Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire, USA

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Abstract Anthropogenic sources of carbon from landfill or waste leachate can promote reductive dissolution of in situ arsenic (As) and enhance the mobility of As in groundwater. Groundwater from residential-supply wells in a fractured crystalline-rock aquifer adjacent to a Superfund site in Raymond, New Hampshire, USA, showed evidence of locally enhanced As mobilization in relatively reducing (mixed oxic-anoxic to anoxic) conditions as determined by redox classification and other lines of evidence. Redox classification was determined from geochemical indicators based on threshold concentrations of dissolved oxygen (DO), nitrate (NO_3^-), iron (Fe^{2+}), manganese (Mn^{2+}), and sulfate (SO_4^{2-}). Redox conditions were evaluated also based on methane (CH_4), excess nitrogen gas (N_2) from denitrification, the oxidation state of dissolved As speciation (As(III) and As(V)), and several stable isotope ratios. Samples from the residential-supply wells primarily exhibit mixed redox conditions, as most have long open boreholes (typically 50–100m) that receive water from multiple discrete fractures with contrasting groundwater chemistry and redox conditions. The methods employed in this study can be used at other sites to gauge redox conditions and the potential for As mobilization in complex fractured crystalline-rock aquifers where multiple lines of evidence are likely needed to understand As occurrence, mobility, and transport.

Introduction

Increased As mobility in groundwater (i.e. from the release of As from the solid to liquid phase) can be a byproduct of the alteration of redox conditions at waste-disposal sites from anthropogenic carbon sources (Delemos et al. 2006; Davis et al. 2004). In this article, this process is referred to as *enhanced As mobility*. Delemos et al. (2006) postulated that mobilization of As, caused by the degradation of subsurface organic contaminants, may be a more widespread problem than previously recognized at waste-disposal sites undergoing natural attenuation. Landfill leachate and other contaminant source materials in the subsurface often produce anaerobic conditions (dissolved oxygen (DO)<0.5 mg/L) in groundwater, which can mobilize As through reductive dissolution and desorption of in situ As from metal oxyhydroxides (Welch et al. 2000; Stollenwerk2003). Arsenic mobilization is species dependent. Under reducing conditions, arsenate, As(V), is reduced to arsenite, As(III), which has a diminished sorption affinity to metal oxyhydroxide (Dixit and Herring 2003).

Groundwater-flow characteristics of fractured crystalline-rock aquifers play a major role in groundwater redox conditions and transport of As. Fractured crystalline-rock aquifers commonly have low groundwater storage capacity and the potential for rapid transport along fractures. Flow in discrete fractures may contain distinct geochemistry based

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on fracture connectivity and mineral composition. Recharge from overburden aquifers can introduce variability in the geochemical and redox condition of groundwater in fractures. Therefore, local As mobilization by anthropogenic carbon sources may be highly variable.

Regional water-quality assessments can facilitate our understanding of local As mobility. The lithochemical composition of bedrock aquifers in New England, USA, has been identified as an important variable in controlling groundwater As concentrations on a regional scale (Welch et al. 2000; Ayotte et al. 2003; Lipfert et al. 2006; Yang et al. 2009). Regional As occurrence in groundwater of New England was studied by the US Geological Survey (USGS) New England Coastal Basins (NECB) study unit, a part of a National Water Quality Assessment (NAWQA) Program for the United States. High As concentrations have been identified in groundwater associated with a band of variably calcareous metasedimentary rocks from central Maine to Massachusetts (Fig. 1; Ayotte et al. 2003).

Arsenic concentrations exceeding the US Environmental Protection Agency (USEPA 2006) maximum contaminant level (MCL) of 10 micrograms per liter (µg/L) have been found in 7–31 % of residential-supply wells set in variably calcareous metasedimentary rocks of southern New Hampshire (Montgomery et al. 2003).

Redox conditions and identification of redox processes are important not only in the evaluation of enhanced As mobility but of several other natural and anthropogenic contaminants including NO_3^- and volatile organic compounds (McMahon and Chappelle 2008). Redox characterization and contaminant occurrence have been described for the principal aquifers of the United States using threshold concentrations of several redox sensitive geochemical constituents (DO, NO_3^-, Mn^{2+}, Fe^{2+}, and SO_4^{2-}) by McMahon and Chappelle (2008). Principal aquifers of the United States include fractured-rock aquifers (McMahon and Chappelle 2008) and glacial aquifers (Thomas 2007). These studies were able to
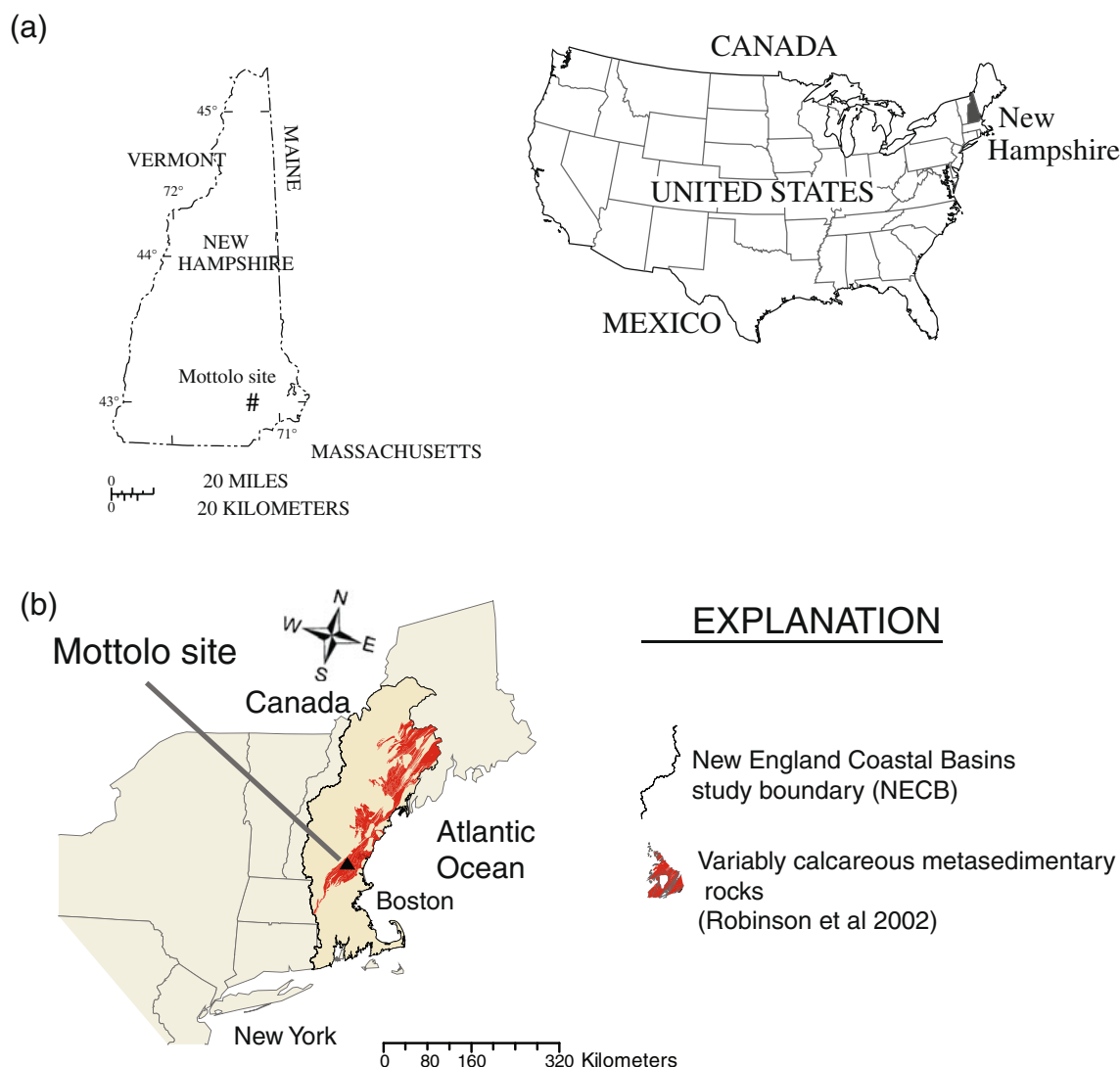

Fig. 1 **a** Location of the Mottolo Superfund site, Raymond, New Hampshire, USA, and **b** extent of variably calcareous metasedimentary rocks within the US Geological Survey, National Water Quality Assessment (NAWQA) study of the New England Coastal Basins (NECB) unit

associate high As concentrations with Fe and Mn reduction. A similar redox characterization method was used to identify the mobility of natural contaminants at water-supply wells in various hydrogeologic settings throughout the United States (Ayotte et al. 2011).

The purpose of the current study was to determine if local conditions near a waste-disposal site, the Mottolo Superfund site in Raymond, New Hampshire, caused enhanced As mobility in the underlying, variably calcareous, metasedimentary fractured-rock aquifer where high dissolved As concentrations above the MCL were found in nearby residential supply wells. An important component of this study was the testing of a variety of redox indicators to assess their utility in understanding the distribution and cause of high dissolved As concentrations. A primary tool was the classification of redox conditions of groundwater samples from wells based on redox sensitive geochemical constituents (McMahon and Chappelle 2008). Additional redox indicators were tested on a subset of the wells. To assist in our evaluation, local redox conditions from the study area were compared to regional redox conditions (NECB study unit) from similar variably calcareous metasedimentary rocks to identify important redox-controlled processes and to help distinguish local and regional differences in As mobility.

Study area description

The Mottolo site and the surrounding study area (Fig. 2) are underlain by thin surficial deposits of glacial origin and by shallow bedrock (less than 10 m from land surface), consisting largely of the Berwick Formation: variably calcareous metasedimentary rocks derived from marine sediments composed of interbedded biotite-plagioclase quartz granofels, schist, and calc-silicate rocks (Lyons et al. 1997; Robinson et al. 2002). The Berwick Formation has been associated with regionally (county scale) high As concentrations although the particular subgroup associated with rocks underlying the study area had regional As concentrations exceeding the MCL only 7 % of the time (Ayotte et al. 2003; Montgomery et al. 2003).

The waste site is a former piggery (1960–1975) and chemical waste disposal dump (1975–1979). During a 4-year period, chemical manufacturing wastes including over 1,600 drums and pails of anthropogenic contaminants such as toluene, xylene, and methyl ethyl ketone, were disposed of in a 1,011 m^2 fill area adjacent to former piggery buildings (US Army Corps of Engineers 2008). Active remediation of the site occurred from 1983 to 1996. Remediation included drum removal, soil remediation, and the installation of interceptor trenches to capture and divert shallow groundwater around a soil vapor extraction system. Since 1993, the groundwater at the site has been undergoing natural attenuation. The interceptor trench was removed in 2001. Soil profiling conducted in 2009 measured soil concentrations for xylene and benzene at approximately 100,000 μg/kg. Groundwater samples from onsite surficial glacial deposits and shallow

bedrock observation wells have detected anthropogenic contaminants including tetrahydrofuran at concentrations as high as 1,000 μg/L (GZA GeoEnvironmental 2010). At an onsite shallow bedrock well, temporal trends in As concentrations positively correlated with organic contaminants (Spearman rho of 0.50, p=.006) indicating As is co-located with organic contaminants (US Army Corps of Engineers 2008). Approximately 200 single family residences border the site and rely on individual residential bedrock wells as a water source (Fig. 2). The residential supply wells are typically constructed with 3 m of well casing set into the bedrock and the remainder of the well uncased leaving long open boreholes in the bedrock (typically 50–100 m in length). The long open boreholes can intercept several fractures with different water chemistry. Trichloroethylene (TCE), a site contaminant, has been detected in residential wells to the west and southwest of the site (GZA GeoEnvironmental 2010). The pH of groundwater in the bedrock ranged from 6 to 8.

The waste site appears to be near a groundwater divide as indicated by a generalized potentiometric head surface map from bedrock water levels collected in 2009 (Fig. 2). The waste site overlies a local, high hydraulic head area and flow is quasi-radial away from the site. The head surface and generalized directions of flow represent an average bulk groundwater flow direction that incorporates the flow-weighted average of the hydraulic heads of discrete fractures that intersect the borehole. Flow in individual fractures may differ from what is presented (Fig. 2). Further, bedrock water levels are dynamic and respond to recharge and withdrawals throughout the day and the potentiometric surface will change as a result.

Arsenic occurrence (2009) in the study area

The spatial distribution of As in groundwater in the fractured-rock aquifer near the Mottolo Superfund site follows a west–east distribution and can be grouped by area (Fig. 2). Highest As concentrations occurred to the west of the waste site, coinciding with one of the general directions of groundwater flow in the bedrock in 2009 (GZA GeoEnvironmental 2010). Some high As concentrations (>10 μg/L) also occurred to the south and north of the waste site. Historically, flow directions in the bedrock were predominantly southwest but have shifted to the northwest as development and residential well pumping has increased in that area. Arsenic concentrations are low and generally below reporting limits (1.0 μg/L) to the east of Brook A (Fig. 2). Residential wells to the east of the site are located on a topographic and hydraulic high.

Uranium (U) concentrations in residential well samples were inversely related to As concentrations, possibly as a result of lithochemical differences in the local bedrock geology (GZA GeoEnvironmental 2010). High dissolved U concentrations (as high as 981 μg/L), above the MCL of 30 μg/L (USEPA 2006), occurred to the east of the site,
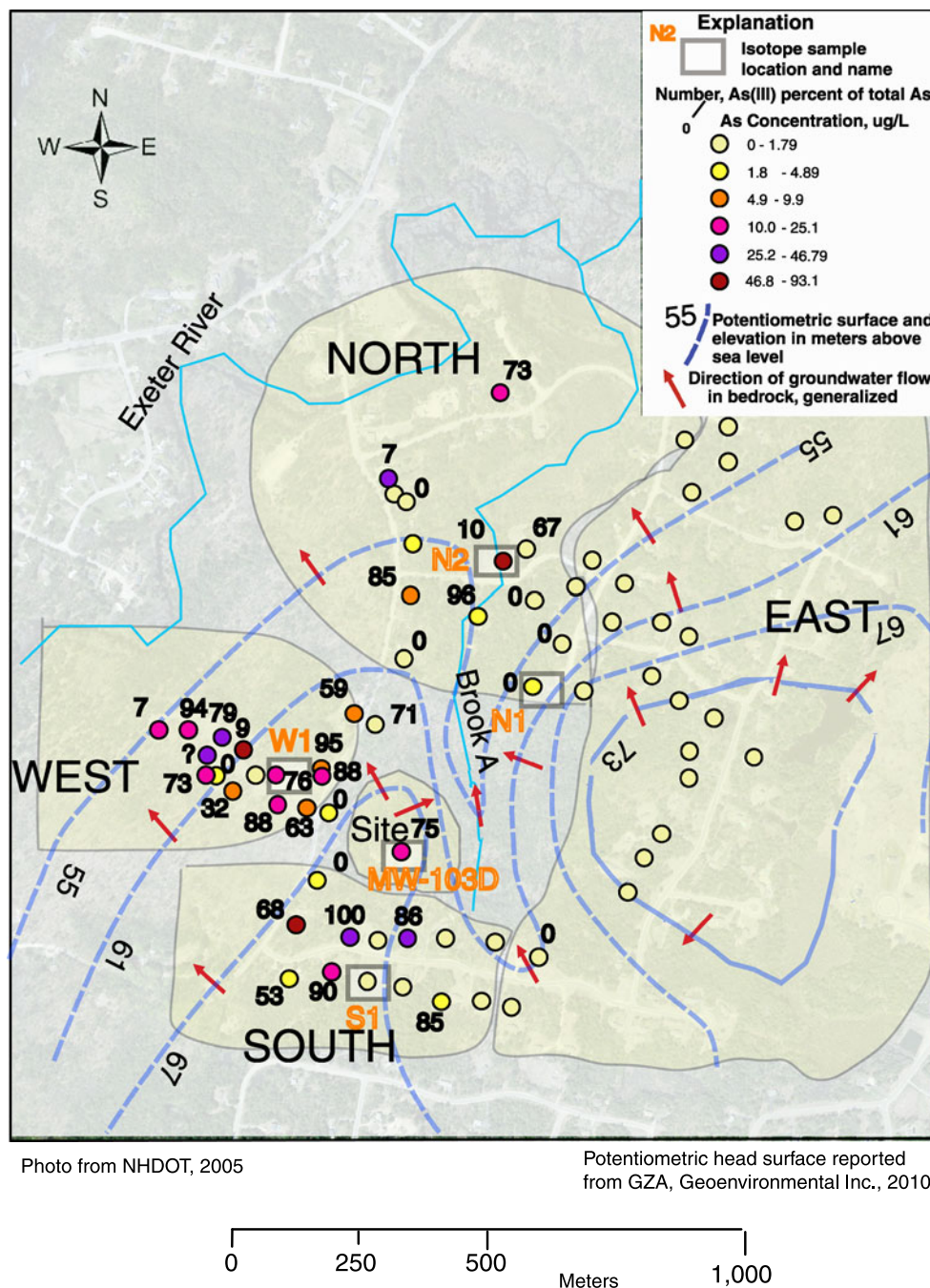
Fig. 2 Map of arsenic (As) concentrations (2009) in well samples from bedrock (photo from NHDOT 2005), As speciation (As(III) as a percent of total As and the potentiometric surface of the bedrock at the Mottolo Superfund site, Raymond, New Hampshire. *North*, *south*, *east*, and *west* subareas generally have different geochemical characteristics, as described in the text

where dissolved As concentrations were low (Fig. 2). Aqueous U occurrence has been shown to correspond with oxic conditions and may indicate the presence of granitic intrusions (Ayotte et al. 2007; Smitherman et al. 2009). The land surface to the east of the site had physiographic features similar to nearby land areas underlain by granitic intrusions (Lyons et al. 1997). Thus, although granitic rocks are not portrayed on the state geologic map of this area, the physiography and the occurrence of low As and high U concentrations in

groundwater indicate that the area to the east (upgradient) of the waste site may be underlain by granitic rocks rather than variably calcareous metasedimentary rocks.

In surficial glacial deposits at the waste site, elevated dissolved As concentrations were related to elevated concentrations of anthropogenic carbon-based contaminants and reduced groundwater conditions (GZA GeoEnvironmental 2010). Arsenic concentrations exceeded 100 μg/L (as high as 585 μg/L) at several wells in surficial deposits in a small area downgradient of the site near a brook (GZA

GeoEnvironmental 2010). At this location, well samples also indicated reduced groundwater conditions (oxidation-reduction potential, ORP, of −156 mV) and the presence of anthropogenic contaminants. Directly underlying the disposal areas, dissolved As concentrations were less (<100 μg/L) than further downgradient; this suggests that the waste is not a direct source of As because higher As concentrations occur further downgradient allowing for the accumulation of dissolved As from the desorption of in situ As. Some high As concentrations in bedrock groundwater may originate from recharge of high As groundwater exposed to reductive dissolution in surficial glacial deposits (Delemos et al. 2006). In the upper (<10 m below bedrock surface) bedrock at the waste site, As concentrations were as high as 85 μg/L in some areas underlying surficial glacial deposits with high dissolved As concentrations.

Methods in redox characterization

An automated version of the redox classification scheme described by McMahon and Chappelle (2008) and developed by Jurgens et al. (2009) was employed to classify local redox conditions and processes in groundwater from well samples in the study area. Also, regional redox conditions were evaluated by performing the same redox classification on previously collected aqueous geochemical data from the USGS NECB study unit. Specifically, the redox program was used to broadly classify groundwater redox conditions as either oxic (DO$\geq$0.5 mg/L), mixed (oxic-anoxic), or anoxic (DO<0.5 mg/L), based on DO concentrations (threshold concentration of 0.5 mg/L) and other key constituents (NO_3^-, Mn^{2+}, Fe^{2+}, and SO_4^{2-}). For a mixed redox designation, groundwater must contain DO $\geq$0.5 mg/L and either Mn^{2+} (>0.05 mg/L) or Fe^{2+} (>0.1 mg/L) above threshold concentrations. Samples were further designated to identify probable electron acceptors undergoing active reduction such as NO_3^-, Mn (IV), Fe (III), and(or) SO_4^{2-}, which may be related to Fe and Mn oxide dissolution reactions, which can release sorbed As. Iron (NECB samples) and Mn (Mottolo and NECB samples) species data were unavailable to assist in redox classification. We used total in its place under the assumption that for the regional and local groundwater in question, total Fe is primarily in the form of Fe^{2+} and total Mn is primarily in the form of Mn^{2+}.

In addition to the automated geochemical redox characterization, As speciation in the Mottolo study was evaluated from measurements of As(III) and As(V) following a field speciation procedure (N.H. Department of Environmental Services, personal communication, 2010). For a limited subset of samples (five) representing different groundwater redox types, additional geochemical and redox evaluations were made using dissolved gases (Ar, N_2, CH_4, CO_2; analyzed in the USGS Dissolved Gas Laboratory in Reston, Virginia; USGS, 2012a; Busenberg et al. 1998), and stable isotopes (H, DO, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), NO_3^-, and N_2; analyzed in the USGS Stable isotope Laboratory in Reston,

Virginia; USGS, 2012b; St. Jean 2003; Sigman et al. 2001; Casciotti et al. 2002; Coplen 1988, Coplen et al. 2004; McMahon et al. 2008; Green et al. 2008). These data provided information about potential redox reactions affecting carbon and nitrogen, which may be associated with As mobility.

Distribution of redox conditions

Based on the geochemical redox characterization, mixed (oxic-anoxic) redox conditions occurred in well samples from 53 % (36 of 68 wells) of residential wells in the Mottolo study area. Oxic (22 %) and anoxic (15 %) redox conditions were less frequently detected. Oxidation-reduction potential (ORP), a commonly used field parameter to discern gross redox conditions, showed a large variation in values for well samples classified as mixed and anoxic and was limited in its utility to decipher redox-As processes.

The high frequency of groundwater with mixed redox conditions appears atypical compared to the low rate of occurrence of groundwater with mixed redox conditions from regional NAWQA studies (8 % of 111 wells) of the crystalline-rock aquifers of New England (McMahon and Chappelle 2008). A subset of wells from the regional NECB study unit of NAWQA, which consisted of 28 wells tapping a similar type of variably calcareous metasedimentary rocks as that found at the Mottolo study area, showed 21 % with mixed redox conditions. Results from the local and regional comparison of redox indicate that residential wells at the Mottolo study area receive recharge from a complex pattern of groundwater flow. Borehole geophysical logging in several residential and onsite wells at the Mottolo study area have shown multiple (typically 3–5) discrete fractures contributing flow under pumped conditions (Hager-Richter Geoscience 2010). Based on the redox indicators, it is likely that groundwaters from these discrete fractures have different chemical and redox characteristics that contribute to the high occurrence of mixed redox conditions in the wells. By itself, the high frequency of mixed redox conditions indicates a high level of chemical redox variability within the aquifer that is potentially induced by anthropogenic carbon and waste disposal.

Redox conditions in the study area varied spatially, with groundwater to the east of the site predominantly oxic and mixed, and to the west predominantly anoxic and mixed (Fig. 3). Thus, it is likely that some wells to the west of the waste site partially captured anoxic groundwater that was affected by waste disposal. TCE has been detected in well samples to the west and historically to the southwest. In addition, an aquifer pump test of a bedrock well at the waste site (onsite) confirmed hydraulic connections with residential-supply wells to the west and south (GZA GeoEnvironmental, personal communication 2010). The potential for westerly transport is supported by the presence of laterally extensive northwesterly dipping fractures underlying the waste site (Hager-Richter Geoscience 2010). To the north and south, redox conditions were similar, with mixed conditions dominating (Fig. 3). Figure 3 shows
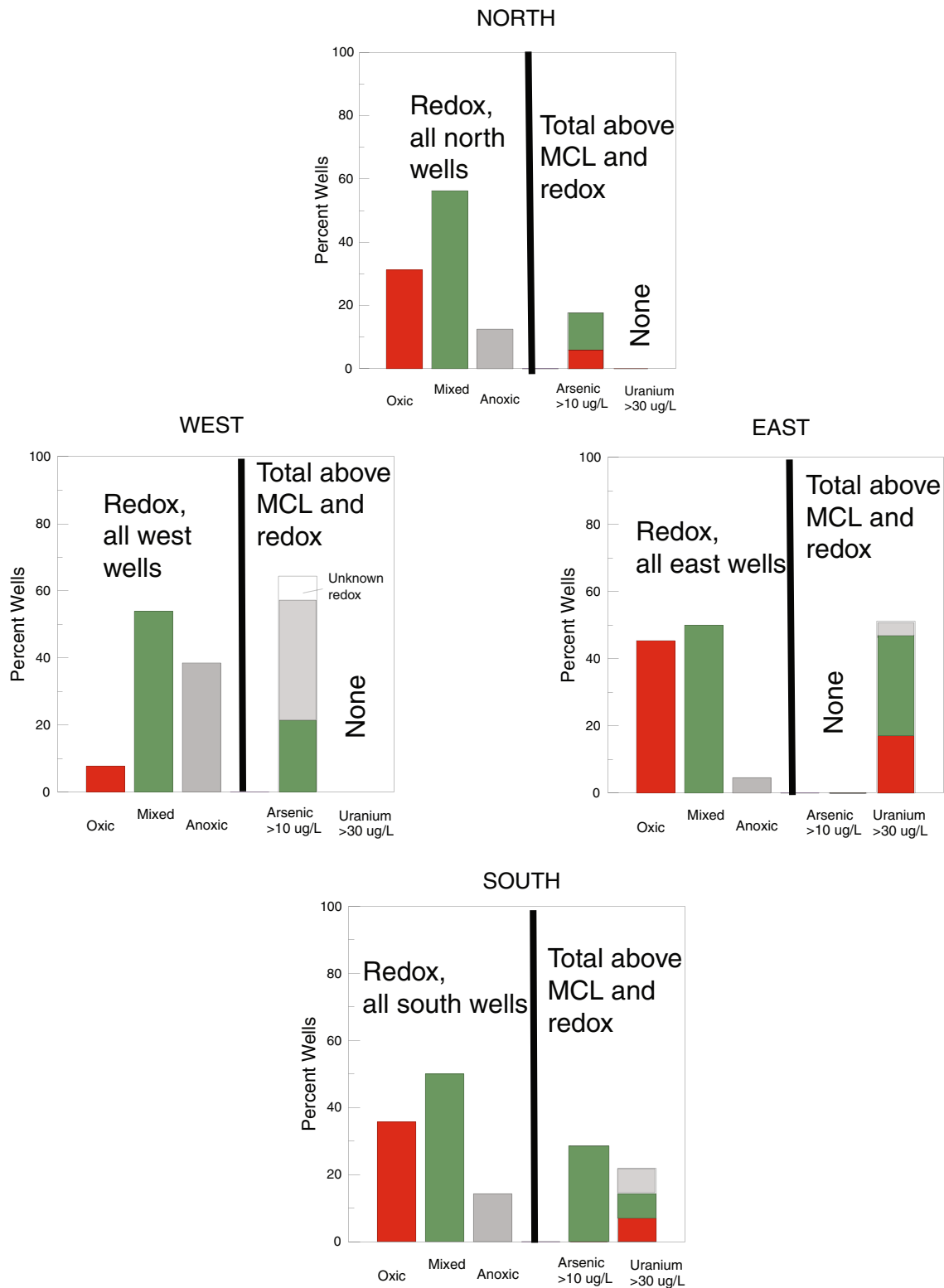
Fig. 3 Graphs showing redox conditions and As and U occurrences above MCL in groundwater from each of four subareas around the waste disposal site (see Fig. 2 for map areas).The *bar sections on the right side* of each graph are color coded as *on the left side* of each graph (*red* for oxic, *green* for mixed, *grey* for anoxic)

redox conditions in each of four subareas north, east, south, and west of the disposal site, and the percentage of wells in each subarea with either As or U concentrations above their respective MCL and their associated redox condition.

Relation between arsenic and redox

The spatial pattern of As and redox conditions is shown in Figs. 2 and 3. Arsenic concentrations in excess of the

MCL were more common to the west (downgradient) of the waste site, corresponding with the greatest occurrence of anoxic and mixed redox conditions (Fig. 3). In contrast, oxic conditions were more prevalent to the east, which also had the lowest As concentrations.

For the entire study area, most samples with As concentrations above the 10 μg/L MCL were associated with either mixed oxic-anoxic (Mn(IV) or Fe(III) reduction) or anoxic (primarily Fe(III) reduction) conditions (Fig. 4a). Fifty percent of samples classified as anoxic had As concentrations exceeding the MCL (Fig. 4a). By contrast, the lowest As concentrations (typically less than 3 μg/L) occurred in samples classified as oxic (Fig. 4a). Only one well sample from the 22 wells characterized as oxic had an As concentration above the 10 μg/L MCL (Fig. 4a).

Median As concentrations at the Mottolo study area were approximately at the MCL for mixed and anoxic redox conditions. Median As concentrations for those same redox groupings from the regional NECB study were below MCL (Fig. 4b). Anoxic waters from Mottolo and NECB studies both had relatively high As concentrations indicating that the variably calcareous metasedimentary rock is a local and regional source of As. By contrast, oxic groundwater had lower As concentrations at the Mottolo study area than from the NECB study area; this is possibly due to regional differences in lithochemistry including the spatial variability of As-bearing sulfide minerals. The oxidation of As-bearing sulfide minerals can mobilize As into solution and lead to high As concentrations under oxic conditions (Welch 2000). In the study
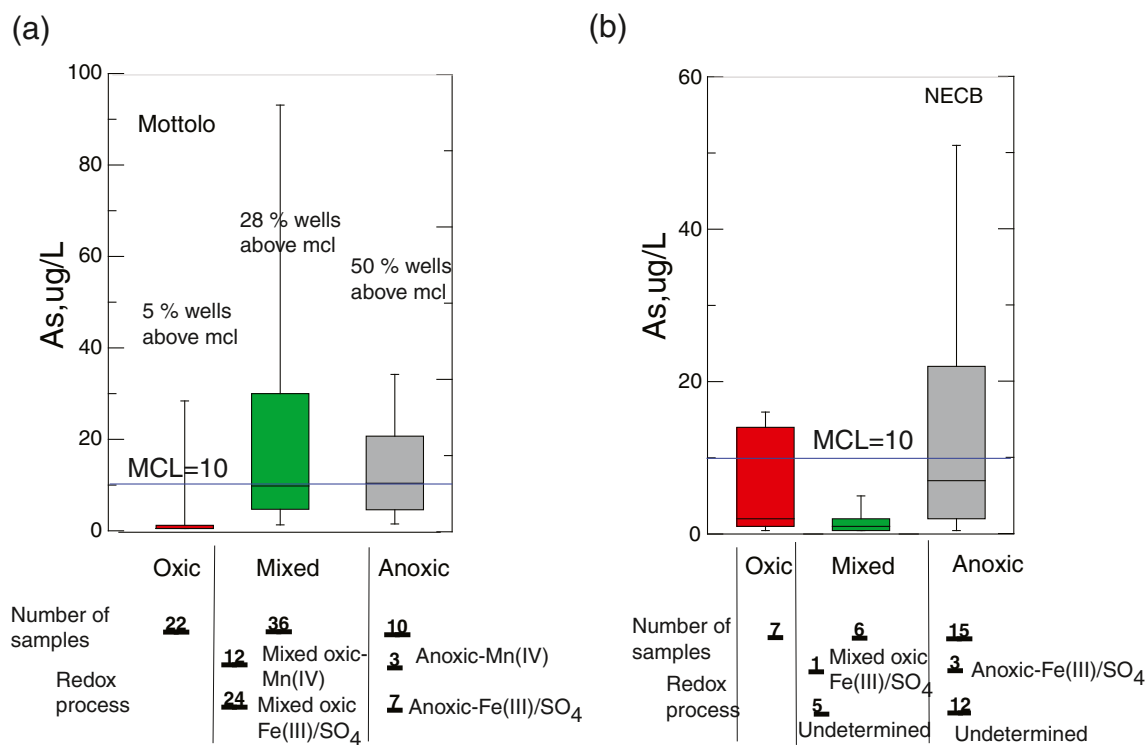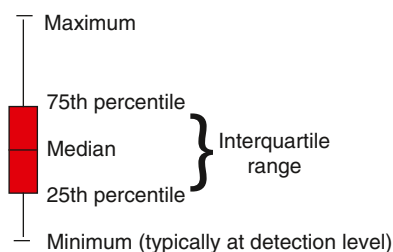

Fig. 4 Arsenic concentration in **a** bedrock groundwater of the study area adjacent to the Mottolo Superfund site and **b** groundwater from similar metasedimentary rocks in the New England Coastal Basins (NECB) study unit of NAWQA, grouped by redox conditions. *Bars* are color coded based on redox conditions, as in Fig. 3. The subcategory numbers under each redox condition (oxic, mixed, and anoxic) refer to the dominant redox process. Undetermined indicates that the subcategory (redox process) could not be identified for that particular redox condition (Fig. 4b.)

area, sulfate concentrations were generally low, ranging from 17 to 28 mg/L, and did not correspond with high (above the MCL) As concentrations. Similar As, redox, and sulfate relations were found by Lipfert et al. (2006) in a study of crystalline-rock aquifers in Northport, Maine, USA. Alternatively, the lack of high As concentrations under oxic conditions in the study area may be indicative of dilution of As concentrations by recently recharged oxic waters with low As concentrations, and (or) the removal of dissolved As by adsorption onto oxhydroxide as suggested by Lipfert et al. (2006).

Additional arsenic-redox characterization

Dissolved inorganic As occurs mainly in two valence states (III and V) and understanding the occurrence of As species in groundwater can provide information on redox processes and As mobilization. Arsenite, As(III), was dominant at 13 of the 17 (76 %) wells with As concentrations above the MCL in the study area; As(III) was particularly prevalent to the west and southwest of the site (Fig. 2). At the four wells where arsenate, As (V), was dominant, DO concentrations were all above 1.0 mg/L and at one of the four wells, the NO_3^- concentration also was high (9.5 mg/L). Low As(III) concentrations in these four wells may indicate As oxidation coupled with either oxygen reduction or denitrification (Sun et al. 2008).

The proportions of As species were related to the redox classifications of the samples. Arsenate, (As(V)), concentrations exceeded As(III) concentrations in the 22 well samples designated as oxic, whereas As(III) concentrations exceeded As(V) concentrations in 9 of the 10 well samples designated as anoxic. Of the 36 well samples designated as mixed redox conditions (53 % of total wells), approximately two-thirds had As(III) ≥ As(V), indicating at least some of the flow to the wells came from fractures containing anoxic groundwater and that the As continued to be in its reduced form even in the presence of some oxic groundwater. The spatial pattern of As speciation was consistent with the distribution of redox conditions. High As(III)/As total ratios were common to the west and south of the Mottolo site, where anoxic conditions were more prevalent (Fig. 3). The median As(III)/As total ratios for samples with As concentrations above 10 μg/L were 0.75 and 0.88 for the west and south areas respectively, but only 0.10 for the north area.

Dissolved gases and isotopes

A subset (four residential wells and one onsite well) of the 68 sampled wells was selected for dissolved gas and stable isotope analyses to provide additional lines of evidence for biogeochemical processes related to As mobility (Table 1). The four residential wells included two wells to the north of the site, one well to the west, and one to the east (Fig. 3). The primary distinguishing feature between the five wells was redox classification (Table 1). Two wells (N1 and S1) with oxic conditions had low As concentrations (less than 3 μg/L). Three wells with mixed redox conditions (N2 well, W1 well, and the onsite well) had As concentrations of 61, 15, and 31 μg/L, respectively. The onsite and W1 well, had detectable concentrations of TCE at 117 and 1.6 μg/L, respectively. The N2 well had the second highest As concentration in the study area.

The detection of CH_4 (methanogenic conditions) is an indicator of anoxic conditions that can promote reductive dissolution of in situ As. Methane was detected in three samples (N2, W1, and the onsite well MW-103D), all of which had total As concentrations above 10 μg/L. At N2 well, the presence of high DO (1.5 mg/L) coupled with detectable CH_4 indicates mixing of oxic and anoxic waters in the borehole and suggests partial capture of groundwater derived from fractures carrying different water chemistry.

Dissolved inorganic carbon $\delta^{13}C$ varied from −12.2 ‰ (N2 well) to −17.8 ‰ (S1 well). The higher DIC $\delta^{13}C$ at N2 could indicate this groundwater was exposed to additional contact with carbonate minerals or perhaps longer residence times, which could be related to its high As concentration (61 μg/L). Arsenic occurrence has previously been associated with rocks containing calcite in the region (Ayotte et. al, 2003).

Anthropogenic sources of nitrogen and biogeochemical processes that affect the nitrogen cycle in groundwater can also affect mobility of trace elements including As (Böhlke 2002; Kirk et al. 2004; Höhn et al. 2006). In the study area, NO_3^- concentrations generally were low (< 0.05 mg/L as N) near the waste site, whereas away from the waste site, NO_3^- concentrations were highest (maximum concentration of 9.5 mg/L) in well samples classified as oxic and mixed and primarily below detection in well samples classified as anoxic. The presence of high NO_3^- in some residential well samples is possibly unrelated to the waste site and instead related to shallow contamination of groundwater from septic fields. Only one of the five wells selected for detailed analysis (S1; As concentration of 1.2 μg/L) had sufficient NO_3^- for reliable isotopic measurement. In that well, which was classified as oxic, the NO_3^- had a relatively low $\delta^{18}O$ value consistent with a nitrification source, and a relatively high $\delta^{15}N$ value that might indicate a wastewater source such as from septic fields or other animal waste-disposal activity, although minor denitrification may have affected these values slightly. Denitrificaton has the ability to suppress As concentrations because of the release of oxygen from nitrate and the potential oxidation of arsenite to arsenate (Sun et al. 2008).

Nitrogen-argon (N_2–Ar) ratios and nitrogen isotopic composition provide insight into denitrification processes. Concentrations of Ar and N_2 in five samples were similar to those of air-saturated water with small amounts of excess air. Sample N2 had relatively high concentrations of Ar and N_2 that could indicate a relatively low recharge temperature near 0°C, possibly indicating seasonal recharge during cold weather. Four other samples had apparent recharge temperatures of around 5–8°C, with some uncertainty related to possible denitrification. Two of the samples (W1 and S1) had slightly elevated N_2/Ar ratios and $\delta^{15}N(N_2)$ values that could indicate small

Table 1 Summary of redox conditions and isotopic composition for representative samples, Mottolo Superfund Site, Raymond, New Hampshire, USA

Sample Name		N1	N2	W1	S1	MW-103D	MW-103D Dup
General location		North of site	North of site	West of site	South of site	Onsite	
Well type		Residential	Residential	Residential	Residential	Onsite	Duplicate
Redox condition		Oxic	Mixed	Mixed	Oxic	Mixed[a]	–
Geochemical water type		Ca–HCO$_3^-$	Ca–HCO$_3^-$	Ca–HCO$_3^-$	Ca-mixed anion	Ca–HCO$_3^-$	–
Constituent	Units						
pH		7.4	7.4	7.4	7.4	9.7[a]	–
Alk as CaCO$_3$	(mg/L)	72.7	74.5	104	61.7	38.5[a]	–
Temperature	°C	14.7	12.8	14.4	10.9	11	–
DO (field)	(mg/L)	6	1.5	0.2	0.9	0.4	–
ORP	(mV)	149	−48	−99	125	–	–
NO$_3^-$	(mg/L as N)	0.011	0.007	0.007	1.8	0.006	0.006
TCE	(ug/L)	<0.5	<0.5	1.6	<0.5	117	–
TOC	(mg/L)	0.51	<0.5	0.51	<0.5	0.54[a]	–
Total As	(ug/L)	2.8	60.9	15	1.2	25.2[a]	–
As(V)	(ug/L)	2.8	54.6	3.6	1.2	6.3	–
As(III)	(ug/L)	<1	6.3	11.4	<1	18.9	–
Fe(II)	(mg/L)	0.02	0.1	0.34	0	0.05[a]	–
Fe	(mg/L)	0.07	23	0.38	0.05	–	–
Mn	(mg/L)	<0.01	7.89	0.22	<0.01	0.06[a]	–
SO$_4$	(mg/L)	12	17	22	14	14[a]	–
N$_2$	(mg/L)	20.18	27.94	23.94	24.49	22.25	22.19
O$_2$[b]	(mg/L)	9.33	4.11	0.36	0.60	0.29	0.30
CO$_2$	(mg/L)	3.16	2.53	5.10	16.06	2.20	2.19
CH$_4$	(mg/L)	0.000	0.002	0.028	0.000	0.029	0.029
Ar	(mg/L)	0.749	0.979	0.804	0.810	0.789	0.784
δD	‰	−60.3	−58.9	−55.5	−55.7	−57.1	−57.5
δ^{18}O	‰	−9.41	−9.18	−8.80	−8.70	−8.97	−8.91
δ^{13}C of DOC	‰	−26.5	−24.3	−26.3	−25.4	−26.1	−24.0
δ^{13}C of DIC	‰	−14.6	−12.2	−14.6	−17.8	−14.9	−14.9
δ^{15}N of NO$_3^-$	‰	–	–	–	9.2	–	–
δ^{18}O of NO$_3^-$	‰	–	–	–	2.6	–	–
δ^{15}N of N$_2$	‰	0.72	0.72	1.00	0.90	0.88	0.88

δ delta; ‰ per mil relative to standard

[a] Sample collected from adjacent onsite well

[b] Dissolved oxygen gas sample; *ORP* oxidation reduction potential; *mV* millivolts; – no data

amounts of excess N$_2$ from denitrification. Sample W1 exhibited the most likely evidence for excess N$_2$ and may originally have had around 1–2 mg/L of NO$_3^-$ (as N) with original δ^{15}N(NO$_3^-$) of around +3 to +5‰. In this case, denitrification was essentially complete, and Fe and Mn reduction were active, possibly releasing As into solution as indicated by relatively high As concentration in W1 (15 µg/L). In contrast, although S1 was classified as oxic and contained NO$_3^-$, its O$_2$ concentration was relatively low (<1 mg/L); therefore, it is possible this sample was partially denitrified or was a mixture of denitrified and undenitrified water. The relatively low As concentration in S1 (1.2 µg/L) is consistent with partial denitrification and little Fe or Mn reduction.

Redox and groundwater flow

Anoxic groundwater, affected by landfill leachate, flows downward into the fractured crystalline-rock aquifer where it is transported rapidly within fractures and by pumping from residential-supply wells. Arsenic adsorbed onto oxyhydroxide surfaces on fractures can readily desorb, or mobilize, as the redox state of the groundwater is geochemically altered towards more anoxic conditions. Once anoxic water from fractures enters the crystalline-rock aquifer, there is little opportunity for re-oxidation, leading to the potential of As desorption and contamination of residential water supplies. High As concentrations will likely persist under anoxic conditions unless precipitation occurs with sulfide minerals.

The residential-supply wells have long (typically 50–100 m in length) open boreholes in the fractured-rock aquifer that can intercept groundwater with variable redox and chemical signatures from multiple discrete fractures. Redox mixing can occur in two ways. First, mixing of oxic and anoxic groundwater can occur outside of the borehole as groundwater in fractures with different redox conditions intersect one another. A conceptual diagram showing mixed redox conditions within a hypothetical fractured-rock aquifer is illustrated in Fig. 5. Mixing within the aquifer is shown for the case of a hypothetical deep residential-supply well that intercepts groundwater from the lowermost mixed redox zone (Fig. 5; left inset). Second or alternatively, mixing can occur entirely within the borehole as groundwater with different fracture-specific redox conditions enters the borehole during pumping. Mixing within the borehole is shown for the case of a hypothetical shallow residential-supply well
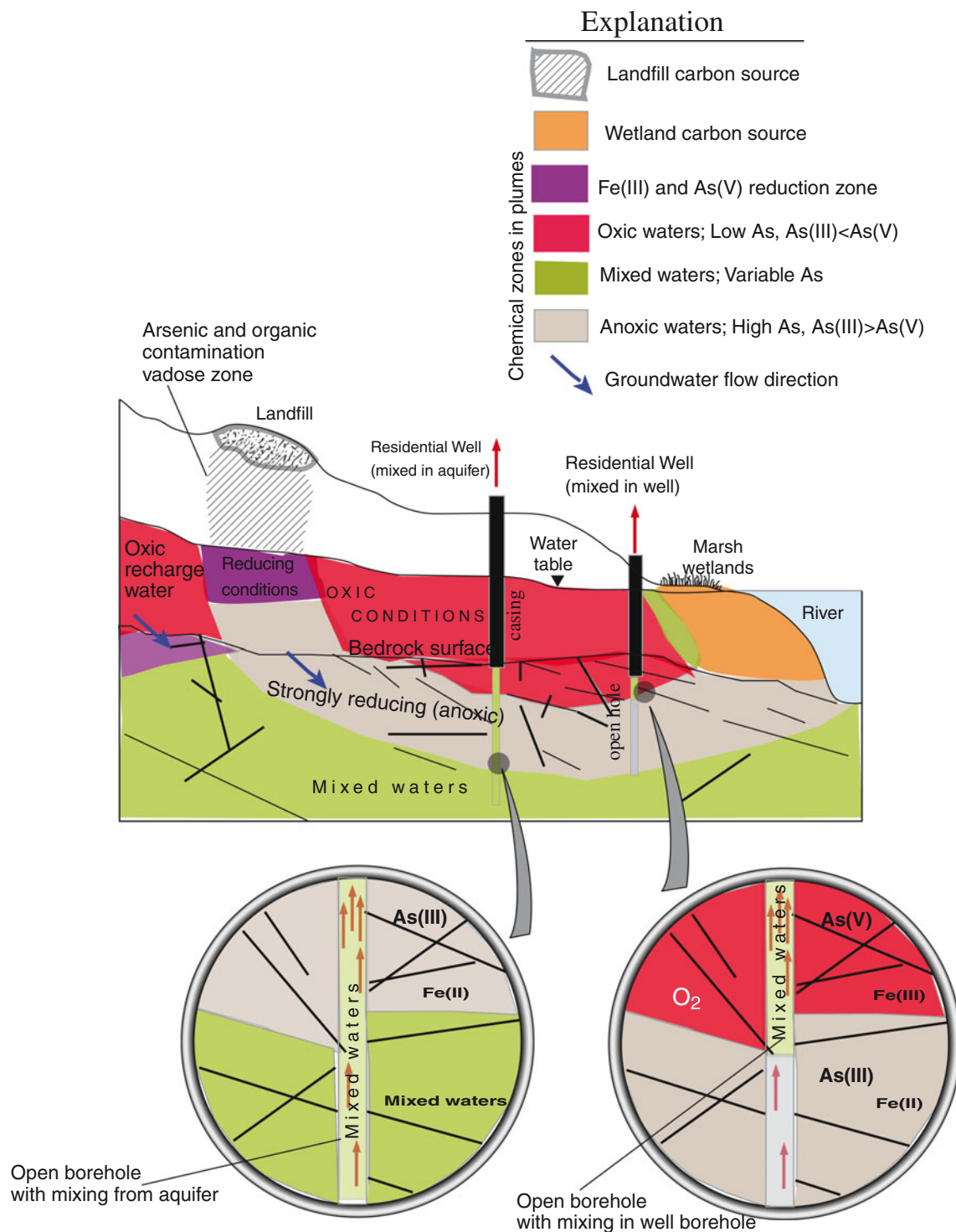
Fig. 5 Conceptual diagram of enhanced As mobility in a fractured crystalline-rock aquifer resulting from waste disposal practices. Mixed redox indicators in well samples can be due to mixing within the aquifer or mixing within the open borehole (*insets*)

that intercepts groundwater from adjacent anoxic and oxic zones (Fig. 5; right inset). Discrete sampling of individual fractures in boreholes could help decipher the dominant mixing process.

Chemical and physical heterogeneity of the groundwater flow system are closely linked and interrelated as presented in Fig. 5. Characterizing redox conditions and

processes can assist in the identification of transport pathways, particularly in flow, in fractured-rock aquifers. Regardless of the variation in natural and anthropogenic carbon inputs of recharged water, redox conditions of groundwater will be affected by fracture patterns and pathways. Residential supply wells commonly intersect a number of discrete fractures and the well sample

integrates the chemical signature of each contributing fracture. Well samples characterized as oxic suggest water derived from shallower and steeply dipping fractures with short pathways. Well samples characterized as mixed suggest water derived from a variety of shallow and deep fractures, either highly interconnected in the aquifer or mixed within the borehole (Fig. 5). Well samples characterized as anoxic suggest water derived from planar dipping or deep fractures with long pathways although significant carbon input could accelerate oxygen depletion in fractures with short pathways. Nevertheless, variability in natural and anthropogenic carbon inputs adds to the complexity of interpreting redox conditions primarily for mixed and anoxic water, whereas oxic water is likely devoid of significant carbon input.

Discussion of redox and arsenic mobility

Residential-supply wells drilled into fractured crystalline-rock aquifers are likely to have a chemically complex mixture of groundwater recharging the well, given the nature of fracture flow and the contribution of groundwater in fractures with different redox states and chemical signatures. Easily obtainable redox characterization can help unravel the complex interaction of hydraulic and redox controls affecting As mobilization from complex groundwater-flow systems such as fractured-rock aquifers. Other information such as As speciation data, dissolved gas concentrations, and stable isotope ratios can provide additional lines of evidence.

Characterization of redox conditions using simple redox indicators showed that the majority of residential-supply bedrock wells in the study area had groundwater with mixed (oxic-anoxic) redox conditions. The high frequency of mixed conditions appears atypical compared to regional redox conditions from similar variably calcareous metasedimentary rocks and provides the first indication that the redox variability found in the study area may be attributed partly to anthropogenic activities and waste disposal. Other factors potentially contributing to the locally high occurrence of redox variability include the local fracture patterns, connectivity, and transmissivity of fractures, and the relatively high density of residential bedrock wells that withdraw groundwater in the study area. Most samples with As concentrations above the USEPA MCL of 10 μg/L were associated with either mixed oxic-anoxic (oxic coupled with either Mn(IV) or Fe(III) reduction), or anoxic (Fe(III) reduction) conditions. This is typical of waters enriched in As by reductive dissolution; i.e., As released from sorption sites by reduction of metal oxyhydroxides and (or) reduction of As(V) oxide. What is not typical is the rate of occurrence of wells with these conditions and with high As concentrations in the study area. The variably calcareous metasedimentary rocks underlying most of the study area, excluding the area to the east that appears to be a granitic intrusion, can have regionally high concentrations of As in groundwater (7–31 % occurrence above MCL). However, in the area downgradient of the waste site, approximately 55 %

of wells had concentrations of As greater than 10 ug/L. This unusual condition is the second indication that mobilization of As may not be entirely natural.

Arsenic speciation provided useful multiple-lines-of-evidence information in identifying As mobilization in groundwater and understanding conditions of As transport under mixed redox conditions. For instance, As(III) was the dominant species in two-thirds of all samples under mixed conditions; therefore, As(III) transport in groundwater likely occurred within fractures under anoxic conditions, later mixing with oxic groundwater from other fractures intersecting the same open borehole of the residential-supply well.

Analysis of dissolved gases and stable isotopes at a subset of wells showed that methanogenic conditions were associated with As concentrations above the 10 μg/L MCL in groundwater. Thus, mapping methane concentrations may prove useful in understanding redox processes and controls on enhanced As mobilization. Isotopic variations in DIC of $\delta^{13}C$ suggest high As concentrations may be associated with increased calcite dissolution and(or) potentially longer residence times of groundwater allowing for greater dissolution of As complexed to calcite. The latter may help explain the high As concentrations (60.9 μg/L) at a well with similar redox conditions to other wells with low (less than 10 μg/L) As concentrations. Nitrate isotopes, which provide insight into the nitrogen cycle, allow for an assessment of nitrogen controls on As mobility caused by denitrification and appear to affect As concentrations at one residential-supply well.

Anoxic redox conditions were most prevalent to the west, often co-occurring with measurable concentrations of TCE. This was the third indication that the concentrations of As in wells to the west of the waste site (downgradient) were caused or enhanced by conditions that arose from the introduction of organic wastes into the local groundwater flow system. The potential for westerly transport is supported by the presence of laterally extensive northwesterly dipping fractures underlying the waste site. Also, the predominance of mixed redox conditions, with a high proportion of As(III)/As total, indicate that anthropogenic carbon sources likely affected groundwater to the west and south as well. In contrast to reduced groundwater, As concentrations were low (typically less than 3 μg/L) in oxic groundwater possibly due to dilution of recently recharged oxic water with low As concentrations and(or) the removal of dissolved As through adsorption of As onto metal oxyhydroxides.

The consideration of any one of the pieces of evidence alone would not necessarily have been sufficient for concluding that the concentrations of As in water samples from wells was related to the waste site activities. The importance of this characterization and the implications of the findings are that fairly simple and easy to obtain information on the redox conditions of samples of groundwater from private wells, combined with measurements of other contaminants (TCE) that would have been collected anyway, resulted in a greater depth of interpretation of the data than is normally possible. Inferred redox conditions of groundwater, including waters potentially

affected by waste disposal can be made relatively easily by analysis of threshold concentrations of key geochemical constituents (McMahon and Chappelle 2008) and this redox characterization can then provide a framework to interpret the likelihood of enhanced As mobilization from reductive dissolution and anthropogenic carbon sources viewed in a local and regional context. Further, selective redox characterization (As speciation, methane gas measurements, and stable isotopes) is beneficial where mixing of oxic and anoxic groundwater occurs at a high frequency, such as fractured crystalline-rock aquifers. At other hydrogeologically complex sites, the list of parameters in Table 1 can used as a starting point to help assess As mobility and pathways.

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