

Redox Conditions in Selected Principal Aquifers of the United States

Introduction

Reduction/oxidation (redox) processes affect the quality of groundwater in all aquifer systems. Redox processes can alternately mobilize or immobilize potentially toxic metals associated with naturally occurring aquifer materials, contribute to the degradation or preservation of anthropogenic contaminants, and generate undesirable byproducts such as dissolved manganese (Mn^{2+}), ferrous iron (Fe^{2+}), hydrogen sulfide (H_2S), and methane (CH_4). 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 predicting the chemical quality of groundwater.

Microorganisms that catalyze redox processes in natural systems compete for limited resources. 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 typically the most common electron donors available in groundwater systems, although reduced forms of nitrogen, iron, sulfur, and possibly other species could be important electron donors. There is also variability in the kinds and amounts of available electron acceptors. Dissolved oxygen (O_2) produces more energy per mole of organic carbon oxidized than any other commonly available electron acceptor, and thus it is used preferentially by subsurface microorganisms. Under anoxic conditions, the next most energetically favorable naturally available electron acceptor is nitrate (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. One consequence of this ecological succession is that redox processes have a tendency to segregate into zones dominated by a single electron-accepting process.

Documenting the consumption of soluble electron acceptors and production of distinctive byproducts along defined flow path segments is the most reliable method for identifying the distribution of redox processes in a groundwater system (Chapelle and others, 1995). But diagnostic redox byproducts like excess nitrogen gas (excess N_2), H_2S , CH_4 , and hydrogen (H_2), which are important components of hierarchical schemes for identifying redox processes (Chapelle and others, 1995; Christensen and others, 2000), are not routinely measured in regional water-quality assessments. Thus, McMahon and

Chapelle (2008) developed a framework for assessing redox processes based on water-quality parameters that are commonly measured in regional water-quality assessments. The redox framework subsequently was used to assess redox conditions in 15 principal aquifer systems (PAs) of the United States using data from the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program (McMahon and Chapelle, 2008). The USGS has identified 62 PAs in the United States (U.S. Geological Survey, 2003; Lapham and others, 2005). This Fact Sheet extends the analysis of McMahon and Chapelle (2008) to additional PAs by applying the framework to a larger set of water-quality data from the USGS national water databases.

Framework for Assessing Redox Processes

The redox framework of McMahon and Chapelle (2008) is based on the dissolved concentrations of five water-quality parameters (O_2 , NO_3^- , Mn^{2+} , Fe^{2+} , and SO_4^{2-}) that are relatively inexpensive and easy to measure. The framework is a modification of those developed by Chapelle and others (1995) and Paschke and others (2007). Although the framework has the advantages of broad applicability and internal consistency, it also is subject to certain limitations that are discussed in detail by McMahon and Chapelle (2008). One limitation of the framework is its inability to distinguish between $Fe(III)$ and SO_4^{2-} reduction. Subsequently, Chapelle and others (2009) proposed an addition to the framework in which Fe^{2+}/H_2S ratios are used to distinguish between $Fe(III)$ and SO_4^{2-} reduction. The updated redox framework is presented in table 1. Jurgens and others (2009) created a Microsoft Excel workbook that automates application of the redox framework to large data sets.

Source of Redox Data

Data for this analysis were retrieved from the USGS Data Warehouse (DW) and State databases of the USGS National Water Information System (NWIS) between January and December 2008. Duplicate samples were removed in instances when data for a well were present in both databases. Only the most recent sample with complete data for all five redox parameters was retained if a particular well was sampled on multiple dates or times.

The analysis in this report includes the 15 PAs and 1,692 wells studied by McMahon and Chapelle (2008), plus an additional 13 PAs and 3,443 wells (fig. 1 and table 2). Only data from domestic wells were considered in this analysis, which is consistent with the approach of McMahon and

Table 1. Threshold concentrations for identifying redox processes in groundwater (modified from McMahon and Chapelle, 2008; Chapelle and others, 2009).

[O₂, dissolved oxygen; NO₃⁻-N, dissolved nitrate as nitrogen; Mn²⁺, dissolved manganese; Fe²⁺, dissolved iron; SO₄²⁻, dissolved sulfate; H₂S, hydrogen sulfide; Mn(IV), oxidized manganese; Fe(III), ferric iron; mg/L, milligrams per liter; —, not applicable; ≥, greater than or equal to; <, less than]

General redox category	Predominant redox process	Distinguishing Fe(III)– from SO ₄ ²⁻ -reduction	Water-chemistry criteria (mg/L)					Fe ²⁺ /H ₂ S mass ratio	Comments	
			O ₂	NO ₃ ⁻ -N	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻			
Oxic	O ₂ reduction	—	≥0.5	—	<0.05	<0.1	—	—	—	
Suboxic	—	—	<0.5	<0.5	<0.05	<0.1	—	—	(1)	
Anoxic	NO ₃ ⁻ reduction	—	<0.5	≥0.5	<0.05	<0.1	—	—	—	
	Mn(IV) reduction	—	<0.5	<0.5	≥0.05	<0.1	—	—	—	
	Fe(III)/SO ₄ ²⁻ reduction	—	<0.5	<0.5	—	≥0.1	≥0.5	—	—	
	—	Fe(III) reduction	—	<0.5	<0.5	—	≥0.1	≥0.5	>10	—
	—	Mix – Fe(III)/SO ₄ ²⁻ reduction	—	<0.5	<0.5	—	≥0.1	≥0.5	≥0.3 and ≤10	—
	—	SO ₄ ²⁻ reduction	—	<0.5	<0.5	—	≥0.1	≥0.5	<0.3	—
Methanogenesis	—	—	<0.5	<0.5	—	≥0.1	<0.5	—	—	
Mixed	—	—	—	—	—	—	—	—	(2)	

¹Further definition of redox processes not feasible.

²Criteria for more than one redox process are met.

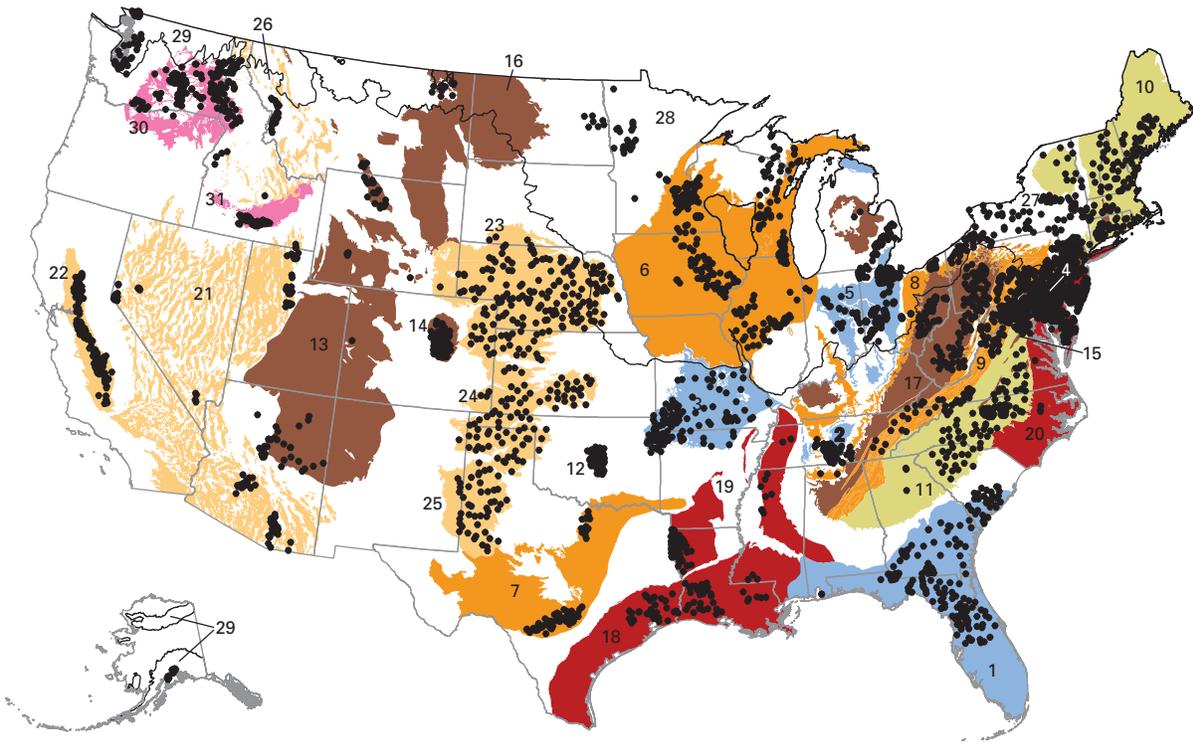
Chapelle (2008). Domestic wells were used for this purpose because they had better spatial distributions in the PAs than the other well types, although it is recognized that none of the well networks is completely representative of entire PAs (fig. 1). Furthermore, only PAs with at least 30 samples were included in the analysis, resulting in a sample size of 5,135 wells. This analysis separates the carbonate-rock and crystalline-rock aquifers of the Piedmont and Blue Ridge and separates the Columbia Plateau and Snake River Plain basaltic-rock aquifers of the western volcanic-rock PAs, whereas those pairs of aquifers were combined by McMahon and Chapelle (2008). Redox assignments in the dataset were based on the framework in table 1, except that Fe²⁺/H₂S ratios were not used to distinguish between Fe(III) and SO₄²⁻ reduction because only a relatively small number of samples has H₂S data and because the exception maintained consistency with the previous analysis of redox processes in PAs (McMahon and Chapelle, 2008).

Redox Processes in Selected Principal Aquifers

The framework presented in table 1 allows for a generalized but internally consistent comparison of redox processes between PAs of the United States. Percentages of water samples from domestic wells that were characterized as being oxic, suboxic, anoxic, or as having mixed redox processes are illustrated spatially in figure 2. The anoxic classification is subdivided further in table 2. Some broad spatial patterns in the distribution of redox processes are apparent in figure 2 that are consistent with the patterns described by McMahon and Chapelle (2008). Oxygen reduction was the predominant redox process in 87 and 84 percent of the samples from nonglacial sand and gravel PAs (excluding alluvial

aquifers) and volcanic-rock PAs in the Western United States, respectively (fig. 2 and table 2). Whereas the number of samples in which O₂ reduction was the predominant redox process ranged from 43 (glacial sand and gravel PAs) to 63 percent (carbonate/sandstone and crystalline-rock PAs) in the remaining PA lithologic groups, many of which were located in the central and eastern parts of the country. Several of those PAs contained relatively large percentages of anoxic samples, with the Silurian-Devonian, central United States glacial sand and gravel, and Cambrian-Ordovician PAs in the upper Midwest containing the largest percentages (fig. 2). Ferric iron/SO₄²⁻ reduction was the most common anoxic redox process in those three PAs (table 2). Suboxic conditions were common in some aquifers containing karst features (Floridan PA) or fractured rocks (New England crystalline-rock PA), as well as in some sandstone aquifers (Denver Basin and Lower Tertiary PAs) (fig. 2 and table 2). Redox conditions were highly variable within some PA lithologic groups. Among the carbonate aquifers, the number of samples that were O₂ reducing ranged from 13 to about 90 percent and the number that were Fe(III)/SO₄²⁻ reducing ranged from 0 to 60 percent.

The spatial variability of redox processes shown in figure 2 likely reflects differences in geology, climate, and hydrology, among other factors, across the United States (McMahon and Chapelle, 2008). Geology, climate, and hydrology influence redox processes primarily through their controls on groundwater 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 (by altering recharge) and electron acceptor/donor availability (for example, agricultural nitrogen applications or gasoline spills).



EXPLANATION

Principal aquifers and reference number

- Domestic well
- Carbonate aquifers
 - Floridan (1)
 - Ordovician (2)
 - Ozark Plateau (3)
 - Piedmont and Blue Ridge (4)
 - Silurian-Devonian (5)
- Carbonate/sandstone aquifers
 - Cambrian-Ordovician (6)
 - Edwards-Trinity (7)
 - Mississippian (8)
 - Valley and Ridge (9)
- Semiconsolidated sand aquifers
 - Coastal Lowlands (18)
 - Mississippi Embayment (19)
 - Northern Atlantic Coastal Plain (20)
- Crystalline-rock aquifers
 - New England (10)
 - Piedmont and Blue Ridge (11)
- Sandstone aquifers
 - Central Oklahoma (12)
 - Colorado Plateau (13)
 - Denver basin (14)
 - Early Mesozoic basins (15)
 - Lower Tertiary (16)
 - Pennsylvanian (17)
- Unconsolidated sand and gravel aquifers, nonglacial
 - Basin and Range basin fill (21)
 - Central Valley (22)
 - High Plains—northern (23)
 - High Plains—central (24)
 - High Plains—southern (25)
 - Northern Rocky Mountains intermountain basins (26)
- Unconsolidated sand and gravel aquifers, glacial
 - Eastern glaciated region (27)
 - Central glaciated region (28)
 - Western glaciated region (29)
- Western volcanic-rock aquifers
 - Columbia Plateau basaltic rock (30)
 - Snake River Plain basaltic rock (31)

Figure 1. Location of domestic wells and principal aquifers included in the redox analysis. 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.

The number of samples with mixed redox processes ranged from about 5 to 20 percent among the eight PA lithologic groups in table 2. In this study and that of McMahon and Chapelle (2008) the semiconsolidated sand PAs and glacial sand and gravel PAs had some of the largest percentages of mixed-redox samples, whereas the nonglacial sand and gravel PAs and the western volcanic-rock PAs had some of the smallest

percentages of mixed-redox samples. Both studies also found that, on average, wells in the semiconsolidated sand PAs and glacial sand and gravel PAs had shorter screens than wells in the other PAs. Thus, samples with mixed redox processes were not necessarily a result of mixing waters in long screen intervals but could reflect the inherent spatial heterogeneity of redox processes in a given hydrologic system.

Table 2. Redox classification of water samples from domestic wells in selected principal aquifers. Only aquifers with at least 30 samples are shown. The High Plains and glacial aquifers, each subdivided in this table, are considered single principal aquifers. Thus, 28 principal aquifers are listed in the table.

[O₂, dissolved oxygen; NO₃⁻, dissolved nitrate; Mn(IV), oxidized manganese; Fe(III), ferric iron; SO₄²⁻, dissolved sulfate]

Principal aquifer (map reference number)	Percentage of samples							
	Number of samples	Oxic conditions	Suboxic conditions	Anoxic conditions				Mixed-redox conditions
		O ₂ reduction		NO ₃ ⁻ reduction	Mn(IV) reduction	Fe(III)/SO ₄ ²⁻ reduction	Methanogenesis	
Carbonate aquifers								
Floridan ¹ (1)	203	49.75	23.15	2.46	2.46	10.35	3.94	7.89
Ordovician (2)	36	50.00	19.44	2.78	0.00	16.67	0.00	11.11
Ozark Plateau ¹ (3)	169	84.02	5.92	2.37	0.00	3.55	0.00	4.14
Piedmont and Blue Ridge ² (4)	106	89.62	4.72	0.94	0.00	0.00	0.00	4.72
Silurian-Devonian (5)	199	13.07	11.06	1.51	2.01	60.29	3.52	8.54
Carbonate/sandstone aquifers								
Cambrian-Ordovician ¹ (6)	179	40.78	3.91	1.12	1.12	37.98	0.56	14.53
Edwards-Trinity ¹ (7)	69	73.91	11.59	1.45	0.00	11.60	0.00	1.45
Mississippian (8)	57	71.93	8.77	1.75	0.00	3.51	0.00	14.04
Valley and Ridge (9)	463	66.09	2.38	0.86	4.75	9.29	0.00	16.63
Crystalline-rock aquifers								
New England ¹ (10)	95	50.53	23.16	1.05	3.16	12.63	0.00	9.47
Piedmont and Blue Ridge ² (11)	743	74.97	1.88	0.67	2.02	5.25	0.00	15.21
Sandstone aquifers								
Central Oklahoma (12)	82	82.93	1.22	2.44	0.00	0.00	0.00	13.41
Colorado Plateau (13)	37	75.68	0.00	2.70	0.00	5.41	0.00	16.21
Denver Basin (14)	74	33.78	39.19	0.00	5.41	13.51	1.35	6.76
Early Mesozoic basins (15)	314	76.11	5.10	2.23	3.50	6.05	0.00	7.01
Lower Tertiary (16)	30	43.33	26.66	6.67	6.67	10.00	0.00	6.67
Pennsylvanian (17)	197	24.37	4.06	1.52	3.05	26.90	1.52	38.58
Semiconsolidated sand aquifers								
Coastal lowlands ¹ (18)	81	54.32	4.94	0.00	2.47	8.64	2.47	27.16
Mississippi embayment (19)	85	34.12	36.47	0.00	0.00	15.29	4.71	9.41
Northern Atlantic Coastal Plain ¹ (20)	392	46.17	4.08	1.02	0.26	23.22	1.02	24.23
Unconsolidated sand and gravel aquifers, nonglacial								
Alluvial ³	82	69.51	0.00	1.22	0.00	6.10	0.00	23.17
Basin and Range basin fill ¹ (21)	121	88.43	2.48	2.48	0.00	2.48	0.83	3.30
Central Valley ¹ (22)	136	80.88	3.68	4.41	2.21	2.21	0.74	5.87
High Plains aquifer–northern ¹ (23)	190	77.37	3.16	2.11	3.16	5.26	0.00	8.94
High Plains aquifer–central ¹ (24)	87	95.40	0.00	1.15	0.00	2.30	0.00	1.15
High Plains aquifer–southern ¹ (25)	46	93.48	0.00	0.00	2.17	0.00	0.00	4.35
Northern Rocky Mountains Intermontane basins (26)	57	87.72	1.75	3.51	1.75	5.27	0.00	0.00
Unconsolidated sand and gravel aquifers, glacial								
Eastern glaciated region ¹ (27)	180	48.33	5.56	2.22	5.00	20.56	2.22	16.11
Central glaciated region ¹ (28)	321	20.25	2.18	0.31	0.00	42.68	9.97	24.61
Western glaciated region ¹ (29)	100	60.00	4.00	1.00	8.00	9.00	4.00	14.00
Western volcanic-rock aquifers								
Columbia Plateau basaltic rock ⁴ (30)	137	67.88	8.76	2.92	1.46	7.30	0.73	10.95
Snake River Plain basaltic rock ⁴ (31)	67	100.00	0.00	0.00	0.00	0.00	0.00	0.00

¹Included in analysis by McMahon and Chapelle (2008).

²Included in analysis by McMahon and Chapelle (2008), but Piedmont and Blue Ridge carbonate-rock and crystalline-rock aquifers were previously combined.

³Results not shown on figure 2.

⁴Included in analysis by McMahon and Chapelle (2008), but Columbia Plateau and Snake River Plain basaltic-rock aquifers were previously combined.

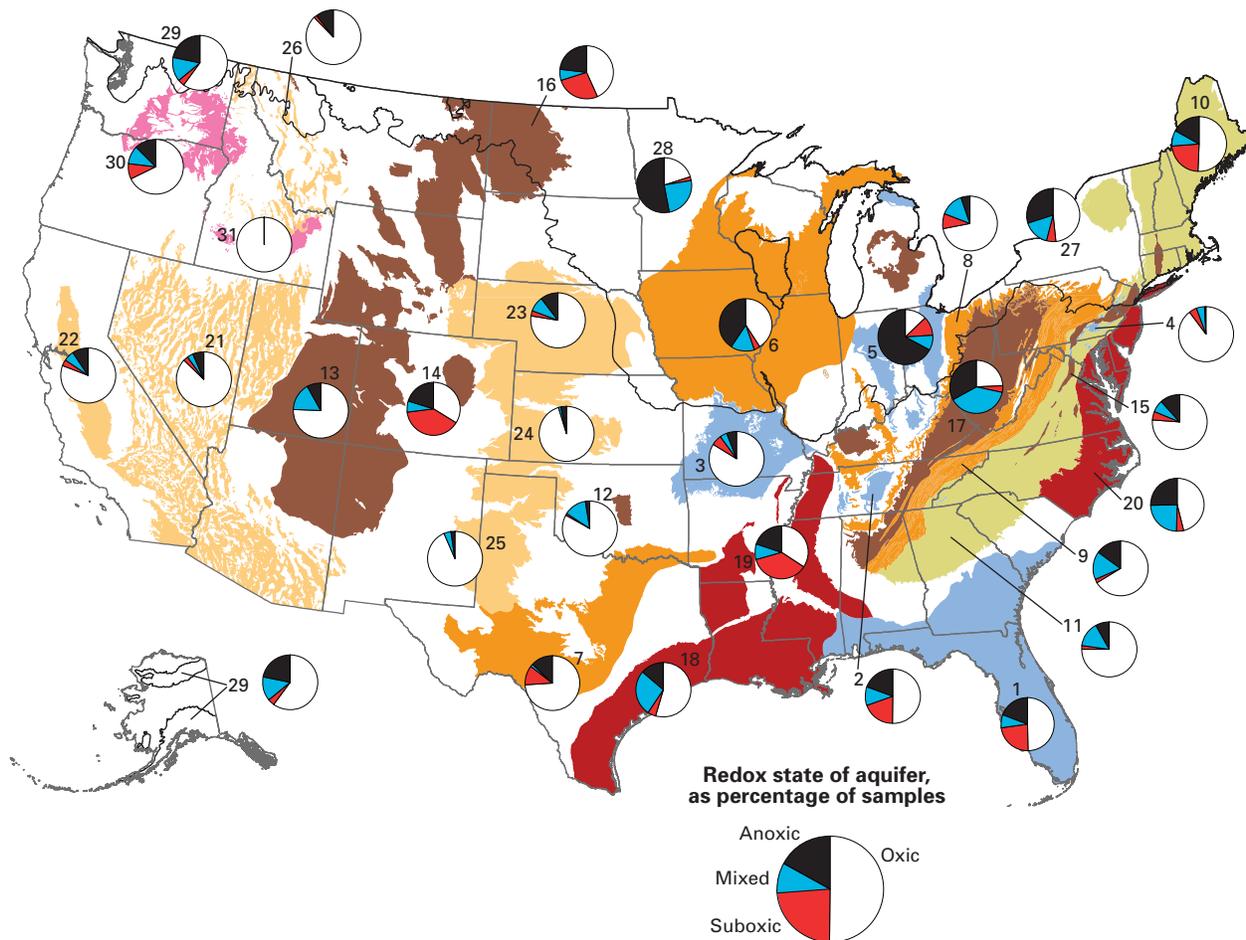


Figure 2. Pie charts indicating the percentages of domestic well samples that were oxic, suboxic, anoxic, or diagnostic of mixed redox processes in selected principal aquifers. See figure 1 for explanation of map reference numbers.

Effect of Redox on Water Quality

A principal reason for assessing redox conditions in groundwater is to address practical water-quality issues. Two such issues are aquifer vulnerability to contamination and contamination of water-supply wells. McMahon and Chapelle (2008) used the redox framework to evaluate the occurrence of arsenic (As), NO_3^- , and volatile organic compounds (VOCs) in selected PAs. Within a given PA, they generally found As concentrations to be larger in samples that were Mn(IV) or Fe(III)/ SO_4^{2-} reducing than in samples that were O_2 reducing. Arsenic tends to adsorb on the surfaces of Mn(IV) and Fe(III) oxyhydroxides commonly present in aquifer materials under oxic conditions. Under Mn(IV)- and Fe(III)-reducing conditions, adsorbed As can be mobilized as metal oxyhydroxides are dissolved. In contrast to As, NO_3^- concentrations were smaller in anoxic samples than in oxic samples, which is consistent with NO_3^- degradation by denitrifying bacteria under anoxic conditions. Detection frequencies for chloroform and tetrachloroethene, two of the most commonly detected VOCs in groundwater (Zogorski and others, 2006), were higher under oxic

conditions than under anoxic conditions. This finding is consistent with the fact that reductive dechlorination of these compounds occurs more readily under more strongly reducing conditions. These examples indicate that aquifer vulnerability to contamination from various natural and anthropogenic chemicals is dependent on redox conditions in groundwater.

Substantial redox heterogeneity in aquifers can have important effects on the distribution of natural and anthropogenic contaminants in groundwater and the placement of water-supply wells. For example, a transition from oxic to anoxic conditions over relatively short distances would not be beneficial to a well owner concerned about As contamination in Fe(III)-reducing sediments because it would be difficult to selectively screen the oxic zones. Conversely, 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 flow paths in the aquifer. Thus, information on the spatial heterogeneity of redox processes in a given hydrologic system could be helpful when designing and operating water-supply wells.

Conclusion

The framework presented in table 1 allows for an analysis of redox processes in aquifer systems using five chemical parameters that are relatively inexpensive and easy to measure. A Microsoft Excel workbook was created to automate implementation of the framework to large data sets. The redox framework can be used to address practical water-quality issues such as aquifer vulnerability to contamination and contamination of water-supply wells. Given the interpretive power of the redox framework and relative ease of application, the five chemical parameters (O_2 , NO_3^- , Mn^{2+} , Fe^{2+} , and SO_4^{2-}) should be included in routine water-quality monitoring programs whenever possible.

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