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# Comparison of $E_h$ and $H_2$ Measurements for Delineating Redox Processes in a Contaminated Aquifer

FRANCIS H. CHAPELLE,<sup>\*,†</sup>  
SHERIDAN K. HAACK,<sup>‡</sup>  
PETER ADRIAENS,<sup>§</sup>  
MARK A. HENRY,<sup>||</sup> AND  
PAUL M. BRADLEY<sup>†</sup>

U.S. Geological Survey, 720 Gracern Road, Suite 129,  
Columbia, South Carolina 29210-7651, U.S. Geological Survey,  
6520 Mercantile Way, Suite 5, Lansing, Michigan 48911,  
Department of Civil & Environmental Engineering,  
University of Michigan, 181 EWRE Building,  
Ann Arbor, Michigan 48109-2125, and National Center for  
Integrated Bioremediation Research,  
4140 East California Street, Oscoda, Michigan 48750

Measurements of oxidation–reduction potential ( $E_h$ ) and concentrations of dissolved hydrogen ( $H_2$ ) were made in a shallow groundwater system contaminated with solvents and jet fuel to delineate the zonation of redox processes.  $E_h$  measurements ranged from +69 to –158 mV in a cross section of the contaminated plume and accurately delineated oxic from anoxic groundwater. Plotting measured  $E_h$  and pH values on an equilibrium stability diagram indicated that Fe(III) reduction was the predominant redox process in the anoxic zone and did not indicate the presence of methanogenesis and sulfate reduction. In contrast, measurements of  $H_2$  concentrations indicated that methanogenesis predominated in heavily contaminated sediments near the water table surface ( $H_2 \sim 7.0$  nM) and that the methanogenic zone was surrounded by distinct sulfate-reducing ( $H_2 \sim 1$ –4 nM) and Fe(III)-reducing ( $H_2 \sim 0.1$ –0.8 nM) zones. The presence of methanogenesis, sulfate reduction, and Fe(III) reduction was confirmed by the distribution of dissolved oxygen, sulfate, Fe(II), and methane in groundwater. These results show that  $H_2$  concentrations were more useful for identifying anoxic redox processes than  $E_h$  measurements in this groundwater system. However,  $H_2$ -based redox zone delineations are more reliable when  $H_2$  concentrations are interpreted in the context of electron-acceptor (oxygen, nitrate, sulfate) availability and the presence of final products [Fe(II), sulfide, methane] of microbial metabolism.

## Introduction

Understanding the distribution of oxidation–reduction processes is fundamental to predicting the fate and

transport of chemical contaminants in groundwater systems. Microbially mediated redox reactions affect the rate and extent of biodegradation processes, which in turn affect the mobility of organic contaminants. In addition, redox processes affect the speciation and solubility of metals. In spite of this importance, methods for evaluating redox processes in groundwater systems are problematic. Platinum electrode measurements of oxidation–reduction potential ( $E_h$ ) are commonly used to evaluate redox conditions in contaminated and uncontaminated aquifers (1–3).  $E_h$  measurements are widely used in spite of the fact that unique redox potentials in natural waters do not exist (4), that electrode-measured  $E_h$  values do not agree with  $E_h$  values calculated from measured concentrations of redox couples (5), that groundwater is seldom, if ever, in a state of full redox equilibrium (6), and that platinum electrodes are subject to a variety of interferences (7). Despite the widely documented problems associated with this technique,  $E_h$  measurements continue to be used, largely because they are easy to make in the field.

The use of dissolved hydrogen ( $H_2$ ) concentrations as an indicator of microbially mediated redox processes (8–10) has provided an alternative method for evaluating redox processes in groundwater systems. Fermentative microorganisms continuously produce  $H_2$  during anoxic decomposition of organic matter. This  $H_2$  is then consumed by respiratory microorganisms that may use Fe(III), sulfate, or  $CO_2$  as terminal electron acceptors. In microbial ecology, this process is referred to as interspecies hydrogen transfer. Significantly, Fe(III)-, sulfate-, and  $CO_2$ -reducing (methanogenic) microorganisms exhibit different efficiencies in utilizing  $H_2$ . Fe(III) reducers are relatively efficient in utilizing  $H_2$ , and thus they maintain lower steady-state  $H_2$  concentrations (0.2–0.8 nM  $H_2$ ) than either sulfate reducers (1–4 nM  $H_2$ ) or methanogens (5–15 nM  $H_2$ ). Because each terminal electron-accepting process has a characteristic  $H_2$  concentration associated with it,  $H_2$  concentrations can be an indicator of predominant redox processes in groundwater systems.

Platinum electrode  $E_h$  measurements are based on the concept of thermodynamic equilibrium and, within the constraints of that assumption, can be used to evaluate redox processes in groundwater systems. The  $H_2$  method is based on the ecological concept of interspecies hydrogen transfer by microorganisms and, within the constraints of that assumption, can also be used to evaluate redox processes. These methods, therefore, are fundamentally different. However, because concurrent  $E_h$  and  $H_2$  measurements have not previously been made in groundwater systems, it has not been possible to directly compare the advantages and disadvantages of each approach. The purpose of this study is to compare platinum electrode-measured  $E_h$  values and  $H_2$  concentrations as indicators of redox processes in a contaminated aquifer.

\* Corresponding author telephone (803) 750-6116; fax: (803) 750-6181; e-mail: Chapelle@dscmb.er.usgs.gov.

<sup>†</sup> U.S. Geological Survey, Columbia, SC.

<sup>‡</sup> U.S. Geological Survey, Lansing, MI.

<sup>§</sup> University of Michigan.

<sup>||</sup> National Center for Integrated Bioremediation Research.

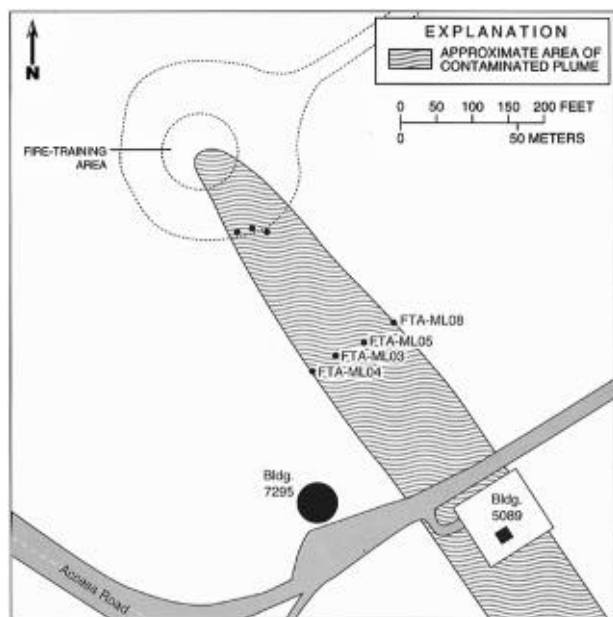


FIGURE 1. Map showing the approximate orientation of the contaminated plume and the location of multilevel wells used to sample groundwater.

## Study Site

The study site is a shallow water table aquifer located on Wurtsmith Air Force Base in Michigan. Historically, a fire-training area known as FT-2 was used to train Air Force personnel in fire-fighting procedures, and a variety of petroleum products and solvents were applied to land surface to start fires. Over the 24-year operational life of FT-2 (1952–1986), organic contaminants seeped to the underlying groundwater system, resulting in the accumulation of contaminants at the water table surface and the production of an extensive plume of contaminated groundwater (Figure 1). Concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX) range from about 1000 to 20  $\mu\text{g/L}$  in the contaminated plume (11). Somewhat lower concentrations (2–100  $\mu\text{g/L}$ ) of dichloroethylene, chloroethane, and vinyl chloride are also present in the contaminated plume (11). The aquifer at this site is comprised of alternating eolian sands and glacial outwash material that is highly permeable and exhibits hydraulic conductivities on the order of 30 m/day. The water table is encountered between 5 and 8 m below land surface.

In order to document the vertical distribution of contaminants in this plume, the National Center for Integrated Bioremediation Research and Development (NCIBRD) installed a series of multilevel sampling wells at this site. The wells were constructed from 2.5 cm i.d. diameter PVC casing with 0.33-m PVC screens. The vertical spacing between the screens varied from 0.5 to 2 m. The multilevel wells were oriented in a line perpendicular to the direction of groundwater flow (Figure 1) and were used to collect groundwater chemistry data for this study.

## Methods

Each 2.5-cm well was pumped with a peristaltic pump at a rate of about 600 mL/min. Groundwater produced from the well was circulated through a closed cell and continuously monitored for  $E_h$ , pH, dissolved oxygen, and specific conductance (QED Environmental Systems, Inc.). When readings for each of these four parameters had stabilized

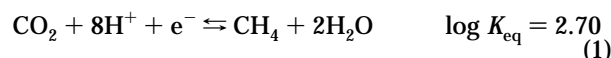
(usually about 15 min), the water was sampled for dissolved  $\text{H}_2$  concentrations using a gas-stripping procedure (10). In this method, a standard 250-mL gas-sampling bulb (Supelco) was continuously purged with groundwater at a rate between 500 and 1000 mL/min. A 20-mL bubble of  $\text{N}_2$  gas was introduced into the gas-sampling bulb through the septum. As the bubble was vigorously agitated by the stream of inflowing water, slightly soluble gases such as  $\text{H}_2$  transferred from the water to the gas phase. As water purged the bulb,  $\text{H}_2$  concentrations in the gas bubble came into equilibrium with the water flowing through the bulb. Previous experience has shown that it takes about 15 min for  $\text{H}_2$  concentrations to stabilize. After 15 min of agitation, a 5-mL aliquot of gas was withdrawn from the bulb into a glass syringe. Another aliquot was withdrawn 5 min later to verify that  $\text{H}_2$  concentrations had stabilized. These gas samples were then analyzed in the field by gas chromatography with reduction gas detection (Trace Analytical, Inc.), and concentrations of  $\text{H}_2$  in the aqueous phase were calculated using the Henry's law partition coefficient. At 1 atm pressure and 10 °C, 1.0  $\mu\text{L/L}$  of hydrogen in the gas phase coexists with 0.8 nmol/L (nM) of  $\text{H}_2$  in the aqueous phase. The detection limit of this method is approximately 0.02 nM.

Concentrations of dissolved oxygen measured by oxygen meter were supplemented by colorimetric analysis (Chemetrics, Inc.). Concentrations of dissolved Fe(II) were determined in the field using ferrozine colorimetric analysis (Chemetrics, Inc.). Concentrations of dissolved methane and carbon dioxide were measured by withdrawing 10 mL of water from the gas-sampling bulb through a syringe and injecting the water through a septa into a sealed 40-mL VOC vial. In the laboratory, methane concentrations in the headspace gas were quantified by gas chromatography with thermal conductivity detection. Aqueous concentrations were determined using Henry's law partition coefficients and reported as milligrams per liter of water. Concentrations of dissolved sulfate, nitrate, and nitrite were measured in the laboratory using ion chromatography with conductivity detection (Dionex).

## Results and Discussion

The distribution of  $E_h$  values measured in a cross section of the plume is shown in Figure 2A. These measurements indicate a core of reducing water ( $E_h$  values < 0 mV) inside the plume surrounded by relatively oxidized groundwater ( $E_h$  values > 0 mV). The reducing groundwater is contaminated by petroleum hydrocarbons (BTEX concentrations on the order of 100–1000  $\mu\text{g/L}$ ) with lesser concentrations (~10  $\mu\text{g/L}$ ) of chlorinated ethenes and ethanes (11). In contrast, the oxidized water lacks measurable contamination (11). The lowest  $E_h$  measurements (–158 mV) were found in the center of the contaminated plume.

One commonly used method for interpreting  $E_h$  measurements is to plot measured values of  $E_h$  and pH on equilibrium stability diagrams constructed for particular redox processes under specified conditions (7). For example, the reduction of carbon dioxide to methane can be described by



From the definitions of pH and  $E_h$ , assuming the ambient temperature of groundwater (10 °C) it follows that

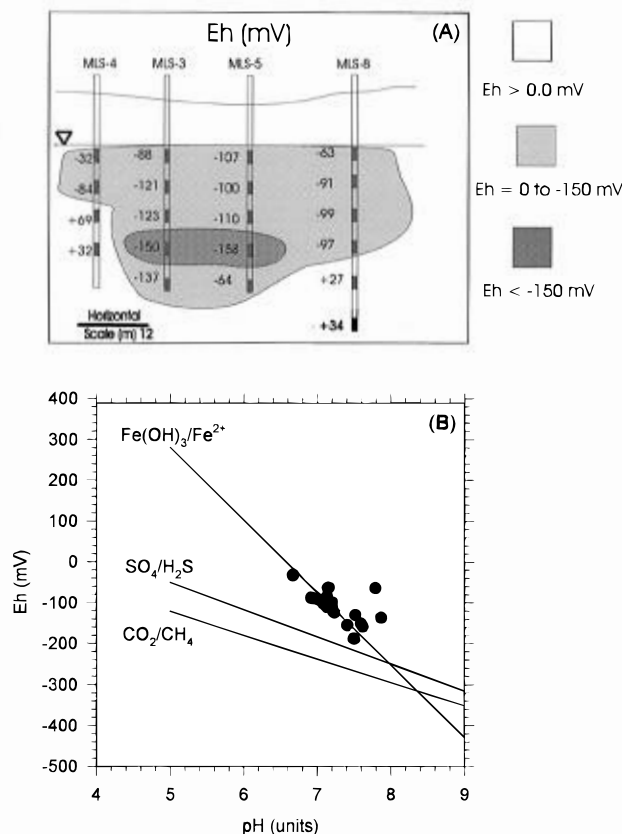


FIGURE 2. (A) Cross section showing the distribution of measured  $E_h$  values, and (B)  $E_h$ -pH diagram showing equilibria for the  $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}/\text{HS}^-$ , and  $\text{CO}_2/\text{CH}_4$  redox couples. (See Table 1 for assumptions used in diagram construction.)

$$E_h = 0.056 \left( 2.70 + \frac{1}{8} \log \frac{[\text{C(IV)}]}{[\text{CH}_4]} + \frac{1}{8} \alpha_o - \text{pH} \right) \quad (2)$$

where C(IV) represents dissolved inorganic carbon of valence IV, and where  $\alpha_o$  describes the pH-dependent speciation of carbon dioxide and bicarbonate (12).

Similar equations can be written for sulfate reduction:

$$E_h = 0.056 \left( 4.25 + \frac{1}{8} \log \frac{[\alpha_{2,\text{S(IV)}}\text{S(VI)}_T]}{[\alpha_{1,\text{S(-II)}}]_T\text{S(-II)}_T} - \frac{9}{8} \text{pH} \right) \quad (3)$$

where  $\text{S(VI)}_T$  and  $\text{S(-II)}_T$  represent total sulfur of valence VI and -II;  $\alpha_{2,\text{S(IV)}}$  and  $\alpha_{1,\text{S(-II)}}$  are pH-dependent dissociation constants (12). The reduction of amorphous ferric hydroxide can be treated similarly:

$$E_h = 0.056(16 - \log [\text{Fe}^{2+}] - 3 \text{pH}) \quad (4)$$

But because the pH-dependent speciation of dissolved iron is complex (12), eq 4 should be regarded as an approximation only. By assuming concentrations of dissolved inorganic carbon, methane, sulfate, sulfide, and ferrous iron appropriate to this site (Table 1), these equations can be plotted in  $E_h$ -pH space (Figure 2B).

To evaluate which redox processes are indicated by the field platinum electrode  $E_h$  measurements, measured  $E_h$  and pH values from anoxic groundwater were plotted on this  $E_h$ -pH diagram (Figure 2B). Most of the measured  $E_h$  and pH values plot along the line derived from the  $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$  redox couple, suggesting that Fe(III) reduction with amorphous ferric hydroxide as the principal reactant is the predominant redox process in the anoxic plume. Note

TABLE 1

Equilibrium Constants and Concentration Assumptions Used To Construct Equilibrium Stability Diagram Shown in Figure 2B

redox couple	$\log K_{eq}$	concentration assumptions
$\text{CH}_4/\text{CO}_2$	+2.70 <sup>a</sup>	$\text{CH}_4 = 6.25 \times 10^{-4} \text{ M}$ (10 mg/L); $\text{C(IV)} = 1 \times 10^{-3} \text{ M}$ (45 mg/L)
$\text{HS}^-/\text{SO}_4^{2-}$	+4.25 <sup>a</sup>	$\text{S(-II)} = 5.56 \times 10^{-6} \text{ M}$ (0.2 mg/L); $\text{S(VI)} = 5.2 \times 10^{-5} \text{ M}$ (5 mg/L)
$\text{Fe}^{2+}/\text{Fe}(\text{OH})_3(\text{amorph})$	+16.0 <sup>b</sup>	unit concn of solid phase is assumed, and concns of $\text{Fe}^{2+} = 1.79 \times 10^{-4} \text{ M}$ (10 mg/L)

<sup>a</sup> From Pankow (12). <sup>b</sup> From Stumm and Morgan (6).

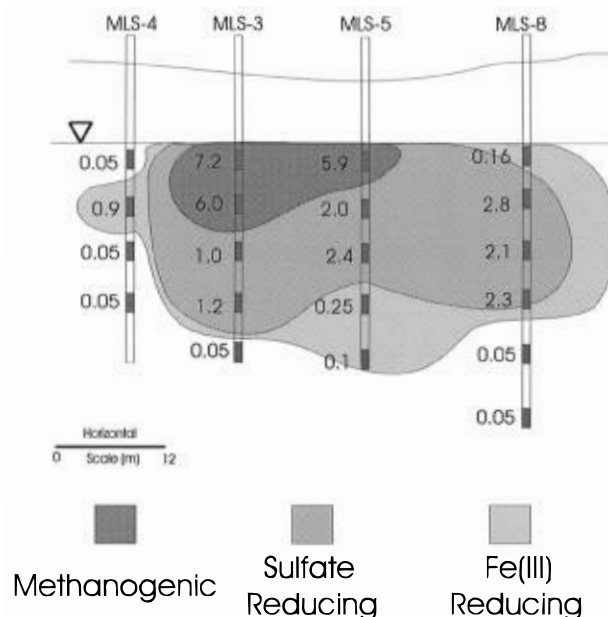


FIGURE 3. Cross section showing the distribution of hydrogen ( $\text{H}_2$ ) concentrations and the zonation of redox processes [ $>5.0 \text{ nM}$ , methanogenic; 1–4 nM, sulfate reducing; 0.2–0.8, Fe(III) reducing] implied by these concentrations.

that none of the measured  $E_h$  values are sufficiently negative to fall in the range characteristic of sulfate reduction and methanogenesis (Figure 2B).

A much different picture of ongoing redox processes at this site is indicated by measured concentrations of dissolved  $\text{H}_2$ . The highest  $\text{H}_2$  concentrations (7.2–5.9 nM) were found in the center of the contamination plume, the water table surface (Figure 3), and are in the range characteristic of methanogenesis (13). Surrounding this apparent methanogenic zone was a zone where  $\text{H}_2$  concentrations were in the 1–4 nM range characteristic of sulfate reduction. Surrounding the apparent sulfate-reducing zone was a zone where hydrogen concentrations were in the 0.1–0.8 nM range characteristic of Fe(III) reduction. Finally, this apparent Fe(III)-reducing zone was surrounded by low hydrogen concentrations ( $\sim 0.05 \text{ nM}$ ), characteristic of nitrate-reducing or oxic environments.

Concentrations of the potential electron acceptors, oxygen and sulfate (Figure 4), and final products, methane and Fe(II) (Figure 5), as well as nitrate and nitrite (Figure 6) can also indicate redox processes in contaminated aquifers (14, 15), and can be compared to the  $E_h$ - and  $\text{H}_2$ -derived redox zonations. At the FT-2 site, the redox zonation indicated by concentrations of these redox-

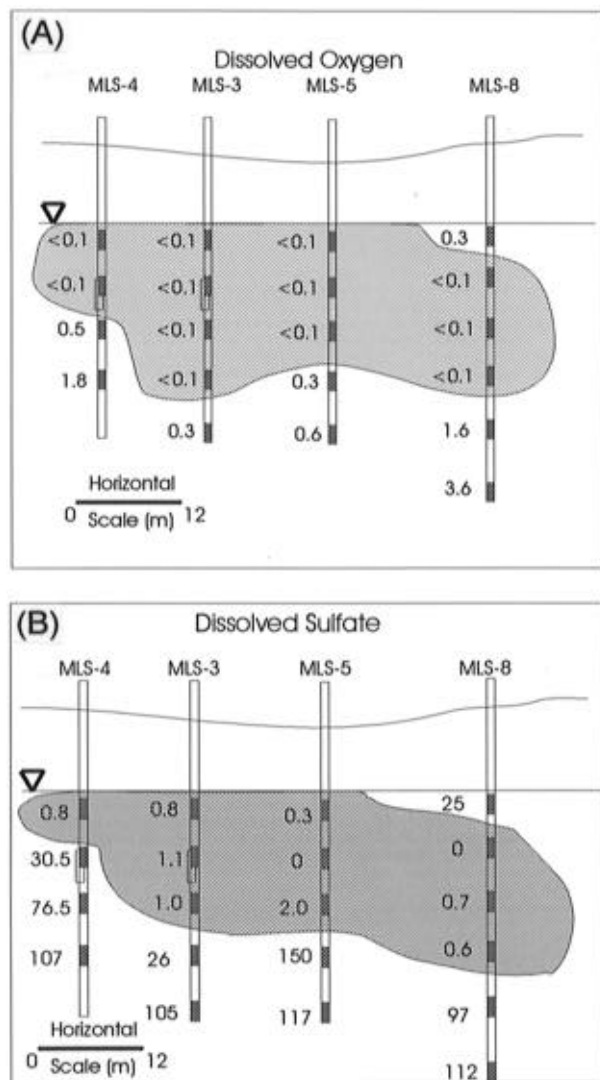


FIGURE 4. Cross sections showing (A) the distribution of measured dissolved oxygen concentrations and (B) the distribution of sulfate concentrations.

sensitive solutes is largely consistent with the  $H_2$ -derived redox zonation. Concentrations of methane are relatively high (up to 15 mg/L) and clearly indicate the presence of active methanogenesis in the contaminated plume. In addition, methane concentrations are higher near the water table surface and decrease with depth in the system as would be predicted from the  $H_2$ -derived redox zonation. Sulfate concentrations were depleted in the anoxic plume relative to surrounding groundwater (Figure 4), which clearly indicates the presence of sulfate reduction. The presence of  $H_2S$  in groundwater and in soil gas overlying the contaminated plume (16) also indicates the presence of sulfate reduction. The presence of dissolved  $Fe^{2+}$  in the contaminated plume indicates that active Fe(III) reduction is occurring as well. Finally, the anoxic plume was surrounded by oxygenated groundwater (Figure 4A) that also contained significant (1–10 mg/L) concentrations of nitrate (Figure 6A). The lack of nitrate in anoxic water and the presence of nitrite (0.2–1.0 mg/L) at the oxic/anoxic boundary (Figure 6B) indicate that nitrate reduction also occurs at this site.

The measurement and interpretation of  $E_h$  and  $H_2$  concentrations in this system provided substantially different views of ongoing redox processes. The  $E_h$  measure-

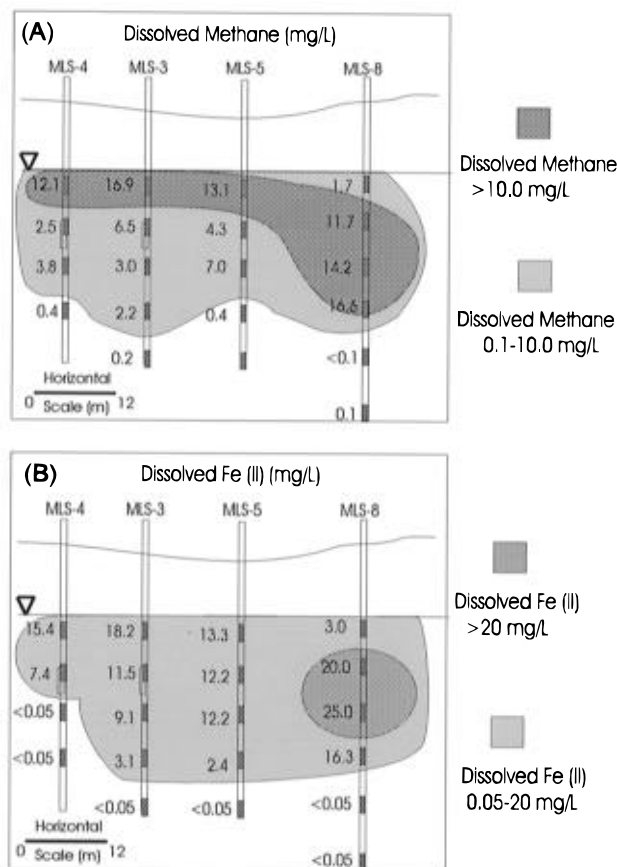


FIGURE 5. Cross sections showing (A) concentrations of dissolved methane and (B) dissolved Fe(II).

ments indicated a zone of oxic water surrounding an anoxic zone apparently dominated by Fe(III) reduction (Figure 2). In contrast, the  $H_2$  measurements indicated the presence of a methanogenic zone near the water table surface, surrounded by discrete sulfate-reducing and Fe(III)-reducing zones (Figure 3). Measured concentrations of methane and sulfate are in substantial agreement with the  $H_2$ -based redox zonation. This, in turn, shows that  $H_2$  concentrations gave a more accurate delineation of redox processes in this hydrologic system than did the  $E_h$  measurements.

The observation that  $E_h$  measurements have difficulty identifying specific redox processes has been noted previously and may reflect the poor electroactivity of some redox species such as  $CO_2$  and  $CH_4$  (6). In contrast,  $Fe^{3+}$  and  $Fe^{2+}$  are highly electroactive on platinum electrodes, which probably explains why electrode-measured  $E_h$  values in this system plot so closely to values predicted by the  $Fe(OH)_3/Fe^{2+}$  redox couple (Figure 2B). This, in turn, may explain why the  $E_h$  measurements overestimate the size of the Fe(III)-reducing zone in this aquifer.

While  $H_2$  concentrations are a better indicator of redox zonation than  $E_h$  measurements at this site, it is important to note that  $H_2$  concentrations have potential drawbacks as well. It was found, for example, that  $H_2$ -based redox zonation was not consistent with all aspects of the observed water chemistry. Specifically,  $H_2$  measurements (Figure 3) indicated the predominance of sulfate reduction in several screened intervals that lacked significant (<1 mg/L) sulfate concentrations (Figure 4). While it is possible that low rates of sulfate reduction, requiring relatively low sulfate concentrations, predominate in those zones, other interpretations are possible. A pumping well may draw water from

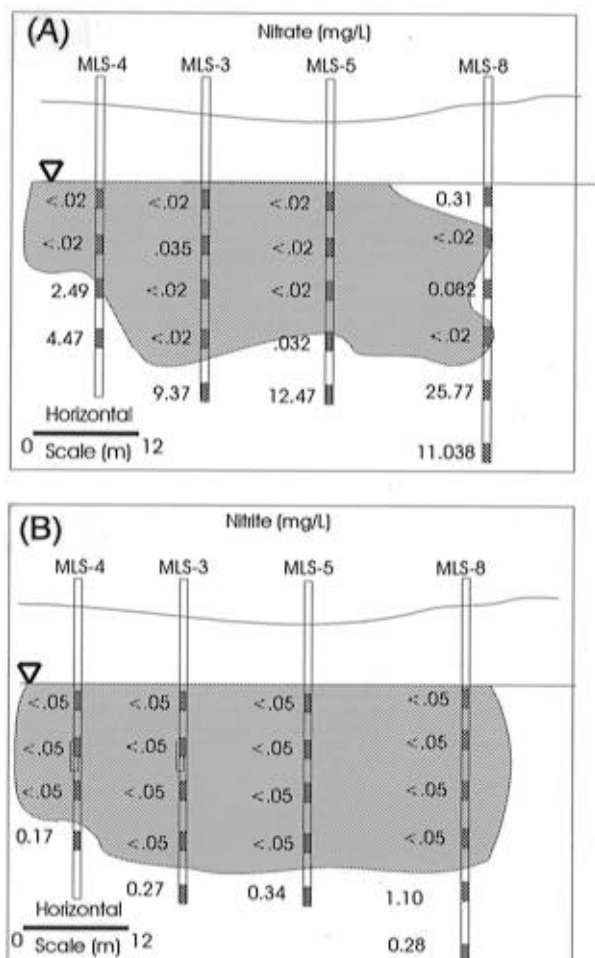


FIGURE 6. Cross sections showing (A) concentrations of dissolved nitrate and (B) dissolved nitrite.

small-scale zones dominated by different redox processes. If a well draws equal volumes of water from closely spaced Fe(III)-reducing ( $H_2 \sim 0.2$  nM) and methanogenic ( $H_2 \sim 7$  nM) zones, the resulting  $H_2$  measurement (3.6 nM) could inaccurately indicate the predominance of sulfate reduction. Such interzonal mixing may complicate the interpretation of  $H_2$  measurements in systems characterized by small-scale redox zone changes and may incorrectly indicate the predominance of sulfate reduction (Figure 3) in parts of the contaminated plume at this site.

Because of these complexities, using  $H_2$  measurements as a sole indicator of redox processes is not appropriate. A more reliable procedure is to interpret  $H_2$  concentrations in the context of electron-acceptor availability and the presence of final products of microbial metabolism. When electron-acceptor availability [dissolved oxygen, nitrate, Fe(III), and sulfate],  $H_2$  concentrations, and the presence of final products ( $Fe^{2+}$ , sulfide, methane) all indicate a similar

redox zonation, proportionally more confidence in the delineation is warranted (10). Conversely, the nonconcurrency of these indicators may highlight specific uncertainties, such as interzonal mixing by pumping wells, that may be encountered in heterogeneous groundwater systems.

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