# ground water

# Redox Processes and Water Quality of Selected Principal Aquifer Systems

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## Abstract

Reduction/oxidation (redox) conditions in 15 principal aquifer (PA) systems of the United States, and their impact on several water quality issues, were assessed from a large data base collected by the National Water-Quality Assessment Program of the USGS. The logic of these assessments was based on the observed ecological succession of electron acceptors such as dissolved oxygen, nitrate, and sulfate and threshold concentrations of these substrates needed to support active microbial metabolism. Similarly, the utilization of solid-phase electron acceptors such as Mn(IV) and Fe(III) is indicated by the production of dissolved manganese and iron. An internally consistent set of threshold concentration criteria was developed and applied to a large data set of 1692 water samples from the PAs to assess ambient redox conditions. The indicated redox conditions then were related to the occurrence of selected natural (arsenic) and anthropogenic (nitrate and volatile organic compounds) contaminants in ground water. For the natural and anthropogenic contaminants assessed in this study, considering redox conditions as defined by this framework of redox indicator species and threshold concentrations explained many water quality trends observed at a regional scale. An important finding of this study was that samples indicating mixed redox processes provide information on redox heterogeneity that is useful for assessing common water quality issues. Given the interpretive power of the redox framework and given that it is relatively inexpensive and easy to measure the chemical parameters included in the framework, those parameters should be included in routine water quality monitoring programs whenever possible.

## Introduction

Reduction/oxidation (redox) processes affect the chemical quality of ground water in all aquifer systems. Redox processes can alternately mobilize or immobilize potentially toxic metals associated with naturally occurring aquifer materials (Lovley et al. 1991; Smedley and Kinniburgh 2002), contribute to the degradation or preservation of anthropogenic contaminants (Korom 1992; Bradley 2000, 2003), and generate undesirable by-products such as dissolved ferrous iron ($Fe^{2+}$), hydrogen sulfide ($H_2S$), and methane ($CH_4$) (Back and Barnes 1965; Baedecker and Back 1979; Chapelle and Lovley 1992).

Determining the kinds of redox processes that occur in an aquifer system, documenting their spatial distribution, and understanding how they affect concentrations of natural or anthropogenic contaminants are central to assessing and describing the chemical quality of ground water (Baedecker and Back 1979; Champ et al. 1979; Thorstenson et al. 1979; Plummer et al. 1990; Vroblesky and Chapelle 1994; Chapelle et al. 1995; Hunter et al. 1998; Christensen et al. 2000). The purpose of this paper was to describe a framework suitable for assessing ambient redox processes in regional ground water systems using a data base of 1692 analyses made as part of the National Water-Quality Assessment (NAWQA) Program of the USGS. This framework then is used to illustrate the effects that redox processes have on several practical water quality issues, including the occurrence and fate of arsenic (As), nitrate ($NO_3^-$), and volatile organic compounds (VOCs) in several principal aquifer (PA) systems of the United States. A PA is defined as a regionally extensive aquifer or aquifer system that has the potential to be used as a source of potable water. The USGS has identified
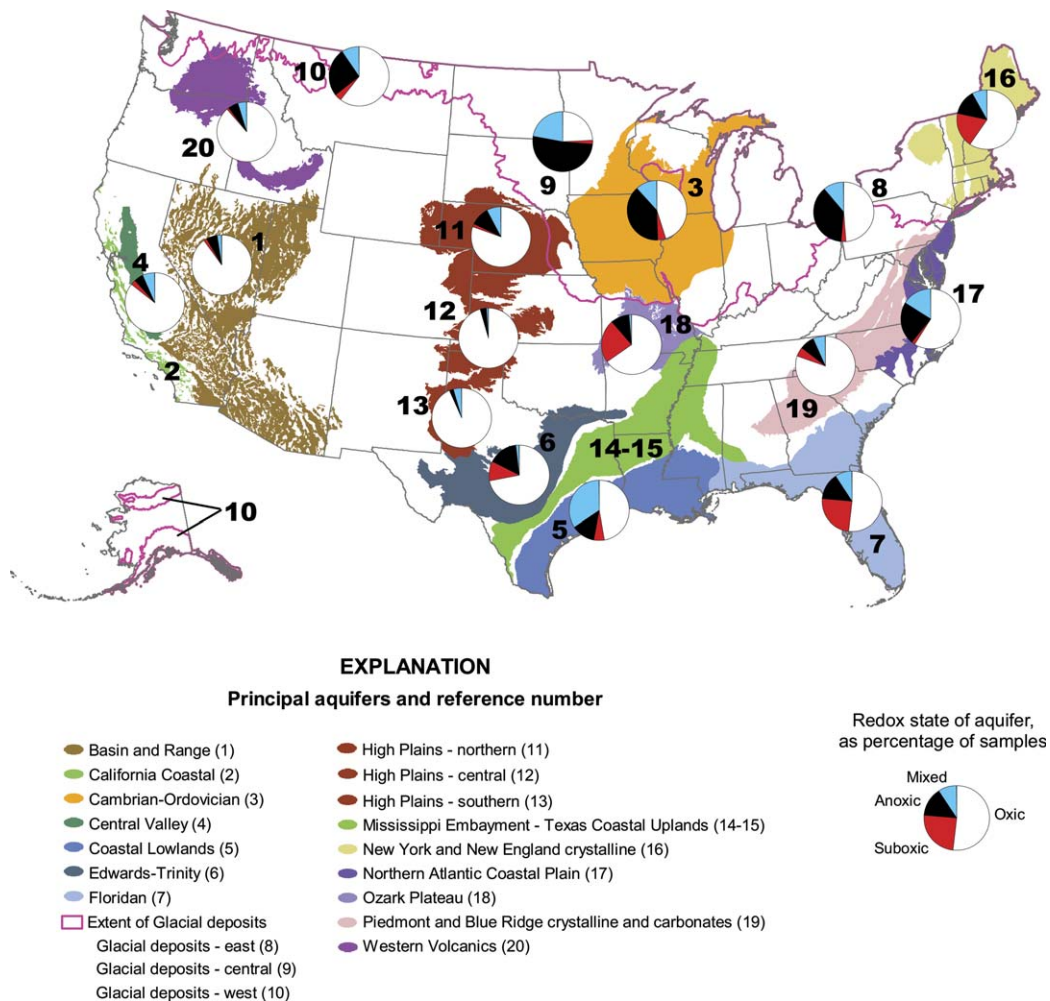
62 PAs in the United States (USGS 2003; Lapham et al. 2005), 15 of which were evaluated in this study (Figure 1).

## Source of Water Quality Data

The water quality data analyzed in this report represent water samples collected from monitoring, domestic, and public-supply wells. The monitoring wells were installed by the USGS near the water table under agricultural and urban land uses. Maps and tables showing the distribution of sampled wells by PA and the number of samples by well type are presented as Supplementary Material. Collection and analysis of samples from the monitoring and domestic wells were done by the USGS from 1991 to 2004 as part of the NAWQA Program using established and consistent procedures (USGS 2006a, 2006b). Data from the public-supply wells were collected from 1993 to 2004 by the USGS for the NAWQA Program using the same procedures as aforementioned or by other agencies. Samples from domestic and public-supply wells were collected at the wellhead upstream from pressure tanks and treatment.

## Framework for Assessing Redox Processes on a Regional Scale

Microorganisms that catalyze redox processes in natural systems compete for limited resources. Because of this competition, microorganisms tend to favor redox processes that generate the maximum amount of available energy. Those microbial processes that couple the most efficient electron donors to the most efficient electron acceptors have a competitive advantage. Dissolved and particulate organic carbon are often the most common electron donors available in ground water systems (Thurman 1985), although some reduced forms of nitrogen, iron, sulfur, and possibly other species could be important electron donors in some cases (Kölle et al. 1985; Straub et al. 1996; Luther et al. 1997; Engstrom et al. 2005). There is similar variability in the kinds and amounts of available electron acceptors. Dissolved oxygen ($O_2$) produces the most energy per mole of organic carbon oxidized than any other commonly available electron acceptor, and thus it is used preferentially by subsurface microorganisms. Because ground water systems



**EXPLANATION**

**Principal aquifers and reference number**

- Basin and Range (1)
- California Coastal (2)
- Cambrian-Ordovician (3)
- Central Valley (4)
- Coastal Lowlands (5)
- Edwards-Trinity (6)
- Floridan (7)
- Extent of Glacial deposits
- Glacial deposits - east (8)
- Glacial deposits - central (9)
- Glacial deposits - west (10)
- High Plains - northern (11)
- High Plains - central (12)
- High Plains - southern (13)
- Mississippi Embayment - Texas Coastal Uplands (14-15)
- New York and New England crystalline (16)
- Northern Atlantic Coastal Plain (17)
- Ozark Plateau (18)
- Piedmont and Blue Ridge crystalline and carbonates (19)
- Western Volcanics (20)

Redox state of aquifer, as percentage of samples

Mixed
Anoxic
Oxic
Suboxic

**Figure 1. Location of PAs included in this analysis. Pie charts show the percentages of domestic well samples that were oxic, suboxic, anoxic, or diagnostic of mixed redox processes (see Table 1 for definitions). The glacial deposit aquifer was subdivided into eastern, central, and western deposits on the basis of geological source of the glacial material (Warner and Arnold 2005). As defined here, the glacial deposit aquifer in the central United States extends from Ohio to central Montana.**

can be isolated from the atmosphere, however, $O_2$ tends to be consumed along aquifer flowpaths. Under anoxic conditions, the next most energetically favorable naturally available electron acceptor is $NO_3^-$, followed by manganese (IV) [Mn(IV)], ferric iron [Fe(III)], sulfate ($SO_4^{2-}$), and finally carbon dioxide ($CO_2$). This order of preferential electron acceptor utilization—$O_2$ > $NO_3^-$ > Mn(IV) > Fe(III) > $SO_4^{2-}$ > $CO_2$—is referred to as the ecological succession of terminal electron-accepting processes. Some common contaminants of ground water systems, such as chlorinated ethenes, may also act as electron acceptors. The ecological succession of some common natural and anthropogenic electron acceptors is shown in Figure 2.

One consequence of this ecological succession is that redox processes have a tendency to segregate into zones dominated by a single electron-accepting process (Froelich et al. 1979; Berner 1980; Lovley and Goodwin 1988). Given the sequential nature of electron acceptor utilization, given the tendency of redox processes to segregate into predominant zones, and given the distinctive end products of some redox processes (dinitrogen gas [$N_2$], ammonium [$NH_4^+$], $Fe^{2+}$, $H_2S$, and $CH_4$), water quality data can be used to assess ambient redox processes in ground water systems.

Documenting the consumption of soluble electron acceptors and generation of distinctive by-products along defined flowpath segments is the most reliable method for identifying the distribution of redox processes in a ground water system (Chapelle et al. 1995). In regional-scale aquifer systems, however, the position of individual wells within the flow system often is uncertain and flowpath analysis cannot always be applied. Furthermore, pumping wells, particularly high-capacity municipal and irrigation wells, can integrate multiple flowpaths that have encountered multiple redox zones. Finally, diagnostic redox by-products like $H_2S$, $CH_4$, and hydrogen ($H_2$), which are important components of hierarchical schemes for diagnosing redox processes (Chapelle et al. 1995; Christensen et al. 2000), are not routinely measured in

regional water quality assessments. Despite these hydrologic and operational realities, a framework for assessing redox processes in regional aquifer systems is possible and is shown in Table 1. The framework is a modification of those described by Chapelle et al. (1995) and Paschke et al. (2007). Among other differences, the frameworks described by Chapelle et al. (1995) and Paschke et al. (2007) do not explicitly include suboxic and mixed categories, do not differentiate between Mn(IV) and Fe(III) reduction (Chapelle et al. 1995), and do not include a methanogenic category (Paschke et al. 2007). The anoxic and suboxic designations in Table 1 differ from those commonly used in the oceanographic literature in which anoxic denotes the absence of $O_2$ and presence of $H_2S$ and(or) $CH_4$, and suboxic denotes the absence of $O_2$ (or very low concentration), $H_2S$, and $CH_4$ (Froelich et al. 1979; Murray et al. 1989). In this study, the anoxic designation has been expanded to include $NO_3^-$, Mn(IV), and Fe(III) reduction. The suboxic designation indicates low $O_2$ conditions, but further definition of redox processes is not possible without additional data.

Parameters included in the framework described in this paper were chosen because they are relatively inexpensive and easy to measure, and most of them are commonly measured in regional water quality assessments. Other redox indicators, such as $N_2$, $NH_4^+$, $H_2S$, $CH_4$, and $H_2$, should be measured whenever possible. The use of $N_2$ to detect denitrification also requires measurements of other dissolved gases such as argon and neon to separate the atmospheric and microbial components of $N_2$ (Vogel et al. 1981; McMahon et al. 2004). The concentration thresholds listed in Table 1 were chosen to be broadly applicable to ambient regional aquifer systems and are based on considerations of microbial physiology (e.g., Knowles 1982; Lovley and Klug 1983), numerous field studies (e.g., Plummer et al. 1990; Chapelle and McMahon 1991; Chapelle et al. 1995; Murphy and Schramke 1998; Elliot et al. 1999; review by Christensen et al. 2000; McMahon et al. 2004), and typical analytical reporting limits for the chosen parameters.

Although the framework shown in Table 1 has the advantages of broad applicability and internal consistency, it also is subject to certain limitations. For example, it is possible that the concentration thresholds are variable and dependent on multiple factors such as microbial species (e.g., Knowles 1982), electron donor availability (Achtnich et al. 1995; Vroblesky et al. 1996), and scale at which sampling occurs (Alewell et al. 2006). The $O_2$ concentration threshold required for the onset of denitrification, for example, generally is considered to be about 0.2 to 0.3 mg/L (Tiedje 1988; Seitzinger et al. 2006) but could be of the order of 2 mg/L in some aquifers (Böhlke et al. 2002, 2007; McMahon et al. 2004) and about 0.2 to more than 1 mg/L for some bacterial strains under controlled laboratory conditions (Skerman and MacRae 1957; Lloyd et al. 1987; Chen et al. 2003). Apparently larger threshold $O_2$ concentrations in some aquifers could result from mixing multiple flowpaths at the sampling scale of well screens.

The threshold concentrations chosen to indicate Mn(IV) reduction (0.05 mg/L) and Fe(III) reduction
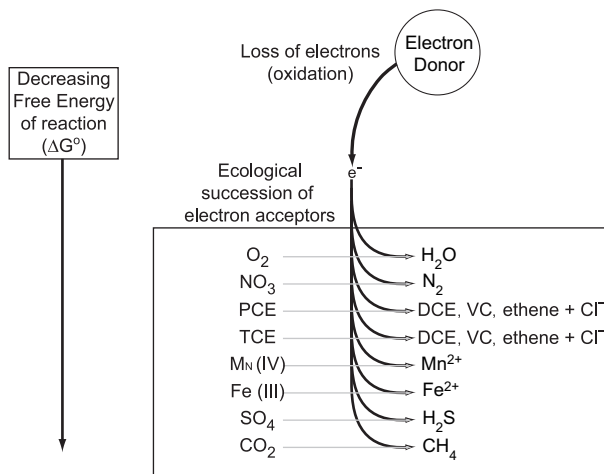


**Figure 2. Ecological succession of electron-accepting processes and sequential production of final products. PCE, tetrachloroethene; TCE, trichloroethene; DCE, dichloroethene; VC, vinyl chloride.**

**Table 1**
**Threshold Concentrations for Identifying Redox Processes in Regional Aquifer Systems**

| Redox Process | Water Quality Criteria (mg/L) | | | | | Comments |
|---|---|---|---|---|---|---|
| | $O_2$ | $NO_3^-$-N | $Mn^{2+}$ | $Fe^{2+}$ | $SO_4^{2-}$ | |
| Oxic | | | | | | |
| $O_2$ reduction | $\geq 0.5$ | — | <0.05 | <0.1 | — | — |
| Suboxic | | | | | | |
| — | <0.5 | <0.5 | <0.05 | <0.1 | — | Further definition of redox processes not possible |
| Anoxic | | | | | | |
| $NO_3^-$ reduction | <0.5 | $\geq 0.5$ | <0.05 | <0.1 | — | — |
| Mn(IV) reduction | <0.5 | <0.5 | $\geq 0.05$ | <0.1 | — | — |
| Fe(III)/$SO_4^{2-}$ reduction | <0.5 | <0.5 | — | $\geq 0.1$ | $\geq 0.5$ | — |
| Methanogenesis | <0.5 | <0.5 | — | $\geq 0.1$ | <0.5 | — |
| Mixed | | | | | | |
| — | — | — | — | — | — | Criteria for more than one redox process are met |

(0.1 mg/L) are also based on the results of numerous field studies (e.g., Plummer et al. 1990; Chapelle and McMahon 1991; Chapelle et al. 1995; Murphy and Schramke 1998; Elliot et al. 1999; review by Christensen et al. 2000). Ferrous iron and $Mn^{2+}$ are reactive species and subject to mineral precipitation (e.g., iron sulfide) and sorption processes; thus, the concentration thresholds may underestimate the extent of Mn(IV) and Fe(III) reduction in some aquifers. In addition, because the energetics of Fe(III) reduction are partly dependent on the crystalline form of solid Fe(III) present in the system, it often is difficult to distinguish between Fe(III) reduction and $SO_4^{2-}$ reduction in ground water systems (Jakobsen et al. 1998). For this reason, the framework of Table 1 does not attempt to distinguish between Fe(III) and $SO_4^{2-}$ reduction. The threshold $SO_4^{2-}$ concentration below which methanogenesis becomes the predominant redox process is likely to be larger than 0.5 mg/L in some aquifers containing abundant electron donors (Chapelle et al. 2002). Underestimation of threshold concentrations would underpredict the occurrence of a particular redox process. While recognizing these limitations, the threshold concentrations listed in Table 1 were chosen to be broadly applicable to different hydrologic systems at the regional scale. Threshold concentrations and the relative importance of each redox process could be further refined using site-specific information, including other redox indicators such as $H_2S$, $CH_4$, and $H_2$ that are not commonly measured in regional assessments.

In some instances, applying the framework to regional water quality data will result in a unique, single-redox diagnosis. In other instances, where aquifer heterogeneities, flowpath complexity, or long-screened wells mix available electron acceptors and/or final products, it is possible only to define a "mixed" redox diagnosis. Even in the case of mixed redox processes, however, the diagnosis may contain information that can be useful in the context of assessing certain water quality issues.

## Redox Processes in Selected PAs of the United States

Water quality data from the domestic, monitoring, and public-supply wells were evaluated using the framework of Table 1 for the purpose of relating redox processes to the occurrence of contaminants in water from those wells (discussed in the next section). Only domestic wells were used, however, for broadly characterizing redox processes in the PAs (discussed in this section). Domestic wells were used for this purpose because they had better spatial distributions in the PAs than the monitoring and public-supply wells, although it is recognized that none of the well networks is representative of entire PAs in most cases (Figure S1 and Table S1), and because they generally had shorter screened intervals than the public-supply wells (median screen lengths of 6.1 and 29.9 m, respectively). The domestic wells were generally shallower, however, than the public-supply wells (median depth to bottom of screen below land surface of 48 and 87 m, respectively).

The framework listed in Table 1 allows for a generalized but internally consistent comparison between the redox processes characteristic of several PAs of the United States. Percentages of the domestic well samples that were characterized as being oxic, suboxic, anoxic, or as having mixed redox processes are illustrated spatially in Figure 1. The samples characterized as being anoxic were subdivided further into $NO_3^-$, Mn(IV), and Fe(III)/$SO_4^{2-}$ reducing and methanogenic in Table 2. Some broad spatial patterns in the distribution of redox processes are apparent in Figure 1. On average, $O_2$ reduction was the predominant redox process in 89% of the samples from sand and gravel PAs and western volcanic PAs in the western United States (Figure 1 and Table 2). However, $O_2$ reduction was the predominant redox process in only 55%, on average, of the samples from the remaining PAs, many of which were located in the eastern half of the

**Table 2**
**Redox Classification of Water Samples from Domestic Wells in Selected PAs**

| PA | Number of Samples | O$_2$ Reduction | Suboxic | NO$_3^-$ Reduction | Mn(IV) Reduction | Fe(III)/SO$_4^{2-}$ Reduction | Methanogenesis | Mixed Redox Processes |
|---|---|---|---|---|---|---|---|---|
| Sand and gravel | | | | | | | | |
|   Basin and Range | 122 | 90.1 | 1.6 | 2.5 | 0.0 | 2.5 | 0.8 | 2.5 |
|   Central Valley | 76 | 85.6 | 2.6 | 2.6 | 1.3 | 1.3 | 0.0 | 6.6 |
|   High Plains, northern | 166 | 80.2 | 1.8 | 1.2 | 3.6 | 5.4 | 0.0 | 7.8 |
|   High Plains, central | 89 | 95.6 | 0.0 | 1.1 | 0.0 | 2.2 | 0.0 | 1.1 |
|   High Plains, southern | 45 | 93.4 | 0.0 | 0.0 | 2.2 | 0.0 | 0.0 | 4.4 |
| Western volcanics | | | | | | | | |
|   Columbia Plateau– Snake River | 107 | 88.7 | 0.9 | 1.9 | 1.9 | 1.9 | 0.0 | 4.7 |
| Carbonate/crystalline | | | | | | | | |
|   New York– New England | 111 | 59.5 | 18.9 | 0.9 | 1.8 | 10.8 | 0.0 | 8.1 |
|   Piedmont and Blue Ridge | 178 | 80.3 | 5.1 | 1.7 | 1.7 | 4.5 | 0.0 | 6.7 |
| Semiconsolidated sandstone | | | | | | | | |
|   Coastal Lowlands | 55 | 47.3 | 5.5 | 0.0 | 1.8 | 7.3 | 3.6 | 34.5 |
|   Northern Atlantic Coastal Plain | 56 | 58.9 | 1.8 | 0.0 | 0.0 | 10.7 | 12.5 | 16.1 |
| Carbonate/sandstone | | | | | | | | |
|   Cambrian-Ordovician | 69 | 45.1 | 4.3 | 1.4 | 1.4 | 36.2 | 0.0 | 11.6 |
|   Edwards-Trinity | 57 | 71.9 | 10.5 | 3.5 | 0.0 | 12.3 | 0.0 | 1.8 |
|   Floridan | 97 | 51.6 | 24.7 | 0.0 | 1.0 | 7.2 | 6.2 | 9.3 |
|   Ozark Plateau | 69 | 65.3 | 23.2 | 1.4 | 0.0 | 5.8 | 2.9 | 1.4 |
| Glacial deposits | | | | | | | | |
|   Eastern | 72 | 48.6 | 2.8 | 2.8 | 8.3 | 25.0 | 1.4 | 11.1 |
|   Central | 270 | 24.1 | 2.2 | 0.7 | 0.4 | 40.0 | 10.4 | 22.2 |
|   Western | 53 | 60.5 | 3.8 | 0.0 | 9.4 | 9.4 | 7.5 | 9.4 |

country. Those PAs contained relatively large percentages of anoxic samples, with the glacial deposit PAs containing the largest percentage followed by the semiconsolidated sandstone, carbonate/sandstone, and carbonate/crystalline PAs (Table 2). On average among those PAs, Fe(III)/SO$_4^{2-}$ reduction was the most common anoxic redox process followed by methanogenesis, Mn(IV) reduction, and NO$_3^-$ reduction. Suboxic conditions were most common in aquifers containing karst features (Edwards, Floridan, and Ozark Plateau aquifers) or fractured rocks (carbonate/crystalline bedrock aquifers in New York and New England) (Figure 1).

The spatial distribution of redox processes shown in Figure 1 likely reflects differences in geology, climate, and hydrology, among other factors, across the United States. A plot of O$_2$ concentrations as a function of PA lithology indicates that geology is a major factor in determining the relative importance of oxic and anoxic redox processes (Figure 3 and Table 2). Geological factors such as sediment source and depositional environment can influence the availability of natural electron acceptors and donors in the subsurface. For example, alluvial fan and fluvial deposits in the western United States contain abundant Fe(III) to potentially support Fe(III) reduction; yet, oxic conditions can persist for thousands of years along kilometer-scale flowpaths in those aquifers because the

deposits generally lack the electron donors necessary to support anoxic redox processes (Winograd and Robertson 1982; McMahon et al. 2004). In contrast, glacial deposits in the northern United States often contain abundant electron donors such as pyrite and buried wood that support robust microbial activity resulting in steep redox gradients that can transition from O$_2$ reduction to methanogenesis along meter-scale flowpaths (Simpkins and Parkin 1993).

A significant ($p < 0.001$) positive Spearman correlation was observed between O$_2$ concentration and depth to water (Figure 4A). Sand and gravel and volcanic PAs in the relatively dry western United States had significantly ($p < 0.001$, Mann-Whitney test) larger depths to water than the aquifers in the relatively wet eastern United States (mean depths 39 and 13 m, respectively). This observation indicates that climate may also influence redox processes, possibly through its control on vegetation, soil development, and recharge. Pabich et al. (2001) reported that concentrations of dissolved organic carbon (DOC) in ground water near the water table in Cape Cod, Massachusetts, decreased as vadose zone thickness increased. A similar inverse relation between DOC concentration and depth to water was observed in the data from water table monitoring wells in this study (Figure 4B). Soil DOC leached to shallow water tables and subsequent microbial mineralization could account for the observed
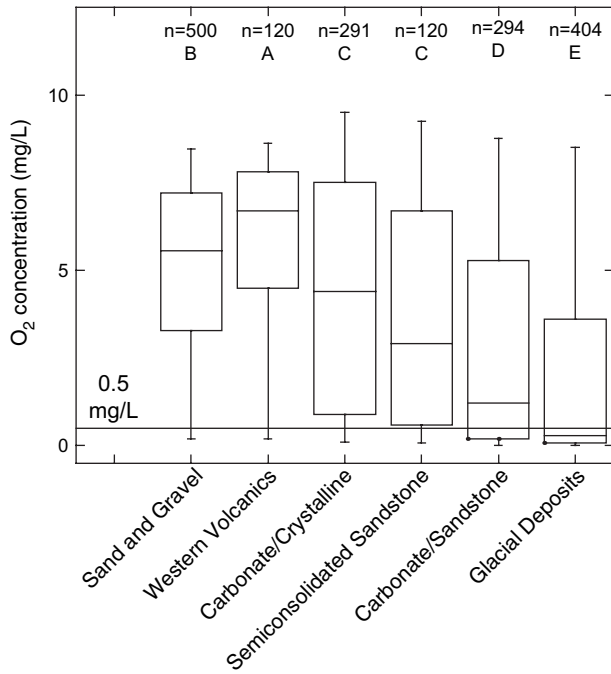
**Figure 3. Concentrations of $O_2$ in water from domestic wells as a function of PA lithology. The box whiskers show 5th and 95th percentile concentrations. The boxes show the 25th, 50th, and 75th percentile concentrations. Boxes labeled with different letters have significantly different $O_2$ concentrations on the basis of the Kruskall-Wallis and Mann-Whitney nonparametric tests. All statistical tests were done using the statistical software package StatView (Abacus Concepts 1996). An α value of 0.05 was used unless specified.**

decrease in $O_2$ concentrations with decreasing depth to water (Figure 4A). Topography probably is important as well because water tables generally are deeper in uplands than in valleys.

Hydrology may influence redox processes in aquifers through its control on ground water residence time. For example, when concentrations of redox reactants and products are plotted vs. depth of the well screen below the water table for domestic wells in the central glacial deposit PA (Figure 5), a distinctive pattern of con-

centration changes with depth emerges. Samples from the shallowest wells were predominantly oxic with $NO_3^-$ concentrations generally ranging from about 1 to 20 mg/L as N. As well depth increased and, thus, presumably ground water residence time, $O_2$ and $NO_3^-$ were the first electron acceptors to be removed from solution (Figure 5). Peak concentrations of $Mn^{2+}$ occurred once $NO_3^-$ concentrations decreased below about 0.5 mg/L as N. A break in slope of the $Fe^{2+}$ concentration trend occurred about 4.5 m deeper than the $Mn^{2+}$ peak, and the percentage of samples with $SO_4^{2-}$ concentrations less than the 0.1 mg/L detection level was seven times larger for samples from depths below the $Fe^{2+}$ slope change (roughly 16 m) than for shallower samples. Those patterns of electron acceptor consumption and final product production mirror the patterns predicted by the ecological succession of terminal electron-accepting processes (Figure 2).

Geology, climate, and hydrology influence redox processes primarily through their controls on ground water residence time and electron acceptor/donor availability. Superimposed on those natural factors are anthropogenic factors like land-use change and chemical applications/releases at the land surface, which also can affect residence time (e.g., by altering recharge, Scanlon et al. 2005) and electron acceptor/donor availability (e.g., agricultural N applications or gasoline spills).

The percentages of domestic well samples with mixed redox processes ranged from 1.1 to 34.5 (Table 2). Although those samples are not diagnostic of a single redox process, they may provide useful information on redox heterogeneity in aquifers. Intuitively, it might be expected that wells with longer well screens would produce more mixed redox diagnoses than wells with shorter screens. In fact, the opposite pattern was observed when mean screen lengths were compared among the different PAs. Figure 6A shows the percentage of samples with mixed redox processes plotted as a function of mean well screen length. Those data indicate that PAs with the most mixed redox samples actually had the shortest screened intervals (Figure 6A). Thus, samples with mixed redox processes are not necessarily a result of mixing waters in long screened intervals. The common occurrence of
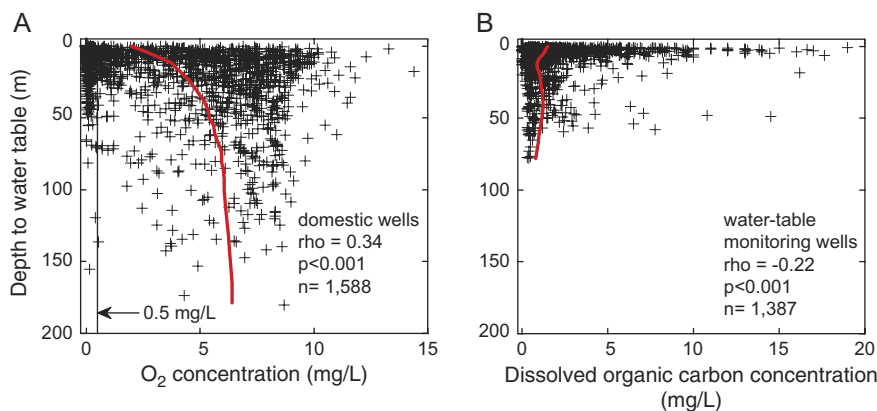


**Figure 4. (A) Concentrations of $O_2$ in water from domestic wells as a function of depth to the water table. (B) Concentrations of DOC in water from water table monitoring wells as a function of depth to the water table. The solid lines in both plots are lowess curve fits to the data. Also shown are Spearman correlation statistics.**
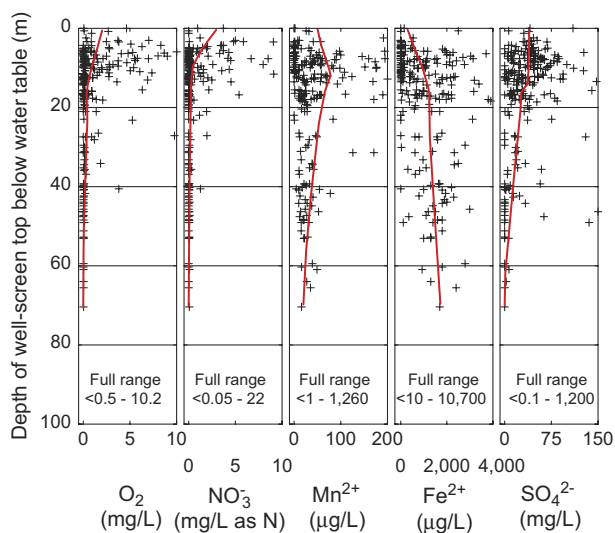
**Figure 5. Concentrations of redox reactants and products as a function of the depth of the well screen top below the water table for domestic well samples from the central glacial deposit aquifer. The solid lines are lowess curve fits to the data.**

mixed redox processes in some short-screen wells could be explained if closely spaced zones with different redox processes were also common in those aquifers. Those environments are known to exist near aquifer/aquitard interfaces (McMahon 2001), near localized zones of electron donor enrichment within aquifers (e.g., lignite fragments, Murphy and Schramke 1998; fuel hydrocarbons, Vroblesky et al. 1996), and in other settings where high electron donor content and slow flow velocity coexist. Increased redox heterogeneity in sediments may be accompanied by increased electron flow because of the diversity of electron acceptors and donors in those environments. A significant ($p = 0.001$) positive Spearman correlation was observed between the percentage of
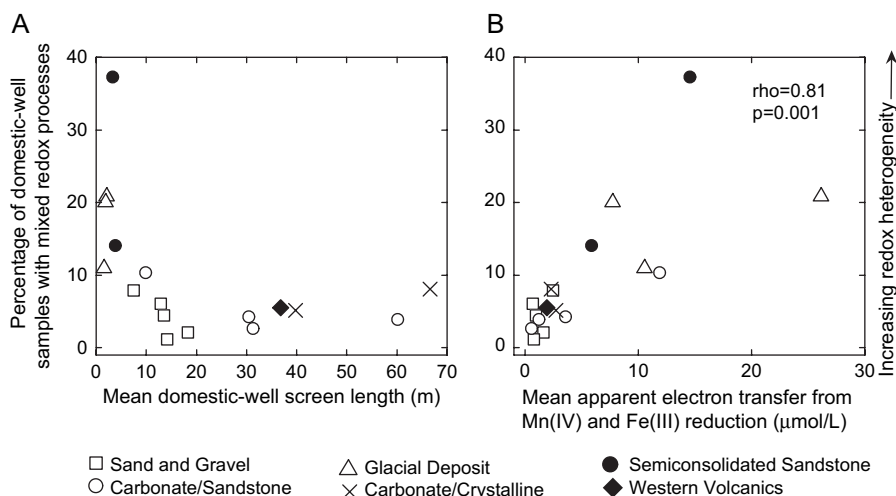
samples with mixed redox processes and the mean apparent electron transfer from Mn(IV) and Fe(III) reduction (Figure 6B). Mn(IV) and Fe(III) electron transfers were calculated using measured $Mn^{2+}$ and $Fe^{2+}$ concentrations and the general redox equations:

$$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad (1)$$

$$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O \quad (2)$$
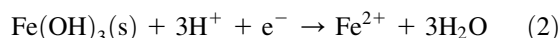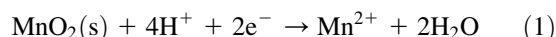
Mn(IV) and Fe(III) electron transfers were assumed to be zero for samples containing less than 0.05 mg/L dissolved $Mn^{2+}$ and less than 0.1 mg/L dissolved $Fe^{2+}$ (Table 1). Although this approach underestimates total electron flow from all redox processes (e.g., electron transfers from $O_2$, $NO_3^-$, and $SO_4^{2-}$ reduction could not be included because their concentrations in the samples at the time of recharge were unknown), the result is consistent with the hypothesis that mixed redox diagnoses reflect the inherent spatial heterogeneity of redox processes in a given hydrologic system. This heterogeneity, in turn, may have important effects on the distribution of natural or anthropogenic contaminants in ground water. If these interpretations are correct, the most heterogeneous distribution of redox processes would be expected in the glacial and semiconsolidated sandstone PAs and the least heterogeneous distributions would be expected in the sand and gravel and western volcanic PAs (Figure 6B).

## Effect of Redox on Water Quality in PAs

The principal goal for having a generalized framework to describe redox processes in regional aquifer systems is to assess their effects on practical water quality issues. The water quality issues addressed for this paper represent natural (As) and anthropogenic ($NO_3^-$ and VOCs) contaminants.



**Figure 6. Percentage of domestic well samples with mixed redox processes as a function of (A) mean well screen length, and (B) mean apparent electron transfer from Mn(IV) and Fe(III) reduction. Electron transfer was assumed to be zero for samples containing less than 0.05 mg/L dissolved $Mn^{2+}$ and less than 0.1 mg/L dissolved $Fe^{2+}$ (Table 1). Also shown in B are Spearman correlation statistics.**

## Redox and the Occurrence of Naturally High Concentrations of As

In some instances, the source of As in ground water comes from the release of anthropogenic wastes. In many instances, however, the source of As is from naturally occurring solid phases that make up the aquifer matrix in ground water systems. Soluble arsenate can be generated by oxidation of As-bearing sulfide minerals such as arsenopyrite. In addition, soluble arsenate complexes tend to adsorb on the surfaces of Mn(IV) and Fe(III) oxyhydroxides also commonly present in aquifer materials under oxic conditions (Dzombak and Morel 1990; Smedley and Kinniburgh 2002). Under Mn(IV)- and Fe(III)-reducing conditions, adsorbed arsenate can be mobilized as metal oxyhydroxides are dissolved. Furthermore, under reducing conditions, arsenate tends to be reduced to soluble arsenite. Thus, depending on the chemical composition of the aquifer matrix and depending on ambient redox conditions, naturally occurring As can be alternately mobilized or immobilized. Other factors that are associated with large dissolved As concentrations in some ground water systems, and that may not be related to redox processes, include high pH, elevated chloride concentrations, aridity, and mixing with geothermal water (Welch et al. 2000; Smedley and Kinniburgh 2002).

Concentrations of dissolved As in ground water from the major PA groups are shown in Figure 7A. The largest concentrations occurred in the sand and gravel and western volcanic PAs, and the smallest concentrations occurred in the carbonate/sandstone PAs. The relative abundance of high-As ground water in the sand and gravel and western volcanic PAs is controlled by several factors, such as pH and evaporative concentration (Welch et al. 2000), in addition to redox. Here the focus is on the apparent effect that redox processes had on As concentrations within PA groups. Even though most samples from the sand and gravel PAs were oxic, there was a significant ($p < 0.05$) difference in As concentrations between samples that were oxic and those that were either Mn(IV) or Fe(III)/$SO_4^{2-}$ reducing, with the anoxic samples having generally larger As concentrations (Figure 7B). The same was true for Mn(IV)- or Fe(III)/$SO_4^{2-}$-reducing samples from the semiconsolidated sandstone and glacial deposit PAs (Figure 7B). In the carbonate/crystalline PAs, the difference in As concentrations between samples that were oxic and those that were Mn(IV) or Fe(III)/$SO_4^{2-}$ reducing was significant at $\alpha = 0.1$ ($p = 0.06$). (There were only three Mn(IV)- and Fe(III)/$SO_4^{2-}$-reducing samples in the western volcanic PAs—too few for the statistical test—and all three concentrations were less than the 1 µg/L common assessment level.) Thus, Mn(IV) or Fe(III)/$SO_4^{2-}$ reducing conditions appear to have produced the largest As concentrations in most of the PA groups. The large As concentrations in ground water of Bangladesh and Vietnam also appear to be produced in anoxic environments characterized by large concentrations of $Mn^{2+}$ and $Fe^{2+}$ (Smedley and Kinniburgh 2002). Whether or not the PAs actually supported Mn(IV) or Fe(III)/$SO_4^{2-}$ reduction as *predominant* redox processes is dependent upon the interactions between climate, geology, hydrology, and anthropogenic factors, as previously discussed. Manganese and Fe(III)/$SO_4^{2-}$
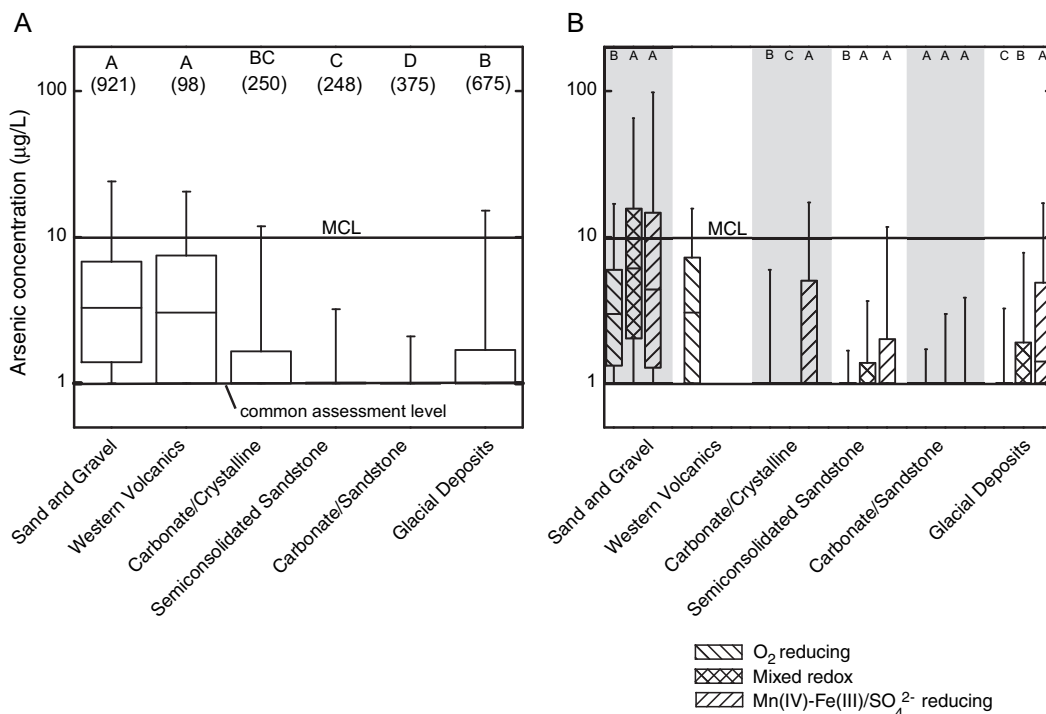


**Figure 7. Concentrations of As in water samples from all well types, by PA, (A) for all samples regardless of redox process and (B) by redox process. See Figure 3 for the definition of box plots and letters at the top of the box plots. A common assessment level of 1 µg/L was used for all PAs. The MCL (maximum contaminant level) line indicates the primary drinking water standard for As. Numbers of samples are shown in parentheses in A.**

reducing conditions occurred most commonly in the glacial deposit and carbonate/sandstone PAs and least commonly in the sand and gravel and western volcanic PAs (Table 2).

In most of the PA groups, As concentrations in samples that were diagnosed as having mixed redox processes were the same as or intermediate between those in oxic and Mn(IV)- or Fe(III)/$SO_4^{2-}$-reducing samples (Figure 7B), which supports the interpretation that those mixed redox samples are characteristic of redox transition zones. If the largest As concentrations occur in anoxic water, then the width of the transition zone from oxic to anoxic conditions has practical implications with respect to the placement of screens in water supply wells. A transition from oxic to anoxic conditions over relatively short distances would not be beneficial to a well owner concerned about As contamination because it would be difficult to selectively screen the oxic zones. Conceptually, the transition between redox zones may be fairly broad, reflecting slower reaction rates and (or) faster rates of ground water flow, such as in relatively homogeneous sand aquifers. Alternatively, the transition between redox zones may be fairly sharp, reflecting faster reaction rates and (or) slower rates of ground water flow, such as at sand/clay interfaces in heterogeneous aquifers. Among the PAs examined in this study, sharp redox boundaries are likely to be more common in those containing greater redox heterogeneity (Figure 6).

### Redox and the Occurrence of Nitrate

The role of redox processes, in particular denitrification, in attenuating $NO_3^-$ in ground water is well known (Korom 1992). Denitrification is a microbially mediated process that reduces $NO_3^-$ to $N_2$ gas in anoxic environments. Nitrate reduction coupled to the oxidation of organic carbon produces $N_2$ and bicarbonate. In some environments, denitrification may be coupled to the oxidation of sulfide minerals instead of, or in addition to, organic carbon (Postma et al. 1991; Böhlke et al. 2002; Beller et al. 2004), which produces $N_2$ and dissolved $SO_4^{2-}$. Dissimilatory $NO_3^-$ reduction to $NH_4^+$ (DNRA) is another possible mechanism for $NO_3^-$ removal under low $O_2$ conditions (Tiedje 1988). In this study, the fraction of $NH_4^+$ to total dissolved N ($NO_3^-$ + nitrite [$NO_2^-$] + $NH_4^+$ + organic N) was zero for 93% of the $NO_3^-$-reducing samples, indicating that DNRA apparently was not an important process under $NO_3^-$-reducing conditions in the assessed hydrogeologic settings.

A comparison of $NO_3^-$ concentrations between PAs shows that the sand and gravel and western volcanic PAs had the largest concentrations and the carbonate/sandstone PAs had the smallest concentrations (Figure 8A). The carbonate/crystalline, semiconsolidated sandstone, and glacial deposit PAs had similar $NO_3^-$ concentrations that were intermediate to those in the other PA groups (Figure 8A). For each PA, $NO_3^-$ concentrations were significantly ($p < 0.001$) larger in water samples containing $O_2 \geq 0.5$ mg/L (and $Mn^{2+}$ and $Fe^{2+}$ concentrations below threshold values, i.e., fully oxic) than in samples containing $O_2 < 0.5$ mg/L (Figure 8B), which is consistent with the understanding of how redox processes affect ground water $NO_3^-$ concentrations. These data indicate the benefit of using $O_2$ measurements, which can be done rapidly in the field, to better understand an aquifer's susceptibility to $NO_3^-$ contamination. Oxygen measurements are not routinely included in many local and state ground water monitoring programs, but those programs are encouraged to do so.

Nitrate concentrations in samples containing $O_2 \geq 0.5$ mg/L and $Mn^{2+}$ or $Fe^{2+}$ concentrations above threshold values (i.e., a mix of oxic and anoxic redox processes) were either the same as or intermediate between those in fully oxic samples and samples containing $O_2 < 0.5$ mg/L (Figure 8B). This is the same type of pattern that was observed in the As data and would be expected if the mixed redox samples are characteristic of redox transition zones. A transition from oxic to anoxic conditions over relatively short distances would be beneficial to a well owner concerned about $NO_3^-$ contamination because it implies that $NO_3^-$ would not persist for long distances along flowpaths in the aquifer. This perspective differs from that of the well owner concerned about As contamination and points to the importance of understanding how redox processes control the fate of different contaminants.

Large $NO_3^-$ concentrations in the sand and gravel and western volcanic PAs are generally consistent with data on N loading from fertilizer and manure at the land surface and with apparent electron transfers from Mn(IV) and Fe(III) reduction. Nitrogen loading was relatively large and electron transfers were relatively small in those aquifers (Figure 8C). Movement of $NO_3^-$ into aquifers would be expected to divert electron flow from Mn(IV) and Fe(III) reduction to denitrification because $NO_3^-$ reduction is higher in the ecological succession of terminal electron-accepting processes (Figure 2). According to that interpretation, the sand and gravel and western volcanic PAs would have relatively little capacity to attenuate $NO_3^-$ inputs from sources like fertilizer and manure. Nitrate concentrations in the carbonate/crystalline, semiconsolidated sandstone, and glacial deposit PAs were not significantly different from each other even though N loading systematically increased among them (Figure 8C). This observation may be explained by the systematic increase in apparent electron transfers from Mn(IV) and Fe(III) reduction that also was observed among those three PA groups that could indicate greater $NO_3^-$ attenuation capacity in the glacial deposit PAs than in the other two PA groups (Figure 8C). The apparent inconsistency between small $NO_3^-$ concentrations in the carbonate/sandstone PAs and the combination of somewhat large N loading and small electron transfer may reflect karst hydrology in the Edwards, Floridan, and Ozark Plateau aquifers that permitted rapid infiltration of dilute recharge containing low N concentrations or containing reduced forms of N rather than $NO_3^-$. Other factors like recharge rates, depth to the water table, contributions from septic systems, and spatial variability in the application of fertilizer and manure also may help to explain the observed differences in $NO_3^-$ concentrations between PA groups (Nolan and Hitt 2006).
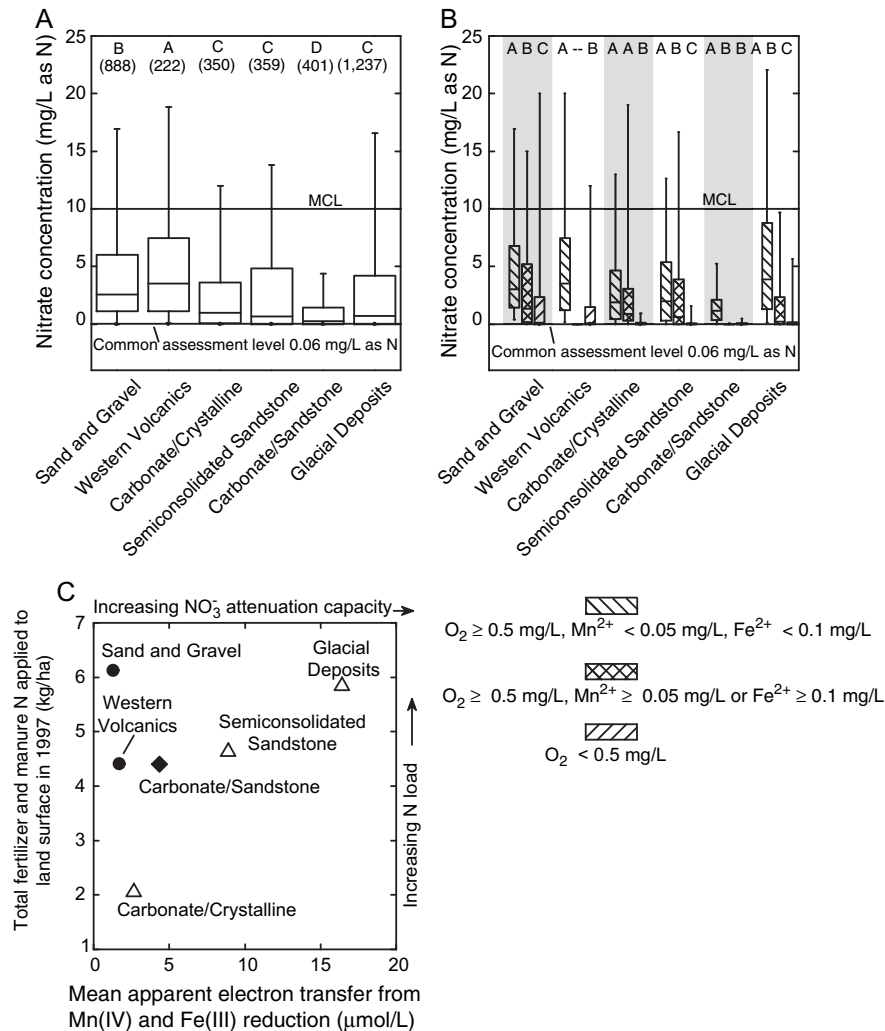
**Figure 8. Concentrations of NO₃⁻ in water samples from all well types, by PA, (A) for all samples regardless of redox process and (B) by redox process. See Figure 3 for the definition of box plots and letters at the top of the box plots. (C) Total fertilizer and manure N applied to the outcrop areas of the PAs as a function of mean apparent electron transfer from Mn(IV) and Fe(III) reduction. Fertilizer and manure data from county-level estimates reported by Ruddy et al. (2006). A common assessment level of 0.06 mg/L as N was used for all PAs. The MCL (maximum contaminant level) line indicates the primary drinking water standard for NO₃⁻. Numbers of samples are shown in parentheses in A.**

## Redox and the Occurrence of VOC

The three most commonly detected VOCs in U.S. ground water are chloroform, tetrachloroethene, and methyl *tert*-butyl ether (MTBE) (Zogorski et al. 2006). Those three compounds plus vinyl chloride and the *cis* and *trans* isomers of 1,2-dichloroethene were analyzed for this study. MTBE is a petroleum hydrocarbon that acts predominantly as an electron donor of microbial metabolism. Chloroform and tetrachloroethene are highly chlorinated (i.e., highly oxidized) compounds that act predominantly as electron acceptors in microbial metabolism and act as the parent compounds of reductive dechlorination (Bradley 2000, 2003). The *cis*-1,2-dichloroethene isomer and vinyl chloride are products of the reductive dechlorination of tetrachloroethene and trichloroethene.

Those VOCs were detected most frequently in samples from urban land-use monitoring wells that were screened near the water table in commercial and residential settings, and they were detected more commonly in

public-supply wells than in domestic wells (Zogorski et al. 2006). The detection frequency of the three classes of VOCs relative to redox diagnoses is shown in Figure 9A. The detection frequencies for chloroform and tetrachloroethene were higher under oxic conditions than under anoxic conditions. This is consistent with the fact that reductive dechlorination occurs more readily under more strongly reducing conditions. As expected, the 1,2-dichloroethene isomers and vinyl chloride, the products of reduction dechlorination, were detected more frequently under anoxic conditions than under oxic conditions. MTBE was detected more frequently under anoxic conditions than under oxic conditions, which is consistent with the observation that MTBE is more readily mineralized under oxic conditions and with the generally slow kinetics of oxic and anoxic MTBE mineralization.

Detection frequencies for chloroform, tetrachloroethene, and MTBE were markedly larger in samples with mixed redox diagnoses than in fully oxic or anoxic water
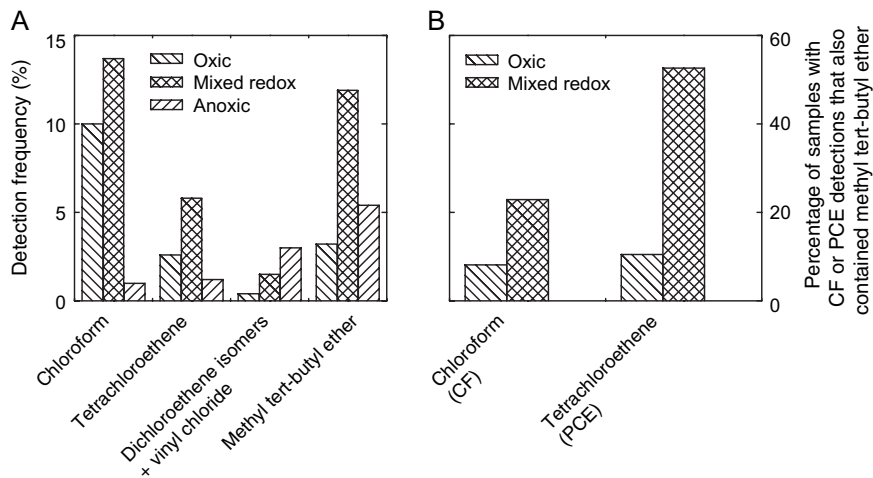
**Figure 9.** (A) Detection frequency for selected VOCs in water samples from domestic, public-supply, and urban land-use wells in all studied PAs, and (B) percentage of samples with chloroform or tetrachloroethene detections that also contained MTBE, by redox process. A common assessment level of 0.2 μg/L was used for all compounds.

samples (Figure 9A). This may reflect the relative preservation of tetrachloroethene and chloroform under conditions that are inadequately reducing to produce efficient reductive dechlorination. In the same manner, this may reflect the relative preservation of MTBE under conditions that are inadequately oxidizing to promote mineralization. Alternatively, the chloroform and tetrachloroethene results could be explained if the detections in mixed redox samples co-occurred with other contaminants that were electron donors, the degradation of which could shift redox conditions toward anoxia or even support multiple anoxic redox processes (Achtnich et al. 1995; Vroblesky et al. 1996). This raises the interesting possibility that redox heterogeneity might be created by contamination rather than reflect heterogeneity inherent in the aquifer sediments. In fact, the mixed redox samples that contained chloroform or tetrachloroethene were at least two times more likely to also contain MTBE than the oxic samples that contained chloroform or tetrachloroethene (Figure 9B). In either instance, further investigation into the reasons for the observed large detection frequencies for chloroform, tetrachloroethene, and MTBE under mixed redox conditions is warranted.

## Conclusions

Despite the inherent difficultly of describing redox processes in large-scale aquifer systems, it is possible to apply an internally consistent set of water quality criteria to assess the occurrence and distribution of redox processes. Applying this framework to a number of PAs in the United States suggests that the occurrence and distribution of redox processes were controlled largely by climate, geology, hydrology, and anthropogenic factors that, in combination, influenced ground water residence time and the availability of electron acceptors and donors. For the natural and anthropogenic contaminants assessed in this study, it appears that considering redox conditions as defined by the framework explained many of the

observed water quality trends at the regional scale of this analysis. An important finding of this study is that samples indicating mixed redox processes provide information on redox heterogeneity that affects the observed fate and transport of natural and anthropogenic contaminants and therefore are useful for assessing common water quality issues. Given the interpretive power of the redox framework and given that it is relatively inexpensive and easy to measure the chemical parameters included in the framework, those parameters should be included in routine water quality monitoring programs whenever possible.

## Acknowledgments

## Supplementary Material

The following supplementary materials are available for this article:

**Figure S1.** Maps showing the distribution of domestic, public-supply, and monitoring (agricultural and urban land uses) wells used in this study.

**Table S1.** Number of samples, by well type, for each Principal Aquifer.

These materials are available as part of the online article from: http://www.blackwell-synergy.com/doi/abs/10.1111/j.1745-6584.2007.00385.x

(This link will take you to the article abstract).

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