O_2 reduction and denitrification rates in shallow aquifers

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[1] O_2 reduction and denitrification rates were determined in shallow aquifers of 12 study areas representing a wide range in sedimentary environments and climatic conditions. Zero- and first-order rates were determined by relating reactant or product concentrations to apparent groundwater age. O_2 reduction rates varied widely within and between sites, with zero-order rates ranging from <3 μmol L^{-1} yr^{-1} to more than 140 μmol L^{-1} yr^{-1} and first-order rates ranging from 0.02 to 0.27 yr^{-1}. Moderate denitrification rates (10–100 μmol N L^{-1} yr^{-1}; 0.06–0.30 yr^{-1}) were observed in most areas with O_2 concentrations below 60 μmol L^{-1}, while higher rates (>100 μmol N L^{-1} yr^{-1}; >0.36 yr^{-1}) occur when changes in lithology result in a sharp increase in the supply of electron donors. Denitrification lag times (i.e., groundwater travel times prior to the onset of denitrification) ranged from <20 yr to >80 yr. The availability of electron donors is indicated as the primary factor affecting O_2 reduction rates. Concentrations of dissolved organic carbon (DOC) and/or sulfate (an indicator of sulfide oxidation) were positively correlated with groundwater age at sites with high O_2 reduction rates and negatively correlated at sites with lower rates. Furthermore, electron donors from recharging DOC are not sufficient to account for appreciable O_2 and nitrate reduction. These relations suggest that lithologic sources of DOC and sulfides are important sources of electrons at these sites but surface-derived sources of DOC are not. A review of published rates suggests that denitrification tends to occur more quickly when linked with sulfide oxidation than with carbon oxidation.

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1. Introduction

[2] Understanding the spatial distribution of redox processes in aquifers is essential when assessing the quality of groundwater [*McMahon and Chapelle*, 2008]. Specifically, the fate of many contaminants in groundwater depends to a large extent on the redox processes that occur along flow paths [e.g., *Tesoriero et al.*, 2000, 2001; *Carlyle and Hill*, 2001; *Cozzarelli et al.*, 2001]. As a result, quantifying redox reaction rates is critical to predicting the fate of many contaminants and delineating redox reaction zones in groundwater (e.g., zones of dominant terminal electron acceptors).

[3] Microbial metabolism depends on the oxidation of organic or inorganic (e.g., FeS_2) species to generate energy for growth and maintainance. The metabolic reaction that yields the most energy will typically dominate over competing reactions [e.g., *Stumm and Morgan*, 1996]. Consequently, microbial processes are expected to change as a function of the redox state of groundwater, progressing to reactions with lower energy yields (Table 1). Organic carbon is the most common electron donor in groundwater. Microbes will first oxidize organic carbon using O_2 as an electron acceptor through aerobic respiration because it is the most energetically favorable reaction (Table 1). When O_2 is depleted, facultative anaerobes begin to use nitrate (NO_3^-) as an electron acceptor during denitrification. Subsequent reactions include the reduction of Mn(IV), Fe(III) and sulfate, and methanogenesis (Table 1).

[4] The rate of O_2 reduction and the amount of O_2 initially present in recharge determine the groundwater travel time in the oxic zone and influence the portion of the aquifer system that is oxic. Consequently, the rate at which O_2 is reduced will have a significant influence on the susceptibility of aquifers to many contaminants. Until recently, aerobic respiration rates were determined using O_2 gradients along flow paths of varying length (e.g., <1–80 km) coupled with approximations of groundwater travel time derived from estimates of groundwater velocity. A review of these studies concluded that the fate of oxygen in groundwater between aquifers depends largely on O_2 consumption rates rather than travel time [*Malard and Hervant*, 1999]. O_2 consumption rates varied widely between aquifers, ranging from <0.02 μmol L^{-1} yr^{-1} in deep sedimentary basins of the Southwestern United States and a sandstone aquifer in Namibia [*Winograd and Robertson*, 1982; *Vogel et al.*, 1981] to ~25 μmol L^{-1} yr^{-1} in a fluvial-sand aquifer in Ontario, Canada [*Jackson and Patterson*, 1982; *Malard and Hervant*, 1999]. Push-pull tests have also been used to determine aerobic respiration rates in groundwater [*Schroth et al.*, 1998] and are particularly useful in aquifers contaminated with organic compounds where rates are expected to

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Table 1. Sequence and Free Energy of Microbial Redox Reactions, Assuming Organic Matter (CH_2O) is Electron Donor[a]

Reaction	Stoichiometry	Free Energy (kJ)
Aerobic respiration	$CH_2O + O_2 = CO_2 + H_2O$	−501
Denitrification	$CH_2O + \frac{4}{5}NO_3^- + \frac{4}{5}H^+ = CO_2 + \frac{2}{5}N_2 + \frac{7}{5}H_2O$	−476
Mn(IV) reduction	$CH_2O + 2MnO_2 + 4H^+ = CO_2 + 2Mn^{2+} + 3H_2O$	−340
Fe(III) reduction	$CH_2O + 4Fe(OH)_3 + 8H^+ = CO_2 + 4Fe^{2+} + 11H_2O$	−116
Sulfate reduction	$CH_2O + \frac{1}{2}SO_4^{2-} + \frac{1}{2}H^+ = CO_2 + \frac{1}{2}HS^- + H_2O$	−102
Methanogenesis	$CH_2O = \frac{1}{2}CO_2 + \frac{1}{2}CH_4$	−93

[a]Data are from *Stumm and Morgan* [1996], *Hedin et al.* [1998], and *Baker et al.* [2000]. Free-energy calculations assume pH = 7 and molar concentrations of other reactants, sequence may vary as a function of reactant and product concentrations [*Hedin et al.*, 1998] as well as the specific Fe-oxide considered [*Postma and Jakobsen*, 1996].

be high. First-order rates ranging from 700 to 15,000 yr^{-1} were determined in contaminated aquifers in the United States [*Schroth et al.*, 1998; *McGuire et al.*, 2002]. Environmental tracers (e.g., chlorofluorocarbons and sulfur hexafluoride) have improved groundwater age estimates of recently recharged water [e.g., *Busenberg and Plummer*, 2000]. The use of these tracers offers an opportunity to refine rates in shallow aquifers. For example, O_2 and tracer-based age gradients along flow paths have been used to estimate aerobic respiration rates in shallow aquifers using multiple wells along a flow path [e.g., *Böhlke et al.*, 2002] or individual well data [e.g., *McMahon et al.*, 2008], with zero-order rates ranging from 0.9 to 190 $\mu mol\ L^{-1}\ yr^{-1}$ and first-order rates ranging from 0.005 to 1 yr^{-1}.

[5] The fate of NO_3^- in groundwater is a major water quality concern both locally and globally. Nitrogen fertilizer applications have increased fourfold since 1960 [*Howarth et al.*, 2002; *Ruddy et al.*, 2006] leading to growing concerns about the consequences of increases in the amounts of reactive N circulating in the atmosphere, hydrosphere, and biosphere in recent years [e.g., *Galloway et al.*, 2003; *Schlesinger et al.*, 2006]. Specifically, increases in reactive nitrogen have led to the degradation of drinking water supplies [*McMahon et al.*, 2008; *Burow et al.*, 2010], nutrient enrichment of terrestrial ecosystems [*Galloway et al.*, 2003; *Vitousek et al.*, 1997], eutrophication of aquatic ecosystems [*Rabalais*, 2002], and contributions to global climate change [*Groffman et al.*, 2000]. Increased nitrogen applications to the land surface have led to a dramatic increase in nitrate concentrations in recharging groundwater in the last 50 yr [*Puckett et al.*, 2011]. Elevated nitrate concentrations in groundwater also pose a risk to streams; groundwater was the dominant source of nitrate in base-flow dominated streams in agricultural watersheds [*Tesoriero et al.*, 2009]. Denitrification is the only process that can remove reactive nitrogen from the hydrosphere and has been suggested as a significant sink for reactive nitrogen in watershed assessments [e.g., *Van Breemen et al.*, 2002; *Vidon and Hill*, 2004].

[6] The many consequences of increased reactive nitrogen in the hydrosphere have led to several studies on denitrification rates in groundwater. In situ denitrification rate calculations have primarily relied on three methods: N_2 gradient, NO_3^- gradient, and injected NO_3^-. Denitrification rates from NO_3^- injection experiments tend to have the highest rates [*Green et al.*, 2008 and references therein], with most occurring in aquifers with strongly reducing conditions either occurring naturally (e.g., *Tesoriero et al.* [2000]; $1.4 \times 10^5\ \mu mol\ N\ L^{-1}\ yr^{-1}$) or from contamination with organic compounds (e.g., *Schroth et al.* [1998]; 2000 yr^{-1}). Nitrate gradient experiments typically have rates ranging from 370 to $3.7 \times 10^5\ \mu mol\ N\ L^{-1}\ yr^{-1}$ [*Green et al.*, 2008 and references therein], while N_2-gradient experiments typically have lower rates, often <370 $\mu mol\ N\ L^{-1}\ yr^{-1}$. Denitrification rates determined from N_2 gradients may better represent aquifer conditions than other methods because they rely on the product of denitrification (excess N_2) occurring under ambient conditions to obtain rates and are not as susceptible as the nitrate-gradient method to artifacts resulting from historical changes in nitrate loadings at the land surface.

[7] Improved estimates of O_2 reduction in shallow aquifers are critical to assess the vulnerability of aquifers to redox-sensitive contaminants. Similarly, improved estimates of the location and rates of denitrification in watersheds [*Boyer et al.*, 2006] and its ability to remove reactive nitrogen from agroecosystems [*Galloway et al.*, 2003] are needed to improve both local and global assessments of the risk posed by reactive nitrogen and other contaminants to aquatic ecosystems and human health. The availability and reactivity of electron donors likely have a major influence on the delineation of redox zones and reaction rates [e.g., *Starr and Gillham*, 1993]. In global assessments of the fate of nitrogen, it has been assumed that the supply of electron donors is largely surface-derived dissolved organic carbon [*Van Drecht et al.*, 2003; *Seitzinger et al.*, 2006], resulting in denitrification estimates that are negligible below 5 m of saturated thickness. An assessment of denitrification rates and the availability of electron donors for denitrification can help refine these global nitrogen budgets.

[8] Age-based tracers and concentration gradients along shallow groundwater flow paths offer the opportunity to expand and improve estimates of O_2 reduction and denitrification rates, and to evaluate how these rates change as a function of hydrogeologic setting. In this study, water chemistry and tracer-based groundwater ages (defined as the time of travel from the water table to the point of sampling) were used to determine redox-reaction rates for surficial aquifers from 12 study areas in the United States and Canada. Objectives of this study were to: (1) determine O_2 reduction and denitrification rates across a range of hydrogeologic settings, (2) examine the importance of electron donors on reaction rates, and (3) estimate groundwater travel time prior to denitrification (denitrification lag time).

2. Study Site Descriptions

[9] Twelve study sites were selected to represent a range of sedimentary environments and climatic conditions

Figure 1. Locations of groundwater flow path studies.

(Figure 1; Table 2). Sites were selected from existing U.S. Geological Survey (USGS) studies that had transects that were approximately parallel to the primary direction of flow and groundwater samples that were analyzed for dissolved O_2 and at least one tracer that could be used to estimate the year of recharge. The 12 study sites selected cover most of the major climatic regions in the contiguous United States and a wide range in recharge rates, from <10 cm yr^{-1} to >70 cm yr^{-1}. The hydrogeologic settings of these sites also cover a range of sedimentary environments, including sites in glacial outwash environments, coastal plain settings, alluvial deposits, and other unconsolidated deposits. Study sites were typically in agricultural areas; however, at some sites, rural residential or suburban areas were present. Details of each site are provided in the references shown in Table 2.

3. Methods

3.1. Groundwater Sampling and Analysis

[10] Monitoring-well transects were installed along hypothesized groundwater flow paths in nests of generally three or four wells at each location. Details of the network locations are provided in the references in Table 2. Well screens were generally 1 m or less in length. The uppermost well was screened near the water table. The remaining wells at each location were screened at various depths to intercept likely flow paths in a transect parallel to the primary direction of flow. Flow paths were determined using measured head values [e.g., *Puckett et al.*, 2002] or hydrologic simulations [e.g., *Saad*, 2008]. Dissolved O_2 and pH were measured while water was being pumped, using electrodes placed in a flow cell chamber to minimize atmospheric interactions. Water samples for nutrients were filtered with a 0.45-μm capsule filter. Samples were age-dated using chlorofluorocarbons (CFC11, CFC12, CFC113), sulfur hexafluoride (SF_6), or tritium-helium using published methods [*Busenberg and Plummer*, 2000; *Plummer et al.*, 2006; *Poreda et al.*, 1988]. Tracer concentrations, coupled with known trends in the atmospheric concentrations of these compounds over time, were used to provide estimates of groundwater age. The tracers were selected based on their suitability for each environment. One potential concern is the degradation of chlorofluorocarbons, which can result in overestimates of groundwater age. Degradation of chlorofluorocarbons does not occur during aerobic conditions but may [e.g., *Hinsby et al.*, 2007] or may not [e.g., *Cook et al.*, 1995] occur under more reducing conditions. Multiple tracers, hydrologic data, and/or modeling were used to identify and exclude age dates derived from tracer concentrations that were appreciably affected by degradation. For example, chlorofluorocarbons degraded under pyrite oxidizing conditions in one of the study sites (Sumas Aquifer, *Tesoriero et al.* [2000]); the age estimates in this study were based on SF_6 analyses of samples collected in 2006 and 2007.

[11] Samples were also collected and analyzed for N_2 and Ar gas to estimate the amount of N_2 derived from denitrification. N_2 and Ar are incorporated into groundwater during recharge by air-water equilibration processes and by entrainment of air bubbles ("excess air") [*Heaton and Vogel*, 1981]. Estimates of excess N_2 from denitrification were calculated by subtracting the estimated concentration of atmospheric nitrogen, derived from both air-water equilibration and excess air, from that of the total amount of nitrogen gas measured in the groundwater sample [*Dunkle et al.*, 1993]. Samples from the Sumas Aquifer site were collected and analyzed for $\delta^{34}S$ of sulfate using methods described by *Révész and Qi* [2006a, 2006b].

3.2. O_2 and Denitrification Rate Calculations

[12] The rate of O_2 reduction in each aquifer was evaluated by relating dissolved O_2 concentrations to groundwater age using the approach described by *Böhlke et al.* [2002]. This technique has the advantage of relying on in situ field conditions, rather than batch or column experiments that may not replicate aquifer conditions. For comparison, apparent zero-order (rate independent of concentration) and first-order (rate dependent on concentration) rate constants were determined. These estimated rates are considered apparent rate constants because of their dependence on tracer-based apparent recharge ages. Zero-order rate coefficients were determined using the following expression:

$$C = C_0 - k_0 t, \quad (1)$$

Table 2. Site Location, Hydrogeologic Setting, and Climate for the Study Areas Included in This Investigation[a]

Location	Setting	Flow Path Length (km)	Saturated Thickness (m)[b]	Upland Surficial Geology	Climate[c]	Reference
Brighton, MI	SE Michigan	4	17	Glacial outwash and till	Humid Continental (Dfa)	*Thomas*, 2000[d]
Chesterville, MD	Delmarva Peninsula Chesterville Br.	1.5	19	Fluvial and marine deposits of sand and gravel	Humid Subtropical (Cfa)	*Böhlke and Denver*, 1995
Kennedyville, MD	Delmarva Peninsula Morgan Ck.	0.5	1.4	Fluvial and marine deposits of sand and gravel	Humid Subtropical (Cfa)	*Böhlke and Denver*, 1995
La Pine, OR	Central Oregon	4	11	Sand	Highland; semiarid steppe (Bsk)	*Hinkle et al.*, 2007
Lizzie, NC	North Carolina Coastal Plain	1.5	13	Marine deposits of medium to fine sand	Humid subtropical (Cfa)	*Tesoriero et al.*, 2005
Mt. Clinton, VA	Virginia Valley and Ridge	1.5	16[e]	Regolith of saprolite, colluvium and alluvium	Humid Continental (Dfb)	*Lindsey et al.*, 2003
Perham, MN	W. Central Minnesota	5	14	Glacial outwash	Humid Continental (Dfb)	*Puckett et al.*, 2002
Polonia, WI	Central Wisconsin	1.5	20	Glacial Outwash	Humid Continental (Dfb)	*Saad*, 2008; *Tesoriero et al.*, 2007
Princeton, MN	Anoka Sand Plain	NA[f]	5	Glacial Outwash	Humid Continental (Dfb)	*Böhlke et al.*, 2002
Stevinson, CA	Central Valley of California	1	24	Alluvial sand, silt and clay	Mediterranean (Csa)	*Green et al.*, 2008
Sumas, WA, Abbotsford, BC	Sumas Aquifer	3	18	Glacial Outwash	Maritime temperate (Cfb)	*Tesoriero et al.*, 2000[d]
York, NE	High Plains Aquifer	9	18	Sand, silt, clay	Humid continental (Dfa)	*McMahon et al.*, 2008; *Landon et al.*, 2008

[a]Additional details on each site are in the references provided.
[b]Based on sample with the largest value for depth below the water table at each site.
[c]Climate designation and code (in parentheses) is based upon the Köppen-Geiger classification system [*Peel et al.*, 2007].
[d]Describes study area only. Data used in this study are from samples collected in 2007 and 2008.
[e]Domestic wells likely screened in bedrock were not used in calculation for this site.
[f]NA, not applicable, vertical transect used.

where C is the concentration of the reactant (i.e., dissolved O_2) at the time of interest, C_0 is the initial concentration of the reactant, k_0 is the apparent zero-order rate constant, and t is time.

[13] Zero-order rate constants were determined by fitting a linear regression curve to a plot of C versus t. Samples with apparent ages exceeding a threshold value, where older samples typically have very low concentrations of O_2 (typically <25 μmol L^{-1}), were excluded from the zero-order analysis because concentration-dependent kinetics were indicated. Large errors in zero-order rates are more likely to occur when reactant concentrations become limiting [*Bekins et al.*, 1997].

[14] Apparent first-order rate constants were determined using the following expression [*Wright*, 2004]:

$$\ln C = \ln C_0 - k_1 t, \tag{2}$$

where C, C_0, and t are as described above and k_1 is the apparent first-order rate constant. First-order rate constants (and C_0 values) were determined by fitting a linear regression curve to plots of ln C versus groundwater age.

[15] Denitrification rates were determined using methods similar to those used for O_2 reduction rates. Zero-order denitrification rates were determined by relating concentrations of N_2 from denitrification, hereafter referred to as excess N_2, with apparent groundwater age. First-order rate expressions were calculated by first determining the initial NO_3^- concentration at the time of recharge, C_0. C_0 was calculated by summing the NO_3^- (C) and excess N_2 concentrations in the sample. Nitrous oxide (N_2O) is also an end product of denitrification but was not included in the calculation of C_0. Excluding N_2O has a minimal impact on C_0 estimates because N_2O is typically very small relative to excess N_2 [e.g., *Weymann et al.*, 2008]. Because C_0 can be estimated, first-order rate constants for denitrification were determined by fitting a linear regression curve to plots of ln C/C_0 versus apparent groundwater age.

[16] Denitrification rates were determined only using samples that were in or near an active denitrification zone, which is defined as having <60 μmol L^{-1} of O_2 and detectable concentrations of NO_3^-. In selected study areas, denitrification rates were so high that no samples were present in the denitrification zone. In these cases, samples on either end of the denitrification zone were used to provide a minimum rate. It should be noted that denitrification rates were not determined in the watersheds with low O_2 reduction rates, resulting in oxic conditions in all samples, even in decades old water. Because of inhibition by the presence of O_2, little or no excess N_2 was detected in any of these groundwater samples resulting in negligible denitrification rates in these systems.

[17] Parameter estimates and fit statistics for first- and zero-order regressions for both O_2 reduction and denitrification rate estimates were calculated using statistical analysis software [*SAS Institute*, 2009]. In cases where rates for these sites have been published previously, rates were recalculated using the methods described above to facilitate comparisons.

4. Results and Discussion

4.1. O_2 Reduction Rates in Groundwater

[18] The relations between dissolved O_2 concentrations and apparent groundwater ages varied widely between sites (Figure 2) resulting in a wide range in O_2 reduction rates (zero-order: <3–140 μmol L^{-1} yr^{-1}; first-order: 0.02–0.27 yr^{-1}, Table 3). Low O_2 reduction rates (i.e., ≤0.03 yr^{-1}) were observed at the Polonia, Wisconsin, Chesterville, Maryland, and York, Nebraska sites (without riparian wells), high rates were observed at sites where lithologic boundaries were crossed (e.g., Sumas Aquifer, Kennedyville, Maryland), with intermediate rates observed at the remaining sites (Table 3).

[19] O_2 reduction rates varied sharply within and between flow paths in some aquifers. For example, O_2 reduction rates were among the lowest measured along most flow paths at the York, Nebraska site (High Plains Aquifer, i.e., 0.02 yr^{-1}, Table 3), but rates were much higher along shallow riparian flow paths near Beaver Creek (i.e., 0.27 yr^{-1}, Table 3). Similarly, in the Sumas Aquifer, O_2 concentrations remained essentially constant in samples that were less than 15-yr old but then sharply declined in samples that were a few years older (Figure 2). These older, more reduced samples coincide with the riparian zone of Fishtrap Creek and a hypothesized relict channel [*Tesoriero et al.*, 2000]. A similar pattern was also observed at the Kennedyville, Maryland site near the riparian zone of Morgan Creek (Figure 2). In contrast, O_2 reduction rates remained low as groundwater entered the riparian sediments adjacent to the Tomorrow River and Chesterville Branch at the Polonia, Wisconsin and Chesterville, Maryland sites, respectively.

[20] The data at the Sumas Aquifer and Kennedyville, Maryland sites suggest that the rate of reduction of O_2 is very low in the upland areas of these sites but increases dramatically once water enters the riparian zone. To better characterize these rates, we estimated zero-order rate constants for the upland, using only samples from this zone in the Sumas Aquifer and Kennedyville, Maryland sites (Table 3). The sharp increase in O_2 reduction rates that occurs as water enters the riparian zones of these watersheds was estimated using the zero-order expression (equation (1)). To describe rates across the upland–riparian boundary, C_0 was assumed to be the median O_2 concentrations in the upland, C was assumed to be the O_2 concentration of the youngest suboxic sample found in the riparian zone, and t was the time period over which O_2 reduction occurs across this interface. Values for k_0 of 140 and 130 μmol L^{-1} yr^{-1} were determined across the upland-riparian boundary for the Kennedyville, Maryland and Sumas Aquifer, respectively. These calculations likely underestimate the rate of O_2 reduction at the upland–riparian zone interface since the period over which O_2 reduction occurs is likely shorter than we could measure with our well network grid. The rates of O_2 reduction at the upland–riparian zone interface are approximately two orders of magnitude higher than in the upland areas of these sites and an order of magnitude greater than the highest rates observed in upland portions of other watersheds. While chemical reaction rates typically vary due to changes in temperature [e.g., *Wright*, 2004], this sharp change in O_2 reduction rates within a study area suggests that temperature may not be a significant factor affecting rates in these study areas. In fact, little of the variance ($r^2 = 0.04$, $p = 0.53$) in O_2 reduction rates can be explained by estimated groundwater temperature (based on mean annual air temperature). It is hypothesized that the availability of electron donors both within and between sites is responsible for the observed range in rates. This hypothesis is explored in section 4.4.

4.2. Denitrification Lag Times

[21] Facultative anaerobes begin to use NO_3^- as an electron acceptor during denitrification (e.g., Table 1) only when O_2 becomes limited. The groundwater travel time that occurs before denitrification occurs is referred to as the denitrification lag time. The rate of O_2 reduction and the initial O_2 concentration influence the denitrification lag time of an aquifer. The O_2 concentration at which denitrification begins to occur was evaluated by examining denitrification reaction progress as a function of O_2 concentration (Figure 3). The LOESS smooth to this relation illustrates the influence of O_2 on denitrification reaction progress. When O_2 concentrations exceed 125 μmol L^{-1}, most samples show little or no denitrification. While denitrification is observed in samples having O_2 concentrations between 60 and 125 μmol L^{-1}, in this study and elsewhere [e.g., *McMahon et al.*, 2004], the large number of samples showing little or no denitrification reaction progress over this interval suggests that 125 μmol L^{-1} may not represent a threshold concentration for denitrification, but rather may be an artifact of mixing of water from both oxic and suboxic zones [*Green et al.*, 2010]. Denitrification occurs in nearly all samples with O_2 concentrations <60 μmol L^{-1}. We suggest that while denitrification may or may not occur at higher O_2 concentrations, denitrification will occur once O_2 concentrations are <60 μmol L^{-1}.

[22] Determining denitrification lag times have important implications for assessing aquifer vulnerability to NO_3^- contamination and other redox-active constituents that are transformed under suboxic conditions. Denitrification lag times were determined using the first-order rate expressions determined from O_2-groundwater age relations (Table 3) and assuming denitrification conditions commence when O_2 concentrations are <60 μmol L^{-1}. While denitrification may occur at higher O_2 concentrations, using an O_2 concentration of 60 μmol L^{-1} for the onset of denitrification results in a conservative (i.e., higher) estimate of the denitrification lag time. Denitrification lag times varied widely between sites, ranging from <20 yr at sites with high O_2 reduction rates to >60 yr at sites with low O_2 reduction rates (Figure 4). Furthermore, lag times may also vary markedly within a site when O_2 reduction rates vary. Lag times of <10 yr and >50 yr observed at the York, Nebraska site illustrate this effect (Figure 4).

[23] Nitrogen applications to the land surface have increased markedly in the last 60 yr, increasing fourfold since 1960 [*Ruddy et al.*, 2006] resulting in sharp increases in NO_3^- concentrations in recharging groundwater [*Tesoriero et al.*, 2007; *Puckett et al.*, 2011]. The extent to which the accumulation of NO_3^- in shallow aquifers affects deeper aquifers and streams depends on the presence of suboxic conditions. Watersheds having long denitrification lag times

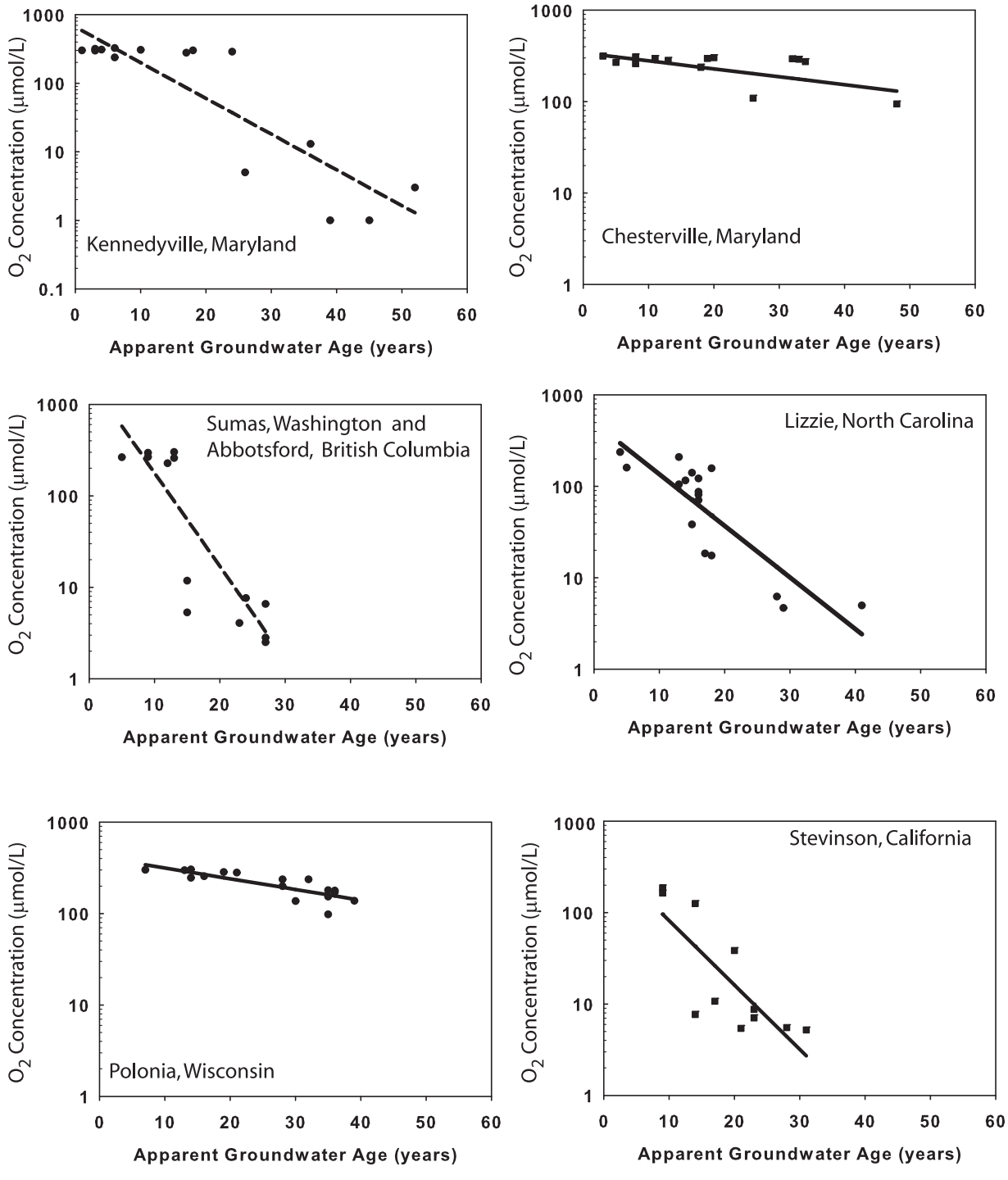

Figure 2. Concentrations of O_2 in groundwater as a function of apparent groundwater age. Regression statistics for the fit of first-order reaction rate expression to the data are provided in Table 3. For Kennedyville and Sumas Aquifer sites, dashed lines are shown because rapid loss of O_2 as groundwater enters riparian zone is not well described by this relation; zero-order rates were estimated for these interfaces (see text and Table 3). Dashed line for York, Nebraska site is fit to riparian flow path data, while solid line excludes riparian samples.

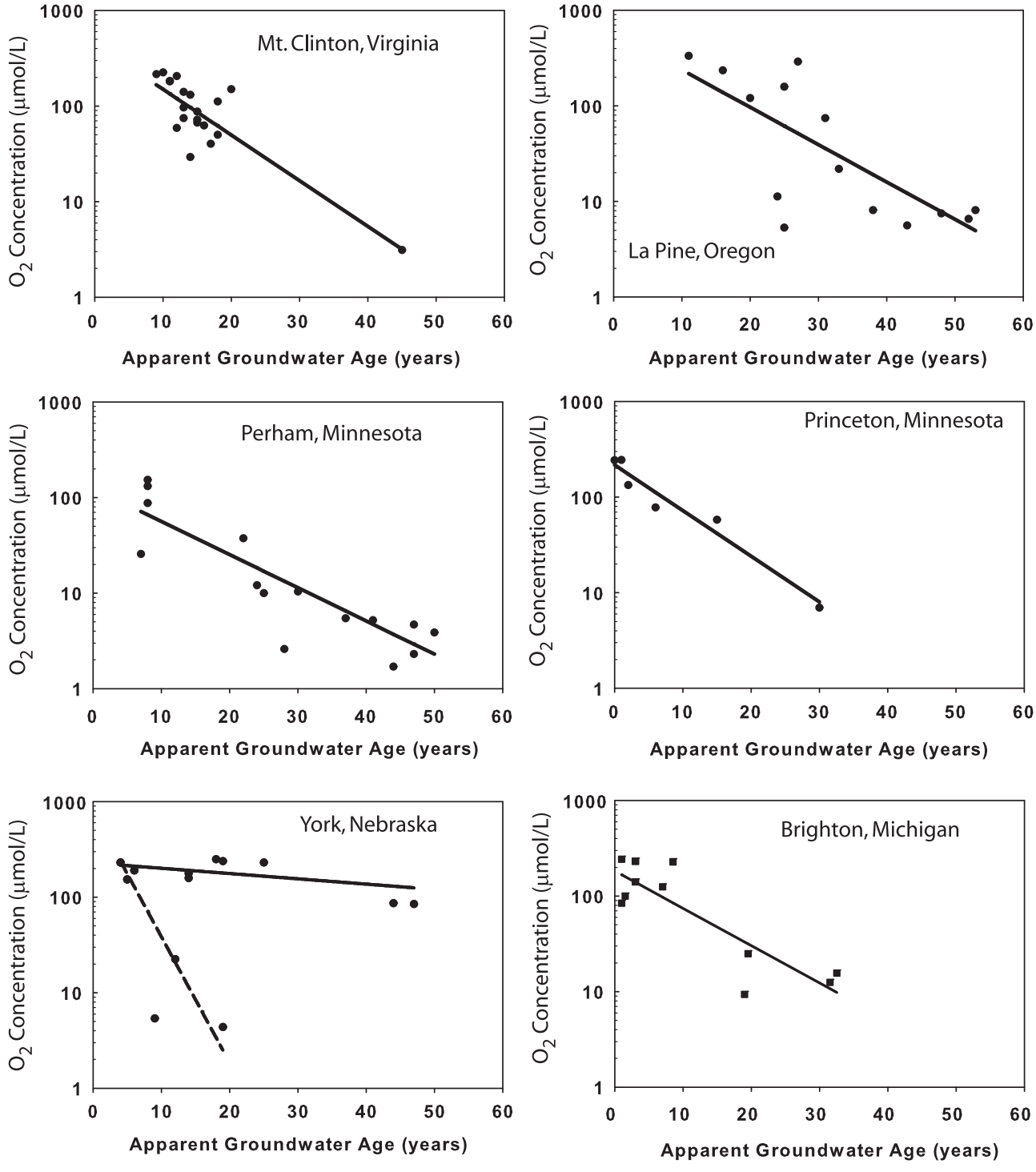

Figure 2. (continued)

are more susceptible to the migration of NO_3^- into deeper portions of the aquifer and into streams.

4.3. Denitrification Rates

[24] Most suboxic systems had zero-order rates ranging from 15 to 70 μmol L^{-1} yr^{-1} (Table 3). One notable exception was the much higher rate (>280 μmol L^{-1} yr^{-1}) that was observed as groundwater entered a hypothesized relict channel in the Sumas Aquifer. The increasing supply of electron donors in the form of iron sulfides and organic carbon (Figure 5) is likely responsible for the quick loss of both O_2 and NO_3^- as groundwater enters these deposits. A similarly high rate may also occur as groundwater enters the riparian zone at Morgan Creek at the Kennedyville, Maryland site; however, only one sample was located in the denitrification zone. These findings suggest that zero-order dentrification rates can be broadly generalized into three categories: low rates (e.g., <3 μmol N L^{-1} yr^{-1}) found in areas having elevated O_2 concentrations, moderate rates (10–100 μmol N L^{-1} yr^{-1}) in most areas with low O_2

Table 3. Zero-Order (k_0) and First-Order (k_1) Apparent Reaction Rate Constants for O_2 Reduction and Denitrification[a]

Location	O_2 Reduction Rates						Denitrification Rates					
	k_0 (μmol L^{-1} yr^{-1})	R^2	p-value	k_1 (yr^{-1})	R^2	p-value	k_0 (μmol N L^{-1} yr^{-1})	R^2	p-value	k_1 (yr^{-1})	R^2	p-value
Brighton, Michigan	7.6	0.41	0.06	**0.09**	0.74	<0.001	>34[b]			**0.29**	0.91	0.05
Chesterville, Maryland	**3.0**	0.31	0.04	**0.02**	0.33	0.03	ND[c]			ND		
Kennedyville, Maryland				**0.12**	0.78	<0.001						
Upland	0.63	0.04	0.57				ND			ND		
Riparian	>140[b]						>30[b]			>0.09[b]		
La Pine, Oregon	11	0.32	0.14	**0.09**	0.55	0.002	NA[d]			NA		
Lizzie, North Carolina	**10**	0.44	0.01	**0.13**	0.68	<0.001	69	0.26	0.15	0.18	0.55	0.09
Mt. Clinton, Virginia	**12**	0.33	0.01	**0.11**	0.72	<.0001	ND			ND		
Perham, Minnesota	4.9	0.50	0.08	**0.08**	0.78	<0.001	**23**	0.92	<0.001	**0.15**	0.76	0.01
Polonia, Wisconsin	**5.6**	0.75	<0.001	**0.03**	0.66	<0.001	ND			ND		
Princeton, Minnesota	29	0.83	0.09	**0.11**	0.96	<0.001	15	0.98	0.06	0.30[b]		
Stevinson, California	**15**	0.65	0.05	**0.16**	0.63	0.003	94	0.83	0.09	**0.06**	0.49	0.05
Sumas Aquifer, WA-BC				**0.24**	0.74	<0.001						
Upland	0.63	0.01	0.86				ND			ND		
Riparian	>130[b]						>**280**[e]	0.99	0.04	>**0.36**[e]	0.69	0.02
York, Nebraska (without riparian)	**2.5**	0.40	0.05	**0.02**	0.53	0.02						
Riparian flow path	**15**	0.65	0.05	**0.27**	0.69	0.04	**32**	0.97	0.01	**0.09**	0.93	0.04

[a]Bold type indicates rate constants are statistically significant ($p \leq 0.05$).
[b]Based on sample pair across or in zone of interest. Fit statistics are not meaningful. See text for details.
[c]ND, not determined. Insufficient number of samples in the denitrification zone due to oxic conditions.
[d]Excess N_2 data not available. Denitrification rates not determined.
[e]Insufficient number of samples in denitrification zone due to high denitrification rate, minimum values reported.

concentrations, and high rates (>100 μmol N L^{-1} yr^{-1}) that occur when NO_3^- crosses a lithologic contact and enters a more reduced zone. The range in denitrification rates observed (10–100 μmol N L^{-1} yr^{-1}) is consistent with rates calculated at other sites using the N_2 gradient method [*Green et al.*, 2008]. First-order rate constant values show a similar pattern, with nondetectable rates in oxic groundwater, rates ranging from 0.08 to 0.30 yr^{-1} in most suboxic systems, and higher rates (>0.36 yr^{-1}) in systems where sharp redox gradients were observed (Table 3).

[25] The heterogeneity of redox conditions between flow paths within an aquifer is exhibited at the York, Nebraska site, where some flow paths remain oxic for 50 yr while others become suboxic in <20 yr (Figure 2). These suboxic wells are shallow and near a stream. It is hypothesized that organic-rich floodplain deposits may lead to suboxic conditions in these areas [*McMahon et al.*, 2008]. A first-order denitrification rate of 0.08 yr^{-1} was observed along suboxic flow paths at the York, Nebraska site, resulting in the loss of most of the initial NO_3^- within 20 yr (Figure 6). This is in contrast to the observation that little or no denitrification occurred along other flow paths in this aquifer that

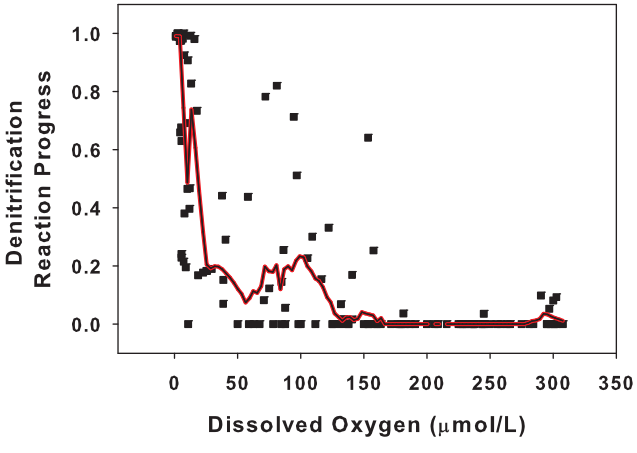

Figure 3. Relation between denitrification reaction progress and O_2 concentrations. Line represents LOESS smooth of the data.

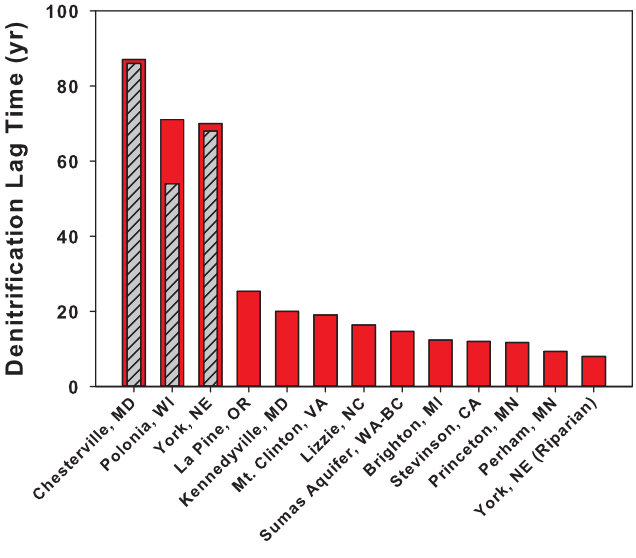

Figure 4. Denitrification lag time for each of the flow path study sites based on apparent first-order rate coefficients determined in this study (solid red bars). Lag time estimates assume denitrification begins when $[O_2] < 60$ μmol L^{-1}. Travel times in Chesterville, York (without riparian), and Polonia sites are extrapolated beyond the age range of available data using first-order (solid red bars) and zero-order rate constants (hatched gray bars).

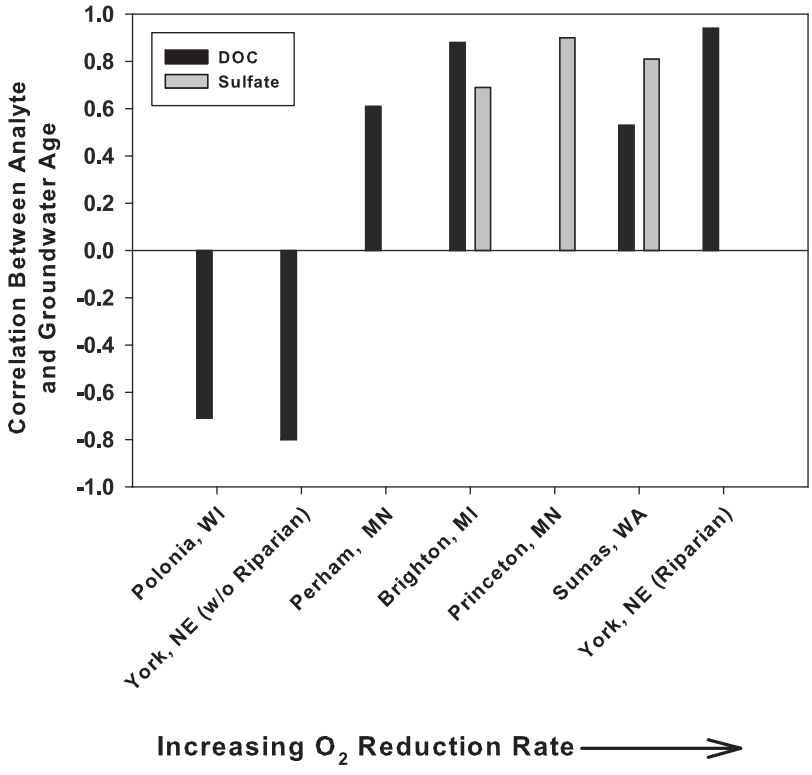

Figure 5. Spearman correlations between sulfate concentrations and groundwater age (gray bars) and dissolved organic carbon (DOC) and groundwater age (black bars). Only sites with significant relations ($p < 0.05$) are shown. Sites are ordered by O_2 reduction rate, with increasing rates from left to right. For the York, Nebraska site, flow paths that are likely influenced by riparian sediments are shown separately from remaining data.

remained oxic even after 50 yr of groundwater travel time (Figure 2).

4.4. Electron Donors

[26] As necessary reactants in the reduction of O_2, the concentration and reactivity of electron donors are hypothesized to be the major factors causing O_2 reduction rates to vary. Organic carbon and iron sulfide minerals have been identified as sources of electrons in groundwater systems [e.g., *Postma et al.*, 1991; *Tesoriero et al.*, 2000; *Visser et al.*, 2009]. It has been suggested that dissolved organic carbon in recharge may be an important source of electrons for reduction reactions [e.g., *Starr and Gilham*, 1993]. Recent global estimates of denitrification assume that DOC from recharge is the primary source of electrons for denitrification [*Seitzinger et al.*, 2006]. Conversely, recharging electron donors have been found to be insufficient to account for losses of O_2 and NO_3^- in groundwater in agricultural areas [*Green et al.*, 2008].

[27] Trends in DOC concentrations were examined as a function of groundwater age to evaluate the importance of surface-derived DOC as a source of electrons in reduction reactions. While concentrations of reactants or products of redox reactions can provide clues that help determine the dominant reactions occurring, more direct evidence may be obtained by examining the changes in concentrations along flow paths. This approach assumes that changes in the composition of recharge are negligible over the time period examined. If surface-derived DOC is a source of electrons for O_2 reduction (e.g., Table 1), a negative correlation between groundwater age and DOC would result as DOC and O_2 are consumed.

[28] Significant ($p < 0.05$) correlations between DOC and groundwater age were observed at five sites (Figure 5). Negative correlations between groundwater age and DOC were observed at the Polonia, Wisconsin and York, Nebraska (without riparian flow path) sites (Figure 5), both sites having very low O_2 reduction rates. The fact that O_2 reduction rates are low in systems where surface-derived DOC is indicated (i.e., a negative correlation between DOC and age) suggests that surface-derived DOC is not sufficient to cause significant amounts of O_2 reduction to occur. In contrast, systems with high O_2 reduction rates (e.g., York, Nebraska riparian, Perham, Minnesota, Sumas Aquifer) have DOC concentrations that increase with groundwater age (Figure 5), suggesting that a lithologic source is needed if carbon oxidation is to supply electron donors for significant O_2 and NO_3^- reduction to occur. Lithologic sources may also be significant even when DOC concentrations do not increase with groundwater age. This may occur if DOC is oxidized rapidly as it enters the aquifer from a confining layer, resulting in no measurable increase in DOC concentrations but still providing a source of electrons to the aquifer [*McMahon and Chapelle*, 1991].

[29] To further evaluate the influence of surface-derived DOC, the amount of O_2 reduction coupled with DOC

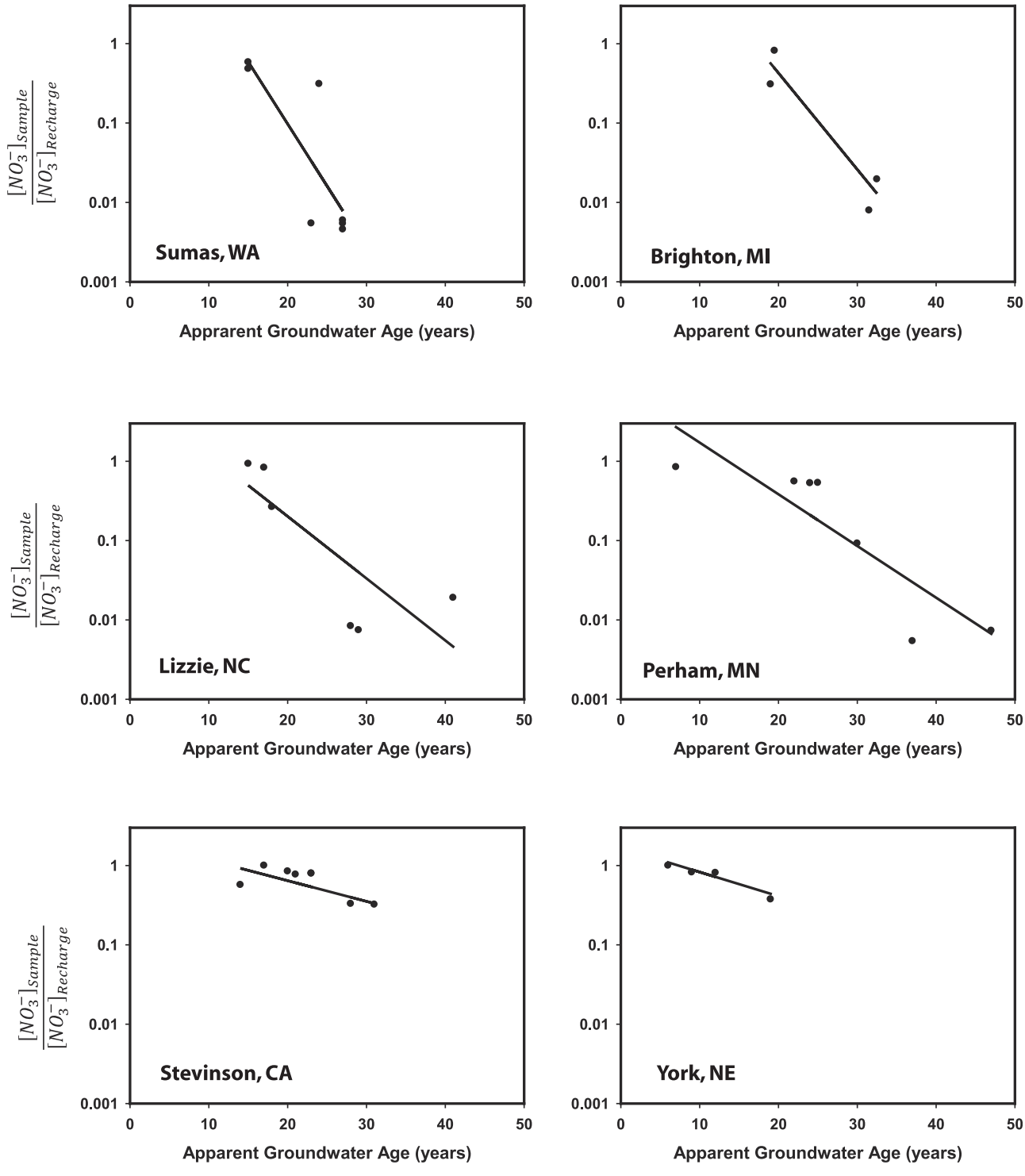

Figure 6. Relation between the fraction of nitrate remaining at the time of sampling (nitrate in sample/nitrate in recharge) and apparent groundwater age. Regression statistics for the fit of first-order reaction rate expression to the data are provided in Table 3.

oxidation was estimated using best fit relations between O_2 and age and DOC and age at the Polonia, Wisconsin site (Figure 7). Assuming the stoichiometry shown in Table 1, 1 mole of DOC oxidized will result in 1 mole O_2 reduced. The number of μmoles of DO lost during the time period examined is more than three times greater than the loss of DOC, indicating that the percentage of O_2 reduction that could be linked to surface-derived DOC oxidation was only 30% for the Polonia, Wisconsin site. This is consistent with the finding that DOC is not a significant source of electrons for O_2 and NO_3^- reduction in agricultural areas [*Green et al.*, 2008].

[30] Additional evidence that DOC at the Perham, Minnesota site is derived from lithologic rather than surface-derived

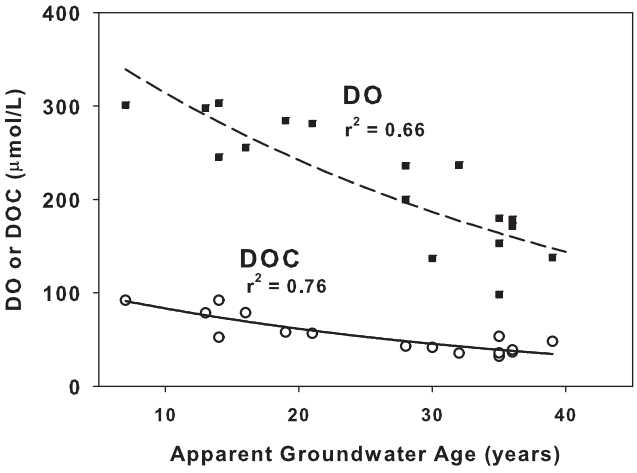

Figure 7. Dissolved oxygen (DO) and dissolved organic carbon (DOC) concentrations in groundwater plotted against apparent groundwater age for samples from the Polonia, Wisconsin site. Dashed and solid lines are first-order regression fits to DO (solid squares) and DOC data (open circles), respectively.

sources is indicated by the increase in ammonium concentrations observed at this site (Figure 8). An increase in ammonium concentrations as apparent groundwater age increases could result from either a dissimilatory reduction of nitrate to ammonium or from the mineralization of organic matter. However, previous nitrogen isotope studies [e.g., *Hinkle et al.*, 2007] and the fact that nitrate is not detected in groundwater where ammonium concentrations are increasing indicate that mineralization of organic matter is the source of ammonium. While ammonium is likely being generated throughout the flow path, it only begins to accumulate in the aquifer after O_2 is depleted; in the oxic portion of aquifers, ammonium is nitrified to NO_3^- or is sorbed to oxide mineral surfaces [e.g., *Hill*, 1990]. DOC does not increase with groundwater age in the oxic portion of the aquifer (Figure 8), suggesting that DOC liberated by the mineralization of organic matter quickly reacts with O_2; however, once the aquifer becomes suboxic, the oxidation of DOC slows and DOC begins to accumulate (Figure 8). Increases in DOC and ammonium concentrations at the oxic/suboxic boundary may also be due to an increase in organic carbon in aquifer sediments; however, soil core data did not indicate a major change in lithology [*Puckett and Cowdery*, 2002]. Other sites examined in this study did not show systematic increases in ammonium concentrations with apparent groundwater age, either because organic matter sources were not as abundant and/or redox conditions were not sufficiently reducing. The Perham, Minnesota site had the highest median DOC concentrations and was one of the more reduced sites, with sulfate-reducing conditions prevalent in older groundwater.

[31] The oxidation of iron sulfides is also a potential source of electrons for reduction reactions [*Tesoriero et al.*, 2000; *Böhlke et al.*, 2002]. Suggested reactions for pyrite oxidation by dissolved O_2 include [*Moses et al.*, 1987]:

$$2FeS_2(\text{pyrite}) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+. \quad (3)$$

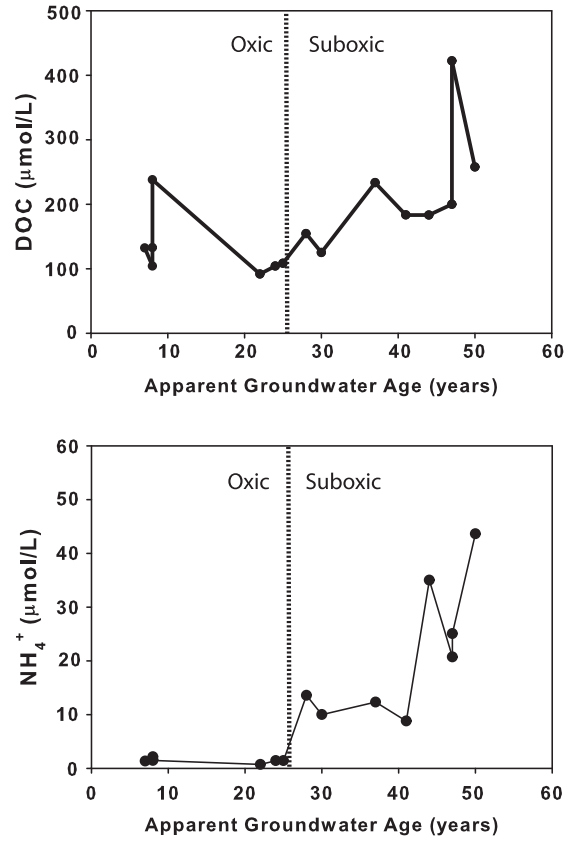

Figure 8. (top) Concentrations of dissolved organic carbon (DOC) plotted against apparent groundwater age. (bottom) Concentrations of ammonium (NH_4^+) plotted against apparent groundwater age. Both graphs show data for the Perham, Minnesota site. Vertical dashed line delineates oxic and suboxic zones.

Suggested reactions where reduced forms of sulfur are electron donors in denitrification reactions include [*Kölle et al.*, 1985]:

$$5FeS_2(\text{pyrite}) + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 7N_2 + 10SO_4^{2-} + 2H_2O. \quad (4)$$

This is often termed autotrophic denitrification since bacteria derive energy from an inorganic source, whereas the denitrification reaction in Table 1 is referred to as heterotrophic denitrification because bacteria use an organic source for growth and maintainance [*Korom*, 1992]. Pyrite occurs in freshwater wetlands and sediments of marine origin [*Marnette et al.*, 1993]. As oxic groundwater moves into portions of aquifers containing iron sulfide deposits, oxidative dissolution of these deposits occurs [e.g., *Poulton*, 2003]. Increases in sulfate concentrations with groundwater age at the Sumas Aquifer, Princeton, Minnesota, and Brighton, Michigan sites (Figure 5) suggest that sulfide oxidation supplies electrons for O_2 reduction and denitrification at these sites.

[32] Electron and mass balance calculations indicate that sulfide oxidation provides most of the electrons needed for O_2 and nitrate reduction at the Sumas Aquifer site [*Tesoriero et al.*, 2000]. Sulfate δS^{34} gradients along flow paths can provide additional evidence into the sources of added sulfate

and electron donors. The sulfate δS^{34} values at the Sumas Aquifer site decrease dramatically across the redoxcline, while sulfate concentrations increase markedly (Figure 9). This pattern is consistent with pyrite oxidation as a source of the added sulfate. While these reversals are not always observed during sulfide oxidation [*Strebel et al.*, 1990], a decrease in sulfate S^{34} content during pyrite oxidation is expected in agricultural areas due to the lower S^{34} content of sulfides than fertilizers [*Moncaster et al.*, 2000; *Böhlke et al.*, 2002] and the potential for fractionation during pyrite oxidation with sulfate-sulfur isotopes lighter than sulfide [*Toran and Harris*, 1989]. Sulfur isotope results from the Princeton, Minnesota site suggest that pyrite oxidation also occurs at this site [*Böhlke et al.*, 2002]. Evidence of sulfide oxidation is not conclusive at the Brighton, Michigan site (e.g., no sulfur isotope data and a weaker correlation between age and sulfate concentrations).

[33] The importance of sulfide oxidation as a source of electrons at the Sumas Aquifer and Princeton, Minnesota sites was examined by estimating the number of electrons donated by this reaction and comparing it to the number of electrons accepted during O_2 and NO_3^- reduction [*Postma et al.*, 1991]. Electrons released during sulfide oxidation at each of these sites were estimated using the increase in sulfate concentrations across the redoxcline and the stoichiometry shown in equations (3) and (4). Similarly, the loss of O_2 and gain in excess N_2 across the redoxcline were used with the stoichiometry shown in equations (3) and (4) to estimate the amount of electrons accepted during O_2 and NO_3^- reduction. Sulfide oxidation could be responsible for most, if not all, of the O_2 and NO_3^- reduction at the Sumas Aquifer site (Figure 10). At the Princeton, Minnesota site, sulfide oxidation may initially supply most of the electrons for O_2 and NO_3^- reduction; however, after ~10 yr, electrons from sulfide oxidation are no longer sufficient to account for the reduction of O_2 and NO_3^-, indicating that another source of electrons must be present (Figure 10). While mass balance calculations suggest that organic carbon is the additional source of electrons at the Sumas Aquifer site [*Tesoriero et al.*, 2000], this was not the case at the Princeton, Minnesota site; however, dissolution of carbonates may have masked the contribution of organic carbon as an electron donor at this site [*Böhlke et al.*, 2002]. Sulfide oxidation may also be an important supply of electrons for O_2 and NO_3^- reduction at other sites where sulfide mineral deposition may occur (e.g., wetlands), but may be masked by other sources or sinks of sulfate.

4.5. Rate Comparisons

[34] O_2 reduction and denitrification rates determined in this study were compared to rates from other studies to further elucidate the factors responsible for the spatial variation in rates. Rates were obtained directly from previous studies or were determined using concentration gradient and travel time estimates provided in these publications (Table 4). Studies examining point source contamination or using injected solutes were not included in this compilation to focus on ambient conditions and to allow a more direct comparison with our results. It should be noted that the rates from this study and those presented in Table 4 represent average rates over the time periods examined. Higher rates have been observed when more discrete zones have been examined using core samples [e.g., *Jakobsen and Postma*, 1994].

[35] While most O_2 reduction rates in this study and previous investigations varied over a similarly wide range (Tables 3 and 4), two previous studies had much lower rates. The presence of O_2 concentrations between 60 and 250 μmol L^{-1} in groundwater >1000-yr old illustrates that very low O_2 reduction rates (e.g., <0.01 μmol L^{-1} yr^{-1}) occur in some systems [e.g., *Winograd and Robertson*, 1982; *Vogel et al.*, 1981]. Low O_2 reduction rates were found in two of our study areas (the uplands of the Sumas Aquifer and the Kennedyville, Maryland sites, Table 3); however, the age range was not sufficient to quantify very low rates.

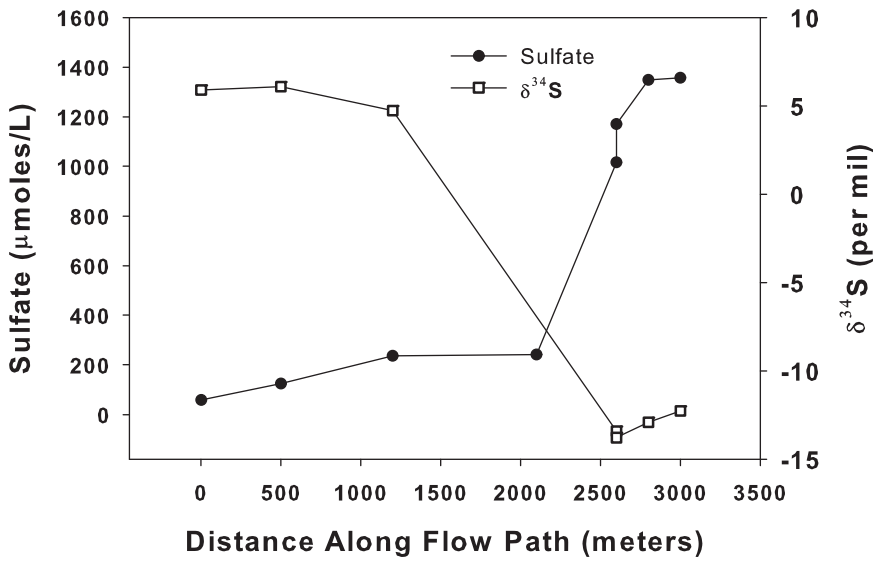

Figure 9. Sulfate concentrations (solid circles) and $\delta^{34}S$ values (open squares) along a shallow flow path at the Sumas Aquifer site.

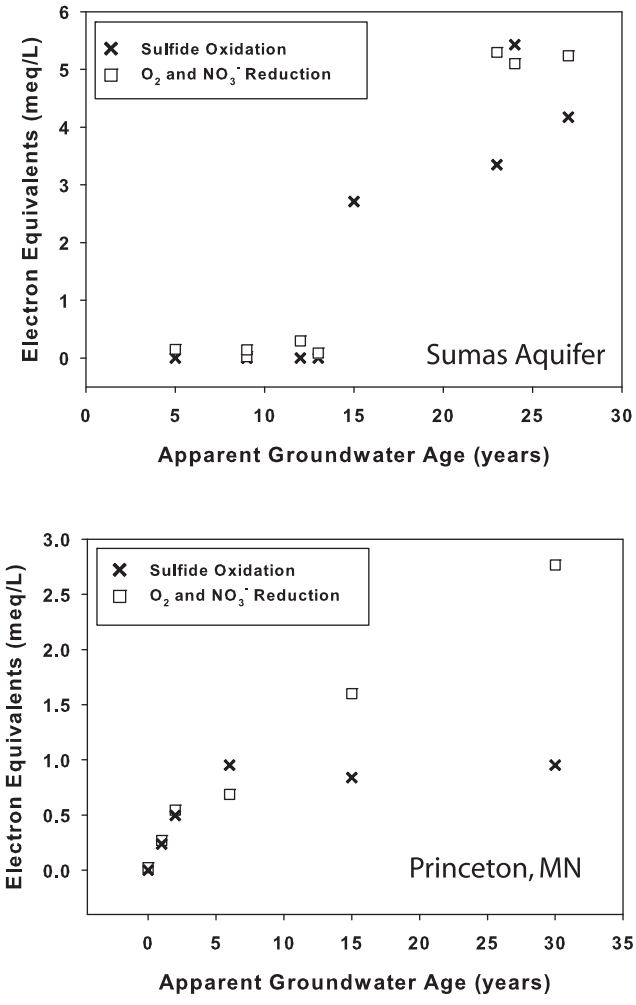

Figure 10. Relation between electron equivalents released from sulfide oxidation (x symbols) and electron equivalents accepted during O_2 and NO_3^- reduction (squares). Data are shown for Sumas Aquifer (top panel) and Princeton, Minnesota sites (bottom panel).

[36] The influence of electron donors on O_2 reduction and denitrification rates was examined by identifying those sites where sulfides were a significant source of electrons. When sulfide oxidation was indicated, zero-order O_2 reduction rates tend toward the upper range of rates observed at other sites (Figure 11; Tables 3 and 4). Similarly, denitrification coupled with sulfide oxidation often occurs at higher rates than at sites where carbon was the dominant electron source for denitrification (Figure 11). High-denitrification rates coupled with sulfide oxidation (e.g., >250 μmol L^{-1} yr^{-1}; Figure 11) were observed at the Führberg Aquifer in Germany [*Böttcher et al.*, 1989], the Oostrum Aquifer in Netherlands [*Zhang et al.*, 2009], the Sumas Aquifer in Canada [*this study*; *Tesoriero et al.*, 2000], and in a sand aquifer in Denmark [*Postma et al.*, 1991]. These results are consistent with the suggestion by *Postma et al.* [1991] that nitrate reduction by pyrite oxidation occurs quickly and can, to a first approximation, be modeled using an equilibrium approach. These findings also suggest that when organic carbon and pyrite are both present, denitrification coupled with pyrite oxidation may be the dominant process even though it is not as favorable thermodynamically [e.g., *Kölle et al.*, 1985]. A possible exception is the high-denitrification rate observed in the Lincolnshire Limestone in the United Kingdom [*Hiscock et al.*, 2011]. While pyrite oxidation occurs in this system [*Lawrence and Foster*, 1986; *Bottrell et al.*, 2000], organic carbon is suggested as the dominant electron source for denitrification [*Hiscock et al.*, 2011].

[37] Sulfate reduction rates also vary widely between studies (Table 4; Figure 11) and over a similar range as O_2 reduction and denitrification rates when sulfide is not an electron donor. However, sulfate reduction rates are typically lower than denitrification rates coupled with sulfide oxidation. This finding is consistent with the electron donor effect on rates stated above since sulfate reduction relies on a carbon source of electrons. An important exception is the rate obtained in a river recharged portion of an aquifer providing young reactive carbon to groundwater [*Massmann et al.*, 2003]. It has been suggested that younger sediments are more likely to contain reactive carbon, resulting in faster redox reaction rates [e.g., *Jakobsen and Postma*, 1994].

5. Summary and Conclusions

[38] O_2 reduction and denitrification rates from 12 study sites were determined using concentration gradients and tracer-based groundwater ages. O_2 reduction rates varied markedly both within and between sites, with first-order rates ranging from 0.02 to 0.27 yr^{-1}. While rates at most sites were generally consistent over decades of groundwater travel time, abrupt increases in reaction rates were often (but not always) observed when riparian sediments were encountered. Identifying these localized areas with high O_2 reduction and denitrification rates is critical to understanding the transport of redox-sensitive contaminants.

[39] The groundwater travel time that occurs before denitrification commences is referred to as the denitrification lag time. Denitrification lag time is an important metric for assessing the susceptibility of aquifers to nitrate and other redox-sensitive contaminants (e.g., arsenic, atrazine, and volatile organic compounds). Measured denitrification lag times varied from <10 yr to >80 yr when low O_2 reduction rates were extrapolated beyond the age range of sampled groundwater.

[40] Denitrification rates were determined assuming zero- and first-order kinetics. Zero-order denitrification rates can be broadly generalized into three categories: low rates (e.g., <3 μmol L^{-1} yr^{-1}) found in areas having elevated O_2 concentrations, moderate rates (10–100 μmol L^{-1} yr^{-1}) in areas with low O_2 concentrations, and high rates (>100 μmol L^{-1} yr^{-1}) when changes in lithology result in a sharp increase in the supply of electron donors. First-order rates show a similar pattern, with nondetectable rates in oxic groundwater, rates ranging from 0.06 to 0.30 yr^{-1} in most suboxic systems, and higher rates (>0.36 yr^{-1}) in systems where a sharp redox gradient was observed.

[41] The availability of electron donors is indicated as the major factor influencing O_2 reduction rates. Likely electron donors at these sites include organic carbon and sulfide deposits. The relations between DOC concentrations and apparent groundwater age suggest that lithologic sources of

Table 4. Compilation of Selected O_2 Reduction, Denitrification, and Sulfate Reduction Rates

Site	Location	O_2 Reduction rates	Denitrification Rates		Sulfate Reduction Rates		Reference[a]
		k_0 μmol L^{-1} yr^{-1}	k_0 μmol N L^{-1} yr^{-1}	k_1 yr^{-1}	k_0 μmol L^{-1} yr^{-1}	k_1 yr^{-1}	
Sand Aquifer, Jutland	Denmark	62	310	>0.35			*Postma et al.*, 1991
Auob sandstone	Namibia	0.02	0.1				*Vogel et al.*, 1981[b]
Perch Lake Basin	Canada	25					*Jackson and Patterson*, 1982[b]
Vekol Valley, Arizona	USA	<0.01					*Winograd and Robertson*, 1982[b]
Lincolnshire limestone	United Kingdom	48	284				*Hiscock et al.*, 2011
Fairmount, Delaware	USA	3					*Denver et al.*, 2010
Willards Site, Maryland	USA	14					*Denver et al.*, 2010
Unconfined N. Platte Aquifer, Nebraska	USA	13	0.5				*Böhlke et al.*, 2007
Oostrum Aquifer	Netherlands		600				*Zhang et al.*, 2009
Unconfined S. Platte Aquifer, Colorado	USA		<11				*McMahon and Böhlke*, 1996[c]
Booholt	Germany				23		*Leuchs*, 1988[d]
Fürberg	Germany		730	0.46	14	0.007	*Böttcher et al.*, 1989; *Frind et al.*, 1990[c,d]
Princeton, Minnesota	USA	3.3–38	16	0.28	8.1	0.085	*Böhlke et al.*, 2002
Black Creek Aquifer, S. Carolina	USA				0.007–0.15		*Chapelle and McMahon*, 1991[d]
Floridan Aquifer	USA				0.1		*Plummer*, 1977[d]
Fox Hills Aquifer, N. and S. Dakota	USA				0.2		*Thorstenson et al.*, 1979[d]
Oderbruch Aquifer	Germany					0.60 (River recharged) 0.014 (confined)	*Massmann et al.*, 2003
Sturgeon Falls	Canada				13	0.23	*Robertson et al.*, 1989; *Robertson and Schiff*, 1994[d]

[a]When published rates were not available, rates were derived from published concentration gradients and groundwater travel times.
[b]Rates were determined from data provided by *Malard and Hervant* [1999].
[c]Also see review by *Groffman et al.* [2006].
[d]Also see review by *Jakobsen and Postma* [1994].

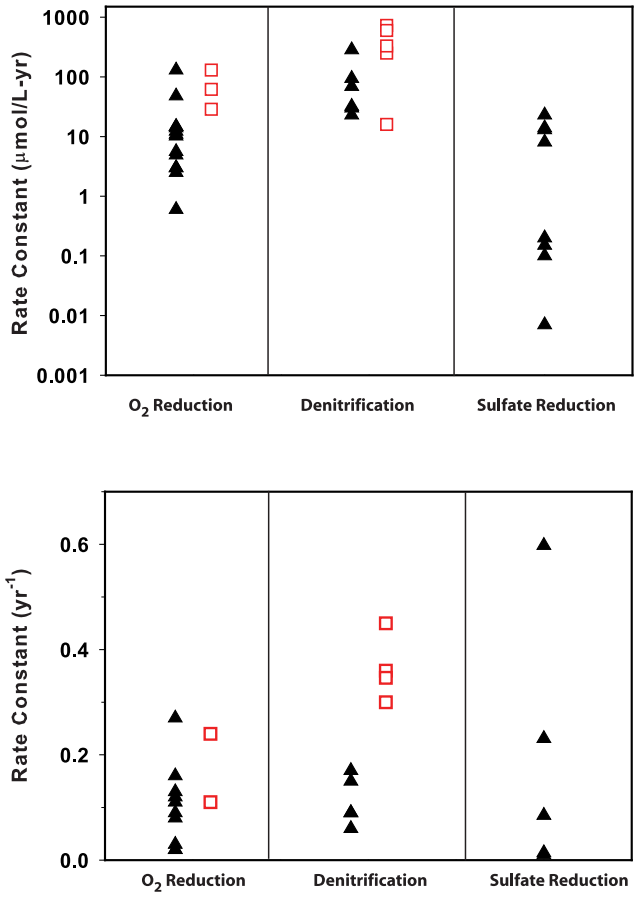

Figure 11. O_2 reduction, denitrification, and sulfate reduction rate constants represented as zero-order (top panel) and first-order (bottom panel) reactions. Data are from Tables 3 and 4. O_2 reduction and denitrification data are shown only if the role of sulfide oxidation as an electron source has been determined. For O_2 reduction and denitrification data: square symbols indicate sulfide oxidation was an important electron source; triangles indicate sulfide oxidation was not suggested as an important electron source.

carbon are a major source of electron donors for O_2 reduction in these aquifers, while surface-derived sources of DOC are not. Sulfide oxidation was indicated as a major source of electrons for O_2 reduction and denitrification at two of the 12 sites studied. A review of published rates suggests that denitrification tends to occur more quickly when linked with sulfide oxidation rather than carbon oxidation.

[42] **Acknowledgments.** This research was funded by the U.S. Geological Survey's (USGS) National Water Quality Assessment Program (NAWQA). L.N. Plummer, E. Busenberg, and their colleagues at the USGS CFC laboratory are gratefully acknowledged for the interpretation and analysis of samples for CFCs, SF_6, and other dissolved gases. The authors thank the many USGS scientists that conducted research on these sites and laid the foundation upon which this work could build, including: J.K. Böhlke, Stephen Hinkle, Peter McMahon, Steven Phillips, David Saad, Gary Speiran, and Mary Ann Thomas. Private landowners are gratefully acknowledged for permitting us to access their land to install and sample monitoring wells. We thank Peter McMahon and Christopher Green (both of USGS) for many helpful suggestions. Three anonymous reviewers and the associate editor of this journal are gratefully acknowledged for their insightful comments on a previous version of this manuscript.

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