Aquifer/aquitard interfaces: mixing zones that enhance biogeochemical reactions

P.B. McMahon

Abstract Several important biogeochemical reactions are known to occur near the interface between aquifer and aquitard sediments. These reactions include O_2 reduction; denitrification; and Fe^{3+}, SO_4^{2-}, and CO_2 (methanogenesis) reduction. In some settings, these reactions occur on the aquitard side of the interface as electron acceptors move from the aquifer into the electron-donor-enriched aquitard. In other settings, these reactions occur on the aquifer side of the interface as electron donors move from the aquitard into the electron-acceptor-enriched, or microorganism-enriched, aquifer. Thus, the aquifer/aquitard interface represents a mixing zone capable of supporting greater microbial activity than either hydrogeologic unit alone. The extent to which biogeochemical reactions proceed in the mixing zone and the width of the mixing zone depend on several factors, including the abundance and solubility of electron acceptors and donors on either side of the interface and the rate at which electron acceptors and donors react and move across the interface. Biogeochemical reactions near the aquifer/aquitard interface can have a substantial influence on the chemistry of water in aquifers and on the chemistry of sediments near the interface.

Résumé Il se produit au voisinage de l'interface entre les aquifères et les imperméables plusieurs réactions biogéochimiques importantes. Il s'agit des réactions de réduction de l'oxygène, de la dénitrification et de la réduction de Fe^{3+}, SO_4^{2-} et CO_2 (méthanogenèse). Dans certaines situations, ces réactions se produisent du côté imperméable de l'interface, avec des accepteurs d'électrons qui vont de l'aquifère vers l'imperméable riche en donneurs d'électrons. Dans d'autres situations, ces réactions se produisent du côté aquifère de l'interface, avec des donneurs d'électrons qui se déplacent de l'imperméable vers l'aquifère riche en accepteurs d'électrons ou en microorganismes. Ainsi, l'interface aquifère/imperméable constitue une zone de mélange capable de supporter une plus grande activité microbienne que chacune des deux unités hydrogéologiques seules. L'extension des réactions biogéochimiques dans la zone de mélange et la largeur de cette zone dépendent de plusieurs facteurs, dont l'abondance et la solubilité des accepteurs et des donneurs d'électrons de chaque côté de l'interface, et le taux de réaction et de déplacement des accepteurs et des donneurs d'électrons au travers de cette interface. Les réactions biogéochimiques au voisinage de l'interface aquifère/imperméable peuvent avoir une influence appréciable sur le chimisme de l'eau des aquifères et sur celui des sédiments au niveau de l'interface.

Resumen Es conocido que varias reacciones biogeoquímicas de importancia pueden tener lugar cerca de la interfaz entre los sedimentos de un acuífero y de un acuitardo. Entre ellas, destaca la reducción del O_2, la denitrificación, y la reducción del Fe^{+3}, SO_4^{-2} y CO_2 (metanogénesis). En algunos casos, estas reacciones se producen en la región cercana al acuitardo, ya que los dadores de electrones se mueven desde éste hacia el acuífero, el cual está enriquecido en aceptores de electrones o en microorganismos. Así, la interfaz acuífero/acuitardo constituye una zona de mezcla que es capaz de sustentar una actividad microbiana mayor que cualquier unidad hidrogeológica por sí misma. El alcance de las reacciones biogeoquímicas en la zona de mezcla y el ancho de esta zona de mezcla depende de varios factores, como la abundancia y la solubilidad de los aceptores y dadores de electrones en ambas caras de la interfaz y la velocidad a la que los aceptores y dadores de electrones reaccionan y se mueven a través de la interfaz. Las reacciones biogeoquímicas cerca de la interfaz acuífero/acuitardo pueden tener una influencia substancial en la hidroquímica de los acuíferos y en la química de los sedimentos cerca de la superficie.

P.B. McMahon (✉)
US Geological Survey, Denver Federal Center,
MS415, Denver, Colorado 80225, USA
e-mail: pmcmahon@usgs.gov
Fax: +1-303-2364912

Introduction

It is widely recognized that microorganisms are important in the chemical evolution of groundwater (Thorstenson

et al. 1979; Chapelle et al. 1987; Murphy et al. 1992; Simpkins and Parkin 1993). Their role primarily involves the transport of electrons from reduced chemical species to those that are oxidized, producing a change in the chemical composition of groundwater. For example, microorganisms couple the oxidation of organic carbon with the reduction of Fe^{3+} at the circumneutral pH and low temperatures of most shallow groundwater systems (Lovley et al. 1991), resulting in an increase in the dissolved concentrations of CO_2 and Fe^{2+} groundwater (Chapelle and Lovley 1992). Aquifers may contain an abundant supply of electron acceptors (including O_2, NO_3^-, Fe^{3+}, SO_4^{2-}) yet support only limited microbial activity because of a lack of suitable electron donors (Winograd and Robertson 1982). In contrast, aquitards may contain an abundance of electron donors (including organic carbon and reduced sulfur species) but support only limited microbial activity (Hendry and Wassenaar 2000), possibly because of small microbial populations (Phelps et al. 1989) or pore-size restrictions (Krumholz et al. 1997). The chemical gradients created between aquifer and aquitard drive the diffusive flux of electron acceptors and donors across the aquifer/aquitard interface (Pucci and Owens 1989; McMahon and Chapelle 1991b). Thus, the aquifer/aquitard interface is a mixing zone capable of supporting greater microbial activity than could be supported in either hydrogeologic unit alone (Krumholz et al. 1997). The mixing zone may vary in width and include sediments on both sides of the physical contact between aquifer and aquitard. The purpose of this paper is to review the major biogeochemical processes known to occur in mixing zones near aquifer/aquitard interfaces.

Biogeochemical Reactions Near the Aquifer/Aquitard Interface

Biogeochemical processes in pristine groundwater systems generally follow a predictable pattern along flow paths (Edmunds 1973; Champ et al. 1979), based on the amount of energy derived from each reaction and the availability of reactants (Stumm and Morgan 1981; Lovley and Goodwin 1988). Accordingly, the most energetically favorable reaction proceeds first, and the less energetically favorable reactions follow in succession. The most common sequence of biogeochemical reactions in groundwater, from most to least energetically favorable, are O_2 reduction, denitrification, Fe^{3+} reduction, SO_4^{2-} reduction, and CO_2 reduction (methanogenesis). Each of those oxidized chemical species may serve as the terminal electron acceptor during the oxidation of reduced chemical species such as H_2 and acetate. The nature and occurrence of each of those terminal-electron accepting processes (TEAPs) near aquifer/aquitard interfaces are discussed in this section. In addition, the function of aquitards in supplying electron donors for biogeochemical reactions near interfaces is examined. Manganese reduction is an important TEAP in some aquifer systems but is not addressed in this paper.

Electron Donors in Aquitards

The extent to which TEAP succession proceeds in aquifer/aquitard systems is dependent on the availability of electron donors to sustain the microbial processes. By far the bulk of electron donors in aquifer/aquitard systems resides in the aquitards. For example, the total organic carbon content in the confined Black Creek aquifer in South Carolina, USA, averages 0.1 wt%, whereas the average in the adjacent aquitard is 0.7 wt% (McMahon and Chapelle 1991a). Hendry et al. (1986) report that weathered and unweathered till in Alberta contains similar amounts of total sulfur, but that reduced sulfur species account for 95% of the total sulfur in unweathered till compared to 65% in the weathered till. Alluvium overlying the Pierre Shale in Colorado, USA, contains 0.06 and <0.01 wt% total organic carbon and sulfide minerals, respectively (McMahon et al. 1999). The shale contains 0.4 wt%, on average, of each component.

The relative lack of electron donors in aquifers is, in part, a function of the permeability of those sediments. Aquifer sediments are more permeable than aquitard sediments; therefore, in aquifer systems having unconfined recharge areas, more pore volumes of water (i.e., dissolved electron acceptors) pass through aquifer sediments than aquitard sediments. Thus, electron donors in aquifers are oxidized to a greater extent than electron donors in aquitards. However, that is not the case for all aquifer systems. The Dalmeny aquifer in Saskatchewan, Canada, is recharged entirely through a surficial glacial till aquitard (Fortin et al. 1991). In that case, the number of pore volumes of water passing through the aquitard and aquifer is the same, and the redox conditions in the aquifer are set by the sediment and water chemistry in the aquitard. Of course, in any aquifer/aquitard system, redox conditions change over time as electron acceptors and donors are depleted or introduced to the system.

Although aquitard sediments are enriched in solid organic carbon and sulfide minerals relative to aquifer sediments, those electron donors are not mobile. One way to couple those electron donors with electron acceptors in adjacent aquifer sediments is transport of electron acceptors into the aquitard. In that scenario, the mixing zone for biogeochemical reactions occurs on the aquitard side of the aquifer/aquitard interface. The transport of dissolved electron acceptors like O_2 and NO_3^- from aquifers to aquitards has been observed in several studies and may be diffusion controlled in unfractured aquitards (McMahon et al. 1999) or advection controlled in fractured aquitards (Keller et al. 1988; Simpkins and Parkin 1993; Martini et al. 1996). At the regional scale, the advective flux of solutes through aquitards can be significant. Models of fluid flow in the Dakota aquifer system in South Dakota, USA, indicate that the majority of flow into and out of the aquifer occurs as leakage through thick aquitards, and that leakage is the predominant source of sulfate in the aquifer (Bredehoeft et al. 1983). Similarly, the advective flux of sulfate-enriched water through a fractured glacial till in Saskatchewan is the
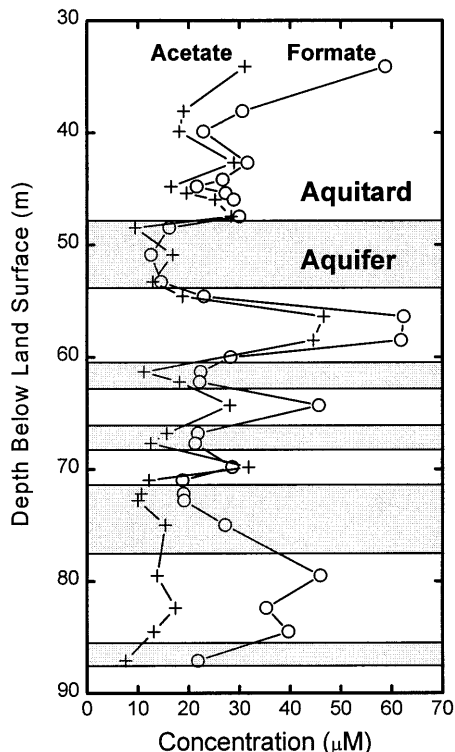
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Fig. 1 Distribution of dissolved formate and acetate in pore water of aquitard and aquifer sediments in the Atlantic Coastal Plain, South Carolina, USA (modified from McMahon and Chapelle 1991b, with permission, courtesy of *Nature*)

predominant source of sulfate in an underlying aquifer (Fortin et al. 1991).

Electron donors in aquitards and solid-phase electron acceptors in aquifers, such as amorphous ferric hydroxide grain coatings, could not be coupled if it were not for the occurrence and production of dissolved electron donors in aquitards and their transport to aquifers. Wassenaar et al. (1990) measured large concentrations of dissolved organic carbon in glacial till aquitards in Canada and concluded that a portion of it was derived from solid carbon sources in the till. Jones et al. (1989) observed that some aquitard sediments from the Atlantic Coastal Plain exhibit a net production of dissolved acetate when incubated under laboratory conditions. McMahon and Chapelle (1991b) and Chapelle and Bradley (1996) measured organic-acid concentrations in pore water squeezed from aquitard sediments in the Atlantic Coastal Plain and note that concentrations of formate and acetate in aquitard sediments are significantly larger than the concentrations in adjacent sands. These results are illustrated in Fig. 1. The chemical gradients shown in Fig. 1 indicate that a potential exists for electron donors in the aquitard to diffuse into the aquifer. In that scenario, aquitard-derived electron donors could be used in the adjacent aquifer, and the mixing zone for biogeochemical reactions would be on the aquifer side of the aquifer/aquitard interface. Solid-phase electron acceptors in aquifers, like ferric hydroxide grain coatings,

could then be coupled with electron donors derived from aquitards. It should not be construed from this discussion that the transport of electron donors in the mixing zone precludes the transport of dissolved electron acceptors. Both chemical species are probably transported simultaneously (possibly in opposite directions), and the precise location of the biogeochemical reaction sites depends on concentration gradients, hydraulic gradients, and which reaction steps are rate limiting, among other factors.

On the basis of diffusion calculations, McMahon and Chapelle (1991b) determined that the concentrations of formate and acetate in the coastal-plain aquitards would be about 200 times less than the observed concentrations if those organic acids were not actively produced in situ. These authors initially proposed that the formate and acetate were the products of microbial fermentation of complex solid organic matter in the aquitard (McMahon and Chapelle 1991b), although no microorganism capable of that fermentation was actually isolated. In a subsequent study, Liu and Suflita (1993) isolated a bacterial strain from aquifer sediments that was capable of degrading a methoxylated aromatic compound (syringate) in the presence of CO_2 and H_2, with the concomitant production of acetate. Methoxylated aromatic compounds are components of lignin, coal, and other forms of complex solid organic carbon, and the acetate produced through their degradation can be used as an electron donor in most TEAPs. The discovery by Liu and Suflita (1993) is important because it supports the microbial-origin theory for organic acids in aquitards and it provides a mechanism for producing dissolved electron donors from complex solid organic matter. One limitation of their work is that the microbial strain was isolated from aquifer sediments, which typically contain only small concentrations of solid organic matter and dissolved acetate. That limitation was overcome by Chapelle and Bradley (1996), who discovered that bacteria in organic-rich aquitard sediments were capable of producing acetate autotrophically (reaction 1) and in the presence of syringate, as shown in Fig. 2:

$$2CO_2+4H_2 \rightarrow CH_3COOH+2H_2O \qquad (1)$$
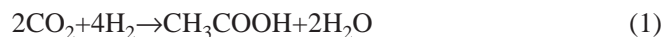
The discoveries of elevated organic-acid concentrations in aquitards and microbial processes for their production provide a mechanism for linking electron-donor-enriched aquitards with microbial activity in aquifers.

Aquitards also may be sources of H_2, another potential electron donor for TEAPs in adjacent aquifers. The production of H_2 in aquitard sediments would be required to support autotrophic acetogenesis in those sediments (Chapelle and Bradley 1996; reaction 1). McMahon and Chapelle (1991b) report a net production of H_2 in aquitard sediments. H_2 could be produced by microbial fermentation of complex organic matter (Lovley and Phillips 1988). It has also been proposed that abiotic rock–water reactions in basalt aquifers could produce H_2 and support microbial activity in deeply buried sediments (Stevens and McKinley 1995, 2000). However, that mechanism of H_2 production has recently
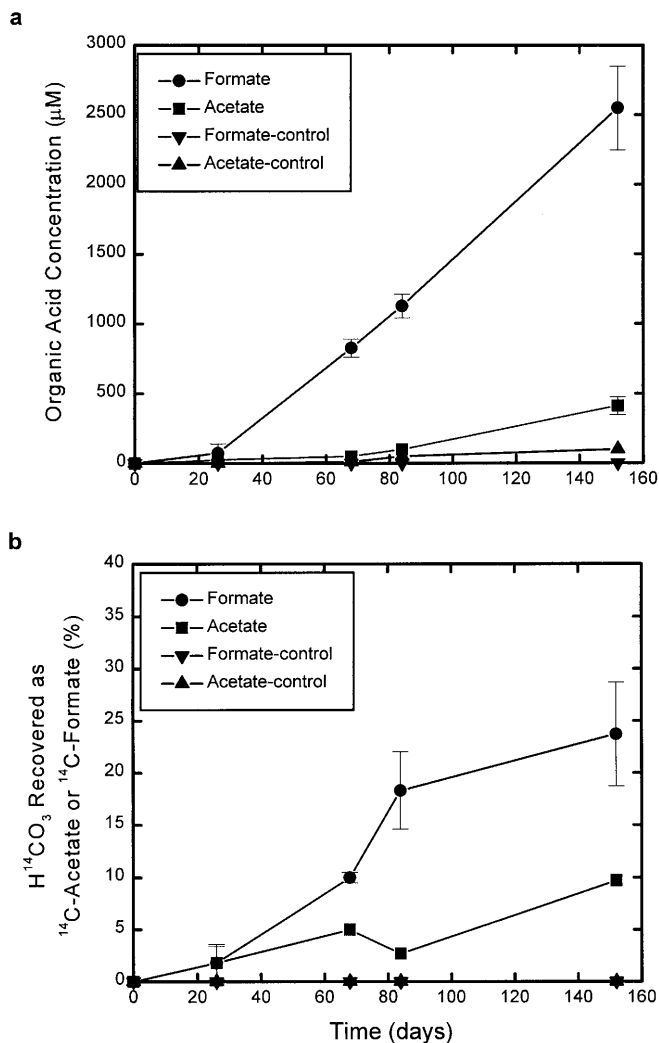

Fig. 2 a Production of organic acids in cultures of aquitard sediments incubated under an H_2 headspace. **b** Incorporation of ^{14}C-labeled bicarbonate in acetate and formate in cultures of aquitard sediments incubated under an H_2 headspace. Sediments were collected from a depth of 148 m in the Atlantic Coastal Plain, South Carolina, USA (modified from Chapelle and Bradley 1996, with permission, courtesy of The Geological Society of America)

their natural state contain sufficient amounts of solid organic carbon, or some other electron donor, to support a variety of TEAPs. Murphy et al. (1992) propose that organic acids and H_2 are produced by fermentation reactions at the surfaces of solid organic carbon disseminated in aquifer sediments. Those dissolved electron donors are transported either by diffusion or advection through the aquifer. The model of Murphy et al. (1992) is similar to that proposed by McMahon and Chapelle (1991b) for organic-acid generation and migration in aquitards, although the scale of investigation is different.

Oxygen Reduction

Dissolved O_2 is commonly present at the water table and at even greater depths below the water table in aquifers if there is a lack of suitable electron donors to support microbial O_2 reduction. For example, the High Plains aquifer, USA, which is unconfined and contains very little organic carbon or reduced sulfur, contains dissolved O_2 under concentrations near saturation to depths of 150 m below the water table (Krothe and Oliver 1982). Winograd and Robertson (1982) report elevated O_2 concentrations in deep (>100 m) groundwater in oxidized valley-fill deposits of the Basin and Range physiographic province, USA. Most of the sampled groundwater is more than 10,000 years old, indicating that rates of O_2 reduction are extremely slow. In contrast, O_2 concentrations decrease relatively rapidly with depth in aquifer systems containing suitable electron donors. Chapelle (1993) reports an O_2 reduction rate of 10^{-4} mmol L^{-1} year^{-1} in the Patuxent aquifer in Maryland, USA. Murphy and Schramke (1998) report O_2 reduction rates of $2 \times 10^{-6} – 6 \times 10^{-4}$ mmol L^{-1} year^{-1} in the Middendorf aquifer in South Carolina. Those aquifer systems were deposited in fluviodeltaic environments and contain organic carbon and reduced sulfur species capable of supporting O_2 reduction.

The loss of O_2 in aquifers is indicative of the presence of organic carbon, or other electron donors, capable of supporting O_2 reduction (reaction 2):

$$2O_2 + CH_3COO^- + H^+ \rightarrow 2CO_2 + 2H_2O \qquad (2)$$
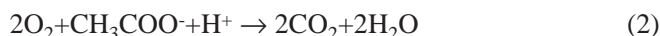
Given the relative abundances of dissolved O_2 in aquifers and electron donors in aquitards, at least some of the O_2 reduction probably occurs in the mixing zone near the interface between those hydrogeologic units. Profiles of O_2 concentrations across aquifer/aquitard interfaces indicate that O_2 probably is transported from aquifers to aquitards, where it is reduced (Simpkins and Parkin 1993; McMahon et al. 1999; Wassenaar and Hendry 1999). An example is shown in Fig. 3. Whether O_2 reduction near the aquifer/aquitard interface is an important component of the O_2 budget in aquifer/aquitard systems probably is dependent on the rate of O_2 transport across the interface. Diffusion is the most likely mechanism for transporting O_2 in unfractured aquitard sediments (McMahon et al. 1999), whereas advection may be important in fractured sediments (Keller et al. 1988).

been questioned (Anderson et al. 1998), but because H_2 is known to occur in gases emanating from volcanic terrain (Taran et al. 1995) such abiotic H_2 production may be important in some hydrologic systems. Regardless of the exact mechanism, H_2 production in aquitards could be an important component in the overall flow of electrons from relatively reduced aquitard sediments to more oxidized aquifer sediments; thus, the possibility warrants further study.
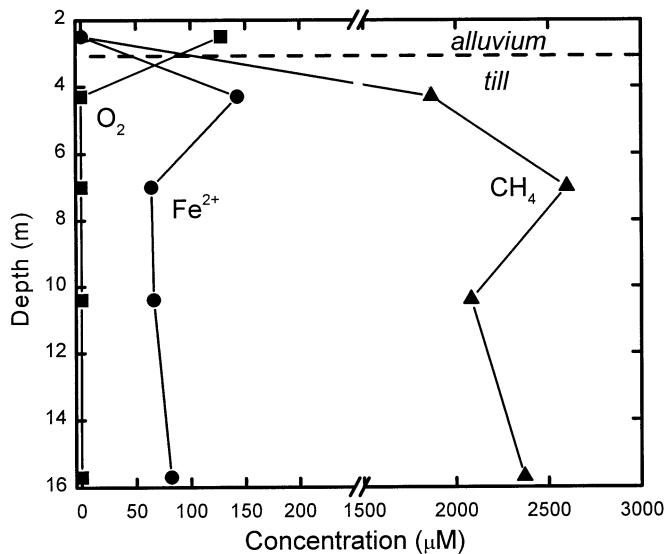
Aquitards are not the only source of electron donors to support microbial activity in aquifers. Dissolved organic carbon produced in the soil zone and leached into aquifers is another source of electron donors to aquifers (Wassenaar et al. 1989, 1990). However, soil-derived organic carbon is probably not an important electron donor in deeply buried and confined aquifers. Some aquifers in

Fig. 3 Profiles of dissolved O_2, Fe^{2+}, and CH_4 in pore water of alluvial and glacial till sediments in Iowa, USA (modified from Simpkins and Parkin 1993, with permission, courtesy of the American Geophysical Union)

Few direct measurements have been made of O_2 reduction rates at the aquifer/aquitard interface. Such measurements are needed to better evaluate the importance of aquifer/aquitard interfaces as sites for O_2 reduction.

Denitrification

Several studies document the occurrence of denitrification near aquifer/aquitard interfaces (Hendry et al. 1984; Robertson et al. 1996; McMahon et al. 1999). Through the use of N_2 and NO_3^- concentration and N-isotope measurements, McMahon et al. (1999) show that NO_3^- from an oxygenated alluvial aquifer is completely reduced to N_2 in adjacent shale. Although NH_4^+ is present in the shale pore water, N-isotope measurements indicate that it is derived from solid N in the shale and not from the dissimilatory reduction of aquifer-derived NO_3^-. A profile is illustrated in Fig. 4.

The rate at which NO_3^- from an aquifer is denitrified in an adjacent aquitard may be limited by the rate of NO_3^- transport into the aquitard. By fitting a one-dimensional diffusion model, including first-order decay, to NO_3^--concentration data at the top of a shale section, McMahon et al. (1999) determined a first-order denitrification rate constant of 0.04–0.4 year^{-1} for the shale. Results are shown in Fig. 5. That in situ rate constant is more than two orders of magnitude smaller than the potential denitrification rate constant (60 year^{-1}), as determined by an NO_3^- injection test. Those results indicate that denitrification in the shale is limited by the slow rate of NO_3^- transport into the shale from the overlying alluvial aquifer.

The predominant electron donor for denitrification in the shale was organic carbon (McMahon et al. 1999). Reduced sulfur species in aquitard sediments also have
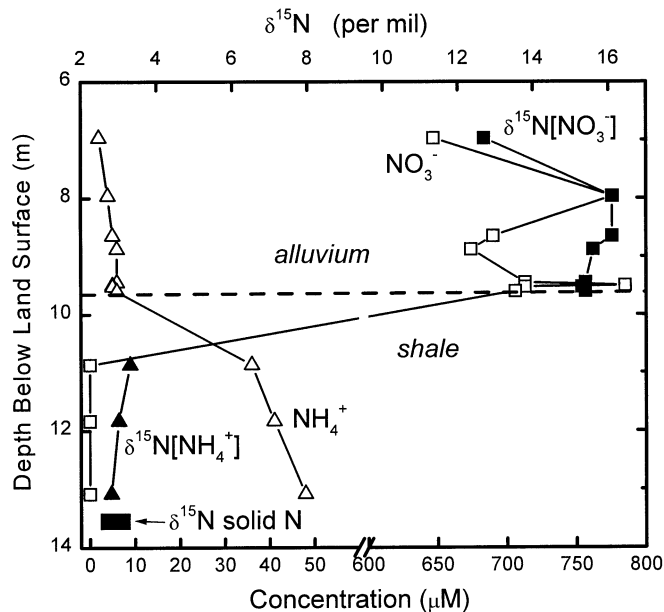

Fig. 4 Profiles of dissolved NO_3^- and NH_4^+, $\delta^{15}N[NO_3^-]$, and $\delta^{15}N[NH_4^+]$ in pore water of alluvial sediments and shale in Colorado, USA (modified from McMahon et al. 1999, with permission, courtesy of the American Geophysical Union)
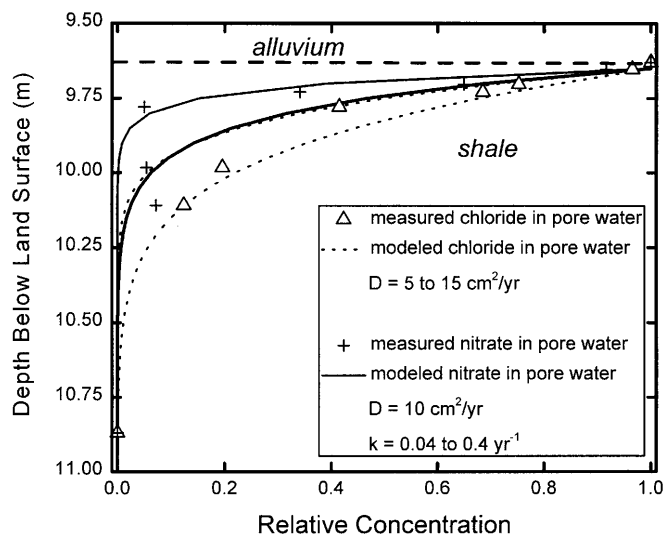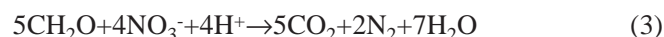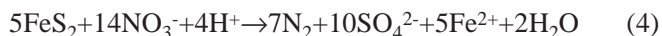

Fig. 5 Models of Cl$^-$ and NO_3^- diffusion in the Pierre Shale, Colorado, USA. The diffusion coefficient, D, was adjusted to obtain the best fit of the diffusion model to the measured Cl$^-$ concentrations in shale pore water. The first-order denitrification rate constant, k, was adjusted to obtain the best fit of the diffusion model to the measured NO_3^- concentrations in the shale pore water, with D=10 cm^2 year^{-1} (modified from McMahon et al. 1999, with permission, courtesy of the American Geophysical Union)

been proposed as electron donors for denitrification (Robertson et al. 1996). Reactions (3) and (4) are examples of denitrification using organic carbon and reduced sulfur, respectively, as electron donors:

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O \qquad (3)$$

$$5FeS_2+14NO_3^-+4H^+\rightarrow7N_2+10SO_4^{2-}+5Fe^{2+}+2H_2O \quad (4)$$

McMahon et al. (1999) conclude that denitrification in aquitards probably is not a significant sink for NO_3^- from overlying contaminated aquifers unless relatively rapid transport of NO_3^- into the aquitard occurs, or the residence time of water in the aquifer is long. However, aquitards may serve to protect underlying uncontaminated aquifers from overlying sources of nitrate (Simpkins and Parkin 1993; Robertson et al. 1996). Aquitards can act as permeable reactive barriers by denitrifying water as it moves through the aquitard to recharge the underlying aquifer. The function of aquitards as permeable reactive barriers could be maintained for extended periods of time if the supply of electron donors in the sediments were sufficient. Robertson et al. (1996) report that the boundary between oxidized and reducing conditions in aquitard sediments in Ontario advanced through the aquitard at a rate of 1 mm year^{-1} because of denitrification. Therefore, an aquitard that is several meters thick might provide protection from nitrate contamination for many years. Similarly, Cambardella et al. (1999) estimate that glacial till in Iowa, USA, has several hundred years of denitrification capacity on the basis of sediment thickness, organic carbon content, and local estimates of N-leaching inputs.

Fe^{3+} Reduction

The aqueous solubility of Fe^{3+} in most groundwater systems is very low (Stumm and Morgan 1981); therefore, Fe^{3+} in aquifers is primarily present in solid phases. Many of those solid phases contain microbially reducible Fe^{3+}, including amorphous ferric hydroxide grain coatings and some structural Fe^{3+} in clay minerals (Lovley and Phillips 1986; Kostka et al. 1999). In some microbes, the enzymes responsible for Fe^{3+} reduction are membrane bound (Lovley and Phillips 1988); thus, Fe^{3+}-reducing microbes must be in direct physical contact with the Fe^{3+}-bearing solid for reduction to take place. The requirement of direct contact between the microbe and Fe^{3+}-bearing solid could limit Fe^{3+} reduction if electron donors are not locally available or if the Fe^{3+} is not easily accessible to the microbe. That limitation can be overcome in several ways. Recent studies have determined that many humic substances are capable of shuttling electrons from the surfaces of Fe^{3+}-reducing microbes to Fe^{3+}-bearing solids, thereby alleviating the need for direct contact between the cell wall and Fe^{3+}-bearing solid (Lovley et al. 1996; Scott et al. 1998). Humic substances are relatively abundant in the pore water of some aquitards (Wassenaar et al. 1990); therefore, it is possible that reduced humic substances in aquitards could shuttle electrons to Fe^{3+}-bearing solids in aquifers. That scenario has not been documented in the field but warrants further study. Acetate and other low molecular weight organic acids, which are dissolved in the pore water of some aquitards (Fig. 1), also can be utilized by Fe^{3+}-reducing microbes (reaction 5):

$$CH_3COO^-+8Fe(OH)_3+15H^+\rightarrow2HCO_3^-+8Fe^{2+}+20H_2O \quad (5)$$
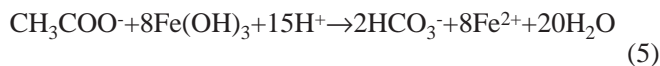
Iron(III)-reducing microbes in aquifers could directly couple the reduction of Fe^{3+} to the oxidation of low molecular weight organic-acids transported from aquitards to aquifers. Studies are needed to determined whether the rate of humic-substance/organic acid transport from aquitards to aquifers would be fast enough to account for observed rates of Fe^{3+} reduction in aquifers. Reported rates of Fe^{3+} reduction in some aquifers range from 10^{-6}–10^{-4} mmol L^{-1} year^{-1} (Chapelle et al. 1987; Murphy and Schramke 1998).

If Fe^{3+}-reducing microbes in aquifers do utilize humic substances or organic acids derived from aquitards, the reduction process might be focused in the mixing zone near the aquifer/aquitard interface. In that case, aquifer sediments in the mixing zone would be depleted in Fe^{3+}. Enhanced SO_4^{2-}-reducing activity occurs near the interface between some sandstones and shales in New Mexico, USA (Krumholz et al. 1997), but studies have yet to directly document enhanced Fe^{3+}-reducing activity near the interface. Reduction spots in red beds are characterized by an Fe^{3+}-depleted zone within an otherwise Fe^{3+}-enriched host rock and may be indirect evidence of enhanced Fe^{3+}-reducing activity near the contact between Fe^{3+}-enriched sandstone and solid organic matter (Mykura and Hampton 1984). Conversely, Hofmann (1991) suggests that the reduction spots are focused around microorganisms to which dissolved electron donors were transported, either by diffusion or advection.

Aquitards may be a source of iron in aquifers. Elevated concentrations of dissolved Fe^{2+}, the end product of Fe^{3+} reduction, have been reported in the pore water of several aquitards relative to the adjacent aquifer (Simpkins and Parkin 1993; Robertson et al. 1996; McMahon et al. 1999; Fig. 3). The Fe^{2+}-concentration gradient thus established would drive the diffusion of Fe^{2+} from the aquitard to the aquifer. Ferrous iron entering an aerobic aquifer from an adjacent aquitard would be oxidized to Fe^{3+} and precipitate from solution. Breit and Goldhaber (1987) describe hematite-enriched deposits in sandstones of the Morrison Formation, southwestern Colorado, as being produced by the oxidation of dissolved Fe^{2+} at the interface between oxidized and reduced zones in the formation. That scenario is analogous to the precipitation of Fe^{3+} in surface-water bodies receiving groundwater discharge enriched in dissolved Fe^{2+}. An abundance of ferric hydroxide grain coatings on aquifer sediments could affect the geochemistry of aerobic aquifers, because of the large capacity of ferric hydroxides to adsorb ions. In addition, focused precipitation of ferric hydroxides near the aquifer/aquitard interface could reduce aquifer permeability in that zone.

SO$_4^{2-}$ Reduction

Aquitards play an important role during SO_4^{2-} reduction in some unconsolidated aquifers by serving as a source
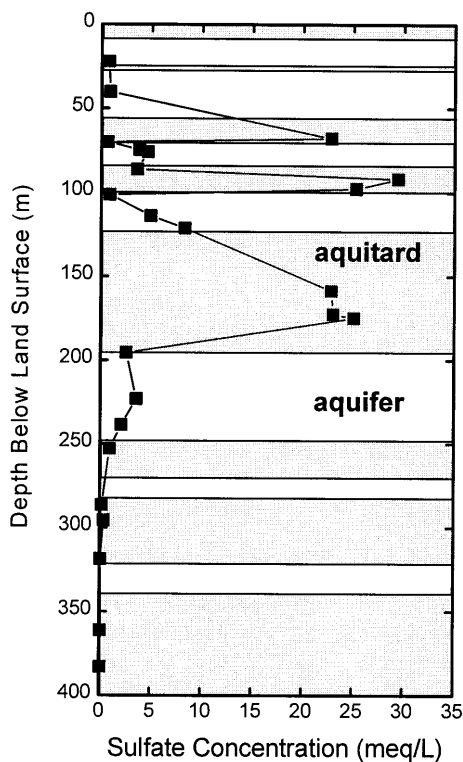
Fig. 6 Profile of dissolved SO_4^{2-} in pore water from aquifer and aquitard sediments in the Atlantic Coastal Plain, New Jersey, USA. Generally, sediments at depths less than about 200 m were reduced and deposited in a marine environment, whereas sediments below 200 m were oxidized and deposited in a mixed fluviodeltaic and marine environment (modified from Pucci and Owens 1989, with permission, courtesy of the National Ground Water Association, Copyright 1989)

Fig. 7a, b Production of reduced sulfur and acetate in incubations of sandstone and shale from New Mexico, USA. *Black bars* and *circles* represent sandstone incubations, *hatched bars* and *squares* represent sandstone and 0.15 g shale per tube, and the *white bars* and *diamonds* represent sandstone and 0.7 g shale per tube (modified from Krumholz et al. 1997, with permission, courtesy of *Nature*)

of SO_4^{2-} and electron donors. For example, Chapelle and McMahon (1991) conclude that SO_4^{2-} reduction was the primary CO_2-producing mechanism in the Black Creek aquifer in South Carolina (reaction 6):

$$SO_4^{2-}+CH_3COOH+2H^+\rightarrow H_2S+2CO_2+2H_2O \qquad (6)$$

This reaction occurs even though the apparent loss of SO_4^{2-} in the aquifer is inadequate to account for the observed CO_2 production. The Black Creek aquifer consists primarily of unconsolidated clastic sediments deposited in a marine environment. A study by Pucci and Owens (1989), and supporting data from Chapelle and McMahon (1991), indicate that concentrations of dissolved SO_4^{2-} in some aquitards of marine origin in the Atlantic Coastal Plain are as much as 30 times larger than the concentrations in adjacent aquifers. A profile is shown in Fig. 6. Chapelle and McMahon (1991) propose that SO_4^{2-} reduction in the Black Creek aquifer might be supported by SO_4^{2-} diffusing from the adjacent aquitards, and they determined that the rate of diffusion is sufficient to account for CO_2 production rates measured in the aquifer (about 10^{-5} mmol L^{-1} year^{-1}). A parallel study by McMahon and Chapelle (1991a, 1991b) concludes that organic acids diffusing from adjacent aquitards to the Black Creek aquifer could satisfy the elec-
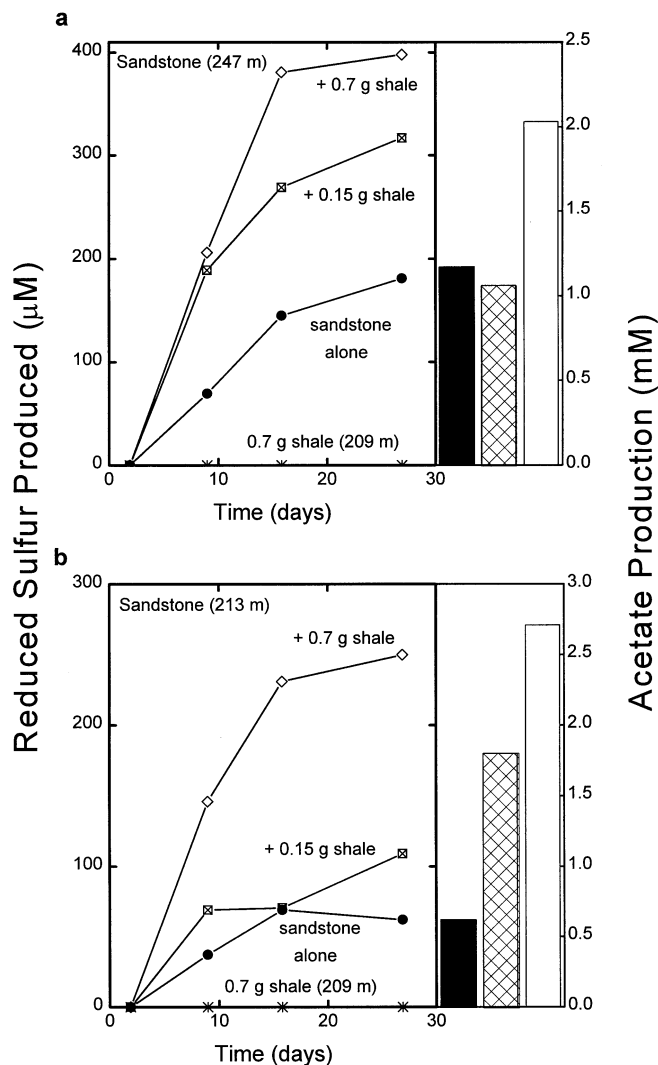
tron-donor requirements of SO_4^{2-}-reducing bacteria in the aquifer.

The study by Pucci and Owens (1989) indicates that dissolved SO_4^{2-} concentrations in aquitards of nonmarine origin in the Atlantic Coastal Plain are small. That is not the case for all aquitards of non-marine origin. Large concentrations of dissolved sulfate also have been reported in glacial till aquitards in Canada (Hendry et al. 1986; Keller et al. 1991).

Krumholz et al. (1997) report that aquifer/aquitard interactions also affected SO_4^{2-} reduction in consolidated sediments. They measured the production of reduced sulfur and acetate in laboratory incubations of Dakota Sandstone and Mancos Shale; results are shown in Fig. 7. No production of reduced sulfur occurred in incubations containing only shale, indicating a lack of SO_4^{2-}-reduc-
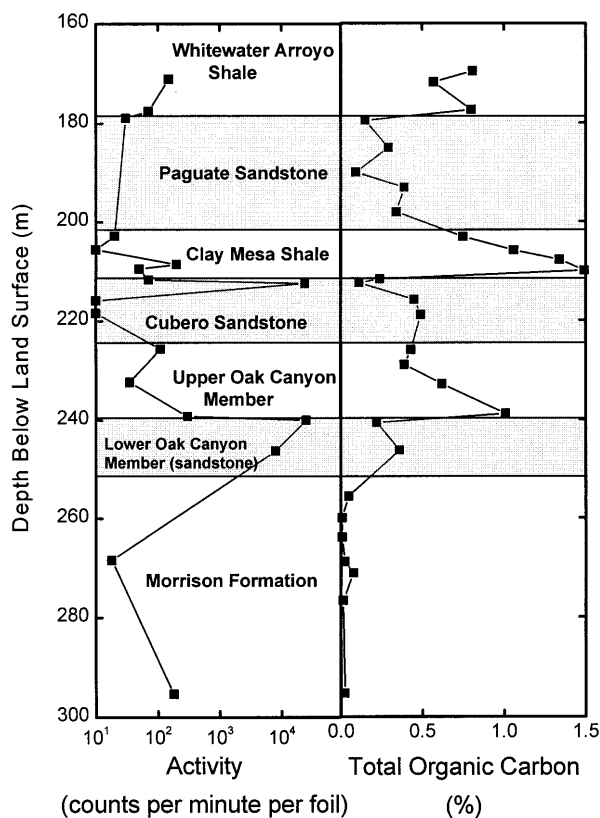
Fig. 8 Profiles of sulfate-reduction activity (*left*) and total organic carbon content (*right*) in Cretaceous sandstone and shale, New Mexico, USA (modified from Krumholz et al. 1997, with permission, courtesy of *Nature*)

ing activity in the shale. Production of reduced sulfur occurred in incubations of sandstone. The amount of reduced sulfur produced in the sandstone increased as the amount of shale mixed with the sandstone increased. The authors conclude that SO_4^{2-} reduction in the sandstone was electron-donor limited and that the shale supplied electron donors to SO_4^{2-}-reducing microbes in the sandstone. That conclusion is supported by increased acetate production in sediment incubations with increasing shale content (Fig. 7). As shown in Fig. 8, the study shows that SO_4^{2-}-reducing activity in the sandstone is largest near sandstone/shale interfaces, with the most microbial activity occurring in sandstone adjacent to the most organic-rich shale. Enhanced activity of SO_4^{2-}-reducing microbes near the interfaces implies that the concentrations of H_2S and CO_2, the products of SO_4^{2-} reduction, are increased near the interfaces. The increased concentrations of H_2S and CO_2 near the interfaces could cause sulfide and carbonate minerals to precipitate, thereby reducing aquifer porosity.

Petrographic study of sediments from the Black Creek aquifer indicated that sulfide- and carbonate-mineral precipitation is focused near aquifer/aquitard interfaces (McMahon et al. 1992). In some samples, authigenic pyrite was present as a mineral replacement, whereas in other samples pyrite cement completely obliterated pri-

mary porosity in the sand at the interface. Most of the authigenic carbonate was present as pore-filling cement. The carbonate cements were depleted in ^{13}C relative to unaltered shell material present in the aquifer, indicating that carbon derived from organic matter was incorporated in the cement. That finding is consistent with the conclusion that aquitard-derived organic acids are used as electron donors by SO_4^{2-}-reducing bacteria near the interfaces. Curtis (1978) also suggests that the carbon in carbonate cements in some sandstones are derived from adjacent aquitards. In contrast to porosity destruction by mineral precipitation, secondary porosity could be generated near the interface as organic acids diffuse into the aquifer. Organic acids can drive mineral dissolution (Surdam et al. 1989; Hiebert and Bennett 1992); however, in the Black Creek aquifer, secondary porosity accounts for only about 1.5% of the total porosity (McMahon et al. 1992).

CO_2 Reduction (Methanogenesis)

Two pathways exist for biogenic CH_4 production. They are the CO_2 reduction pathway (reaction 7) and the acetate fermentation pathway (reaction 8; Games et al. 1978):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{7}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{8}$$

Measurements of $\delta^{13}C[CH_4]$, $\delta^{13}C[CO_2]$, $\delta^2H[CH_4]$, $\delta^2H[H_2O]$ in groundwater can be used to determine which pathway is the predominant CH_4-producing mechanism in the subsurface (Whiticar et al. 1986; Sugimoto and Wada 1995). On the basis of those measurements, the CO_2 reduction pathway appears to be the dominant CH_4-producing mechanism in aquifer/aquitard systems representing various depositional settings, including Pleistocene glacial deposits in Canada; and Tertiary coal beds in Washington, Tertiary coastal-plain deposits in Texas, and Upper Devonian shale in the Michigan Basin, all in the USA (Grossman et al. 1989; Aravena and Wassenaar 1993; Johnson et al. 1993; Martini et al. 1996).

Significant biogenic CH_4 production can occur in aquitards. Martini et al. (1996) report that CH_4 production via the CO_2 reduction pathway resulted in economic accumulations of CH_4 at depths less than 600 m in the Antrim Shale of the Michigan Basin. Simpkins and Parkin (1993) report CH_4 concentrations larger than 2,500 µM in glacial till in Iowa (Fig. 3). Those large CH_4 concentrations indicate that aquitards could be a significant source of biogenic CH_4 to adjacent aquifers. Based on measured hydraulic gradients and CH_4 concentrations, Parkin and Simpkins (1995) calculated a downward advective flux of 0.21 mol CH_4 m^{-2} year^{-1} moving from Pleistocene till and loess to underlying Mississippian bedrock aquifers. That calculation is consistent with the presence in the Mississippian aquifer of CH_4 that was generated from Pleistocene-age organic carbon

(Simpkins and Parkin 1993). Methane entering aquifers from adjacent aquitards could affect the chemistry of groundwater in the aquifer, particularly if methane-oxidizing microbes were active in the aquifer. Methane oxidation at the interface separating a strong CH_4 source from an aquifer could be a significant source of CO_2 to drive geochemical reactions in the aquifer. Little is known about the fate of aquitard-derived CH_4 in shallow aquifers, and this should be a topic for future studies.

Aquitards also could be a source of electron donors for methanogenesis in aquifers. Aravena and Wassenaar (1993) used ^{14}C and $\delta^{13}C$ measurements on CH_4 and dissolved organic carbon to show that organic-rich Pleistocene sediments are the source of C for CH_4 in a Pleistocene-age aquifer in Canada. They also concluded that the CO_2 reduction pathway was the predominant CH_4-producing mechanism. Aravena and Wassenaar (1993) are not specific about the location in the aquifer system of the solid organic carbon used by the methanogens, but two possibilities exist. One is organic matter incorporated in the aquifer sediments during deposition, and the other is the glaciolacustrine clay that confines the aquifer from above. Regardless of the carbon source, the methanogens would be dependent on other microbial populations to degrade the complex solid organic matter into simpler compounds (e.g., H_2 and CO_2) for subsequent use in CH_4 production.

Conclusions

Studies indicate that important biogeochemical reactions occur near the interface between aquifer and aquitard sediments, including O_2 reduction; denitrification; and Fe^{3+}, SO_4^{2-}, and CO_2 (methanogenesis) reduction. In some settings, biogeochemical reactions occur on the aquitard side of the interface as electron acceptors move from the aquifer into the electron-donor-enriched aquitard. In other settings, biogeochemical reactions occur on the aquifer side of the interface as electron donors, and sometimes electron acceptors, move from the aquitard into the electron-acceptor-enriched, or microorganism-enriched, aquifer. The extent to which biogeochemical reactions take place in the mixing zone near aquifer/aquitard interfaces depends on several factors, including the abundance and solubility of electron acceptors and donors on either side of the interface and the rate at which electron acceptors and donors react and move across the interface. Although several detailed studies of biogeochemical reactions at the aquifer/aquitard interface have been conducted, more work is needed, particularly in the areas of organic-acid and H_2 generation from solid organic carbon in aquitards, biogeochemical reaction rates in aquitard sediments, and mechanisms and rates of electron-donor and electron–acceptor transport across the interface.

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