenic concentrations further along a flow path in comparison to both anthropogenic and mixed sources because of the cumulative effect of dissolution or desorption from native sediments (Exhibit 1c). Therefore, the high arsenic concentration zone could be disconnected from the landfill. The distance between the high concentration zone and landfill could be very small and much smaller than that shown in Exhibit 1c. The highest mass transport of arsenic, assuming a reductive driven process, would occur along deep flow paths. Shallow zones, although likely having the greatest groundwater velocities even under homogeneous conditions, would be affected by surficial recharge of oxygenated waters that would depress dissolved arsenic concentrations.

At many landfill sites, the current monitoring network may not be robust enough to identify the arsenic plume or internal patterns of zonation as those illustrated in Exhibit 1.

ALTERNATIVE CONCEPTUAL MODELS

Anthropogenic and *in situ* sources that behave differently under the same geochemical redox condition will provide a much different distributional pattern than the ones provided in this paper. An inverse pattern may develop between oxygenated and reduced zones where each zone is dominated by a different arsenic source. Understanding geochemical signatures of groundwater for the various redox zones would help clarify sources. Heterogeneity can create a complex distributional pattern that can obscure arsenic sources. Integration of advanced geologic mapping can assist in attributing effects of heterogeneity on arsenic transport.

AN EXAMPLE OF MAPPING OF ARSENIC PLUME

At many landfill sites, the current monitoring network may not be robust enough to identify the arsenic plume or internal patterns of zonation as those illustrated in Exhibit 1. Additional mapping tools may be necessary, including surface and borehole geophysical surveys (Degnan & Harte, 2013). Geophysical surveys can provide information on the hydrogeologic framework of aquifers to determine map layers, preferential pathways, and recalcitrant arsenic contamination zones that could serve as reservoirs for back diffusion. In some cases, if the arsenic is colocated with an electrically conductive leachate, such as chloride, electrical-based geophysical surveys could directly map the arsenic distribution. Further, if the leachate is also colocated with reduced waters, then geophysical surveys can provide information on redox zonation.

Direct current (DC) resistivity imaging provides information on the subsurface electrical properties. An example is provided from a survey of a landfill site in New Hampshire that contains an arsenic plume (Exhibit 2). The site consists of a glacial-sediment aquifer (sands and silts), a thin (less than 10 ft) basal till layer, and an underlying fractured, meta-sedimentary, bedrock aquifer. Dissolved arsenic is attributed primarily to *in situ* sources (Degnan & Harte, 2013). The survey shows several conductive (low resistivity) and resistive (high resistivity) zones. The section is drawn orthogonal to a flow path originating from the landfill, and the landfill is upgradient from the section. The complex geometry of the conductive zone, which defines areas of transported landfill

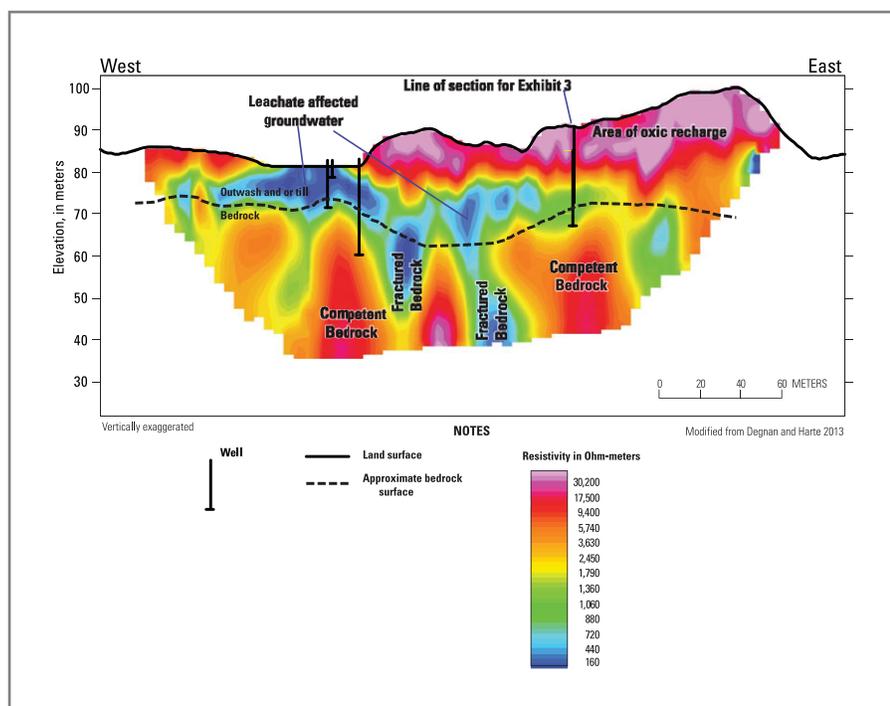


Exhibit 2. Direct current resistivity imaging of subsurface, orthogonal to flow, showing low and high resistivity zones (modified from Degnan and Harte, 2013)

leachate and is colocated with elevated arsenic concentrations from a theorized, primarily *in situ* source, illustrates the complexity of flow. Aquifer heterogeneity and preferential flow paths can obscure arsenic distributional patterns from proximal to distal locations unless high-resolution mapping is performed. Conductive zones (as indicated by blues and greens on Exhibit 2) are located in the glacial-sediment aquifer and underlying fractured-rock aquifer. Also important to note is the preponderance of resistive zones at land surface along the eastern section of the survey line (Exhibit 2) that correspond to recharge of oxygenated water. In the resistive zones, arsenic concentrations are low owing to the lack of dissolution of sorbed arsenic (Degnan & Harte, 2013).

The geophysical surveys were used with the formulation of geochemical-redox zones, which were generated from commonly collected chemical data from well samples and analyzed according to methods described by Jurgens et al. (2009), to generate a more complete picture of the arsenic plume (Exhibit 3). This section runs along a flow path from the landfill. Redox zones were mapped and interpolated between wells with the assistance of DC resistivity imaging (Degnan & Harte, 2013). High concentrations of dissolved arsenic were found in the methanogenic and iron/sulfate reducing zones. The zone of depressed arsenic concentrations in Exhibit 3 corresponds to the high resistivity zone mapped in Exhibit 2. Prior to the study by Degnan and Harte (2013), the reason for the low arsenic concentrations in this area was not well understood.

CONSEQUENCES FOR REMEDIATION

The effect of surficial recharge of oxygenated water on dissolved arsenic concentrations indicates that increasing oxygen levels in groundwater could be an effective remedial

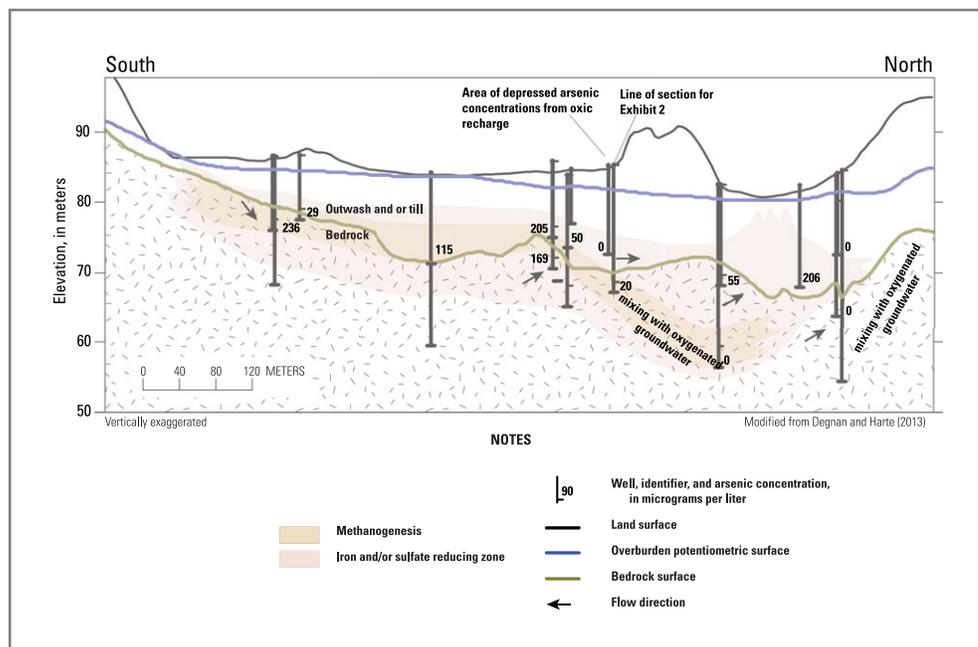


Exhibit 3. Synthesized redox zonation from resistivity imaging and geochemical-redox data showing co-occurrence of arsenic concentrations (modified from Degnan & Harte, 2013)

strategy. At the example site, regulators can use this information to plan for more specific follow-up work to assess the feasibility of air sparge technology or other processes to raise oxygen levels in groundwater. Other sites could benefit from advanced mapping techniques as well. Sites that are primarily anthropogenic driven could use advanced mapping like DC resistivity imaging to identify preferential pathways and zones where pump and treat would effectively capture dissolved arsenic.

CONCLUSIONS

The distributional pattern of arsenic provides important information on sources and has implications for remediation at landfill sites. Under idealized scenarios, the distributional pattern of arsenic affected by anthropogenic and *in situ* sources will potentially look different. Methods that allow for high resolution mapping of dissolved arsenic distribution in a quick and efficient manner offer a great benefit to remediation professionals tasked with finding solutions to complex problems. More than just for academic reasons, arsenic mapping provides clues about arsenic source, fate, and transport that can be used to help select appropriate remedial strategies.

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