ground water

Methods Note/

Distinguishing Iron-Reducing from Sulfate-Reducing Conditions

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Abstract

Ground water systems dominated by iron- or sulfate-reducing conditions may be distinguished by observing concentrations of dissolved iron (Fe^{2+}) and sulfide (sum of H_2S, HS^-, and $S^=$ species and denoted here as "H_2S"). This approach is based on the observation that concentrations of Fe^{2+} and H_2S in ground water systems tend to be inversely related according to a hyperbolic function. That is, when Fe^{2+} concentrations are high, H_2S concentrations tend to be low and vice versa. This relation partly reflects the rapid reaction kinetics of Fe^{2+} with H_2S to produce relatively insoluble ferrous sulfides (FeS). This relation also reflects competition for organic substrates between the iron- and the sulfate-reducing microorganisms that catalyze the production of Fe^{2+} and H_2S. These solubility and microbial constraints operate in tandem, resulting in the observed hyperbolic relation between Fe^{2+} and H_2S concentrations. Concentrations of redox indicators, including dissolved hydrogen (H_2) measured in a shallow aquifer in Hanahan, South Carolina, suggest that if the Fe^{2+}/H_2S mass ratio (units of mg/L) exceeded 10, the screened interval being tapped was consistently iron reducing (H_2 ~0.2 to 0.8 nM). Conversely, if the Fe^{2+}/H_2S ratio was less than 0.30, consistent sulfate-reducing (H_2 ~1 to 5 nM) conditions were observed over time. Concomitantly high Fe^{2+} and H_2S concentrations were associated with H_2 concentrations that varied between 0.2 and 5.0 nM over time, suggesting mixing of water from adjacent iron- and sulfate-reducing zones or concomitant iron and sulfate reduction under nonelectron donor–limited conditions. These observations suggest that Fe^{2+}/H_2S mass ratios may provide useful information concerning the occurrence and distribution of iron and sulfate reduction in ground water systems.

Introduction

Reduction/oxidation (redox) processes affect the chemical quality of ground water in all aquifer systems (Lovley et al. 1991; Smedley and Kinniburgh 2002; Barbash and Reinhard 1989; Korom 1992; Bradley 2000, 2003; Mazur and Jones 2001; Barbash 2007; Back and Barnes 1965; Baedecker and Back 1979; Chapelle and Lovley 1992). Identifying redox processes that occur in an aquifer system, documenting their spatial distribution, and understanding how they affect concentrations of natural or anthropogenic contaminants are central to assessing and describing the chemical quality of ground water (Baedecker and Back 1979; Champ et al. 1979; Thorstenson et al. 1979; Plummer et al. 1990; Vroblesky and Chapelle 1994; Hunter et al. 1998; Christensen et al. 2000).

Methodologies for identifying redox processes (Berner 1981; Lovley et al. 1994) typically document the consumption of electron acceptors (i.e., oxygen, nitrate, sulfate), concentrations of unstable intermediate product concentrations (i.e., dissolved molecular hydrogen [H_2]), and the production of final products (i.e., Fe^{2+}, H_2S, methane) along aquifer flowpaths (Chapelle et al. 1995). However, information about individual flowpaths is not always available for routine water quality investigations.

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A framework for identifying redox processes in the absence of precise flowpath information based solely on observed concentrations of electron acceptors and final products of microbial metabolism has recently been proposed (McMahon and Chapelle 2008). Because the data sets used in that study did not include concentrations of dissolved H_2S, the characteristic final product of sulfate reduction, it was not possible to distinguish iron-reducing from sulfate-reducing conditions. The purpose of this note was to extend the methodology of McMahon and Chapelle (2008) by suggesting an approach for distinguishing iron- and sulfate-reducing conditions based on measured concentrations of dissolved Fe^{2+} and H_2S.

Methods

Ground water chemistry data were collected from two sites, a chlorinated ethene-contaminated site located in Pensacola, Florida (Bradley et al. 2007), and a petroleum hydrocarbon site located in Hanahan, South Carolina (Petkewich et al. 1997). Prior to the collection of water samples, each monitoring well was pumped at a rate of approximately 0.5 L/min and the temperature, pH, and specific conductance monitored continuously until stable values were obtained. Concentrations of dissolved oxygen were made in the field using colorimetric methods (Chemetrics Inc., Calverton, Virginia). The detection limit for this method is 0.05 mg/L dissolved oxygen, and the variability of replicate analyses is typically less than $\pm 10\%$. Concentrations of Fe^{2+} (Stookey 1970) and H_2S (U.S. EPA method 376.2) were measured in the field using colorimetric methods with spectrophotometric detection (Hach Inc., Loveland, Colorado). The detection limit for these methods is 0.01 mg/L dissolved Fe^{2+} or H_2S, and the variability of replicate samples is typically less than $\pm 10\%$. The assay for dissolved sulfide does not distinguish between the sulfide species H_2S, HS^-, or $S^=$.

Concentrations of dissolved hydrogen (H_2) are an indicator of predominant redox processes under electron donor–limited conditions (Lovley et al. 1994), particularly when supplemented with other redox indicator data (Chapelle et al. 1995). Redox data, including concentrations of H_2 from the Hanahan site, were measured and redox diagnoses made according to methods described by Chapelle et al. (1995).

Hyperbolic Relation between Fe^{2+} and H_2S Concentrations

Ground water chemistry studies conducted on either regional or local scales often show a hyperbolic relation between concentrations of Fe^{2+} and H_2S. This is illustrated in Figure 1A, which shows concentrations of Fe^{2+} plotted vs. H_2S for the Madison Aquifer, a regional confined system located in Montana, Wyoming, and South Dakota (data from Plummer et al. [1990]), and a small-scale water table aquifer located at Naval Air Station, Pensacola, Florida (Figure 1B, a site that has been previously described by Bradley et al. [2007]). Only wells located outside the sulfuric acid plume described by Bradley et al. (2007) were used in the present study.

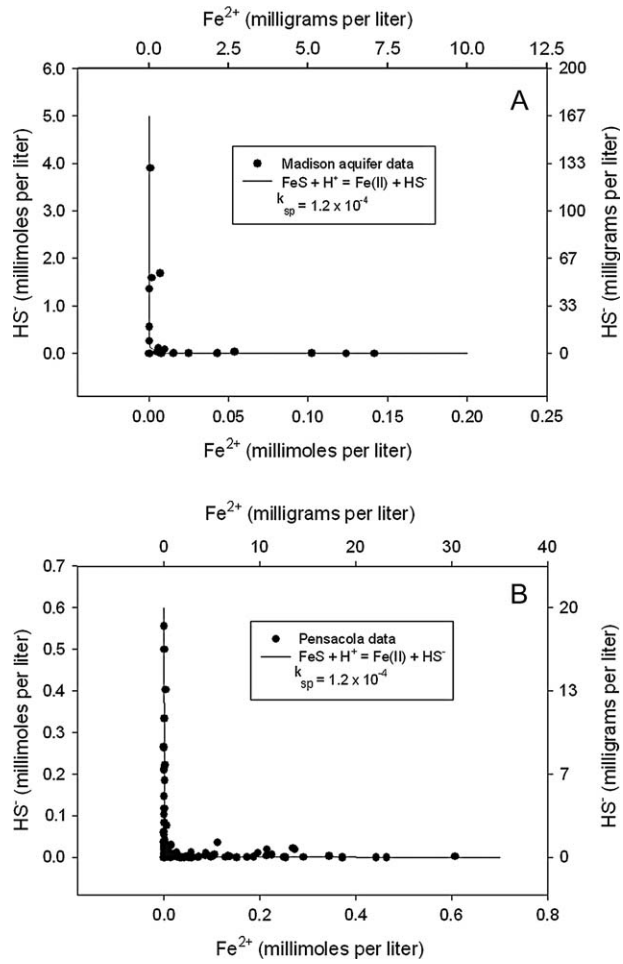

Figure 1. Concentrations of dissolved Fe^{2+} plotted vs. sulfide for (A) the regional-scale Madison Aquifer, Montana (data from Plummer et al. 1990), and (B) a water table aquifer at Naval Air Station, Pensacola, Florida.

There are at least two chemical and/or biochemical processes that may contribute to this observed hyperbolic relation. The first process is the reaction of Fe^{2+} and H_2S to produce solid-phase ferrous sulfide (FeS). For the reaction:

$$FeS_{(s)} + H^+{}_{(aq)} \leftrightarrow Fe^{2+}{}_{(aq)} + HS^-{}_{(aq)} \quad (1)$$

the solubility product for freshly precipitated FeS (mackinawite) is approximately 1.2×10^{-4} (Parkhurst and Appelo 1999):

$$K_{sp} = \frac{[Fe^{2+}][HS^-]}{[H^+]} = 1.2 \times 10^{-4} \quad (2)$$

Thus, at pH = 7.0:

$$[Fe^{2+}] = \frac{(1 \times 10^{-7})(1.2 \times 10^{-4})}{[HS^-]} \quad (3)$$

or

$$[Fe^{2+}] = \frac{1.2 \times 10^{-11}}{[HS^-]} \quad (4)$$

Equation 4 is a hyperbolic algebraic expression relating concentrations of Fe^{2+} and HS^-, which is consistent with observed field data (Figure 1). Furthermore, the low solubility product suggests that when Fe^{2+} is present in excess, H_2S concentrations will be low. Conversely, when H_2S is present in excess, Fe^{2+} concentrations will be low (Figure 1). The relatively fast rate at which FeS precipitation occurs—on the order of minutes or hours (Davidson 1991; Davidson et al. 1999)—suggests that near-equilibrium between Fe^{2+}, H_2S, and FeS will be the most common condition in ground water systems.

Another process that may contribute to the observed hyperbolic relation between Fe^{2+} and H_2S involves microbial competition for electron-donating substrates. It has been shown that iron-reducing microorganisms can outcompete sulfate-reducing microorganisms under electron donor–limited conditions when bioavailable Fe(III) is present in a system (Lovley and Phillips 1987; Achtnich et al. 1995). When Fe(III) reduction predominates, the rate of Fe^{2+} production will outpace H_2S production and Fe^{2+} concentrations will be greater than H_2S concentrations. Conversely, when metabolizable Fe(III) is not available and sulfate reduction predominates, production of H_2S will outpace Fe^{2+} production leading to higher H_2S concentrations relative to Fe^{2+} concentrations. In other words, microbial competition between iron- and sulfate-reducing microorganisms may also contribute to the observed hyperbolic relation between Fe^{2+} and H_2S.

In ground water systems, it is expected that concentrations of Fe^{2+} and H_2S will be affected by both mineral solubility and microbial competition processes. But because both processes lead to a similar relation, they tend to act in tandem, reinforcing the observed hyperbolic relation between Fe^{2+} and H_2S concentrations observed in the field (Figure 1).

Distinguishing Iron from Sulfate Reduction

The hyperbolic nature of Fe^{2+} and H_2S concentrations observed in the field suggests an approach for distinguishing predominantly iron- and sulfate-reducing ground water systems. Specifically, if concentrations of Fe^{2+} are substantially higher than H_2S concentrations, the production of Fe^{2+} must have outpaced the production of H_2S, suggesting predominant iron reduction. Conversely, if H_2S concentrations are substantially higher than Fe^{2+} concentrations, the production of H_2S must have outpaced Fe^{2+} production, suggesting predominant sulfate reduction. When concentrations of Fe^{2+} and H_2S are interpreted in the context of concentrations of other redox-sensitive parameters such as dissolved oxygen, nitrate, manganese, and sulfate (McMahon and Chapelle 2008), the Fe^{2+}/H_2S mass ratio may indicate the relative predominance of iron or sulfate reduction.

In some ground water systems, the clear hyperbolic patterns shown in Figure 1 can be more complex. This is illustrated with Fe^{2+} and H_2S concentrations in ground water from multiple wells that screened a shallow petroleum hydrocarbon–contaminated aquifer in Hanahan, South Carolina (Vroblesky and Chapelle 1994; Petkewich et al. 1997). While high Fe^{2+} concentrations generally coincide with low H_2S concentrations and vice versa, there are also wells producing water where concentrations of these species are roughly similar (Figure 2A). Because concentrations of dissolved hydrogen (H_2), an independent indicator of predominant redox conditions (Lovley et al. 1994), were measured at this site, it is possible to investigate the causes of these deviations. When H_2 concentrations indicated constant iron reduction over a 3-year period (H_2 concentrations staying in the 0.2 to

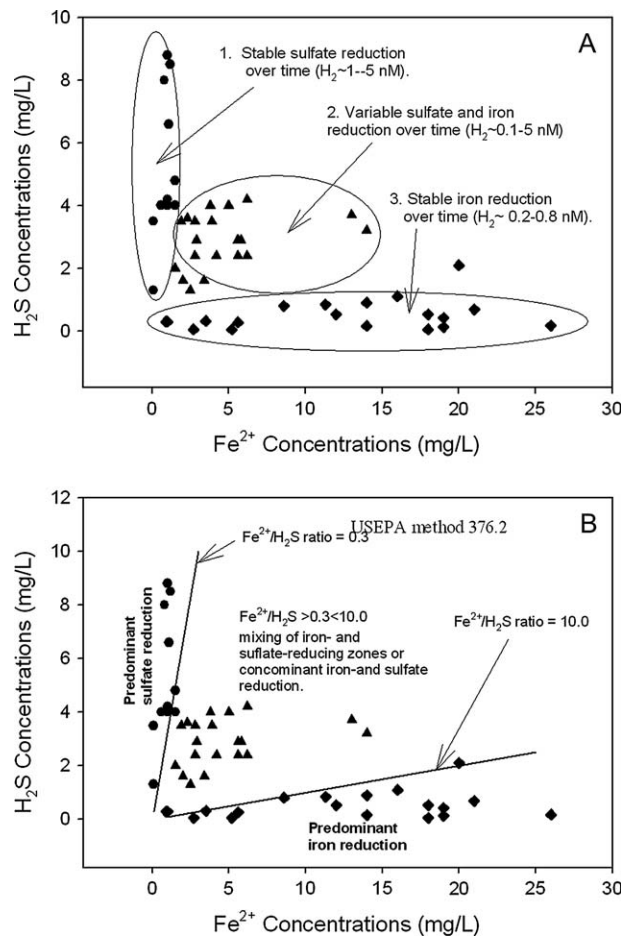

Figure 2. (A) Concentrations of H_2S plotted vs. Fe^{2+} for conditions of (1) stable sulfate reduction over time (H_2 ~1 to 5 nM); (2) transient iron and sulfate reduction over time (H_2 varying between 0.1 and 5 nM); and (3) stable Fe(III) reduction over time (H_2 ~0.2 to 0.8 nM); and (B) observed Fe^{2+}/H_2S mass ratios differentiating predominant iron reduction, predominant sulfate reduction, and wellbore mixing of iron- and sulfate-reducing zones or concomitant iron and sulfate reduction under nonelectron donor–limited conditions.

0.8 nM range, with sulfate concentrations > 0.5 mg/L), Fe^{2+} concentrations were consistently greater than H_2S concentrations (Figure 2A). Conversely, when H_2 concentrations indicated constant sulfate reduction over the same 3-year period (H_2 concentrations ~1 to 5 nM and sulfate concentrations > 0.5 mg/L), H_2S concentrations were consistently greater than Fe^{2+} concentrations (Figure 2A). When similar concentrations of Fe^{2+} and H_2S were observed, concentrations of H_2 indicated that redox conditions shifted back and forth over time between sulfate and iron reduction (Figure 2A). Because the observation wells at the Hanahan site have relatively long screened intervals (3.1 m), and because the vertical zonation of iron and sulfate reduction has been observed to change over time (Vroblesky and Chapelle 1994), simultaneously high concentrations of Fe^{2+} and H_2S may reflect the mixing of water drawn from different discrete redox zones tapped by the sampling wells. Alternatively, because the energetics of iron reduction are similar to those of sulfate reduction (Jakobsen et al. 1998), it may indicate the simultaneous occurrence of the two processes under nonelectron donor–limited conditions. In petroleum-contaminated aquifers such as the Hanahan site, conditions are not necessarily electron donor limited. This relieves competition for electron donors such as H_2, making it possible for concomitant redox process to occur. Furthermore, it has been shown that alternative electron donors can affect the kinetics of H_2 consumption, which in turn may affect ambient H_2 concentrations (Brown et al. 2005).

These observations suggest that Fe^{2+}/H_2S mass ratios may be useful for distinguishing iron from sulfate reduction when concentrations of sulfate are greater than the lower threshold (0.5 mg/L) required to support sulfate reduction (McMahon and Chapelle 2008). Specifically, if Fe^{2+}/H_2S mass ratios (i.e., units of mg/L) are greater than approximately 10 (16 if molar units are being used), predominant iron reduction is suggested. Conversely, if Fe^{2+}/H_2S ratios are less than 0.30 (0.5 if molar units are being used), predominant sulfate reduction is suggested (Figure 2B). Just as importantly, concomitantly high concentrations of Fe^{2+} and H_2S (Fe^{2+}/H_2S greater than 0.3 but less than 10) suggest either the mixing of water from adjacent redox zones in a pumping well or the simultaneous occurrence of iron and sulfate reduction under nonelectron donor-limiting conditions (Figure 2B). Thus, this method may allow the identification of not only relatively homogeneous iron- or sulfate-reducing conditions (Figure 1) but also heterogeneous redox conditions where multiple redox processes affect water chemistry (Figure 2). While H_2 concentrations improve the reliability of redox process diagnoses (Lovley et al. 1994), these results suggest that Fe^{2+}/H_2S mass ratios can also be useful in the context of a multiple line of evidence approach.

Table 1
Threshold Concentrations for Identifying Redox Processes in Water (modified from McMahon and Chapelle, 2008)

General Redox Category	Predominant Redox Process	Distinguishing Fe(III)- from SO_4-reduction	Water Chemistry Criteria (mg/L)						
			O_2	NO_3^-	Mn^{2+}	Fe^{2+}	SO_4^{2-}	Fe^{2+}/H_2S ratio	Comments
Oxic									
	O_2 reduction		≥0.5	—	<0.05	<0.1	—		—
Suboxic									
	—		<0.5	<0.5	<0.05	<0.1	—		Further definition of redox processes not feasible
Anoxic									
	NO_3^- reduction		<0.5	≥0.5	<0.05	<0.1	—		—
	Mn(IV) reduction		<0.5	<0.5	≥0.05	<0.1	—		—
	Fe(III)/SO_4^{2-} reduction		<0.5	<0.5	—	≥0.1	≥0.5		—
		Fe(III) reduction	<0.5	<0.5	—	≥0.1	≥0.5	>10	
		Mix - Fe(III)/SO_4^{2-} reduction	<0.5	<0.5	—	≥0.1	≥0.5	≥3≤10	
		SO_4^{2-} reduction	<0.5	<0.5	—	≥0.1	≥0.5	<3	
	Methanogenesis		<0.5	<0.5	—	≥0.1	<0.5		—
Mixed									Criteria for more than one redox process are met

The sensitivity of this approach is constrained by the ecological succession of redox processes observed in ground water systems (Lovley et al. 1994), the stoichiometry of Fe^{2+} and H_2S production, and the potential downgradient transport of Fe^{2+} and H_2S. Specifically, iron reduction generates significantly more Fe^{2+} per mole of organic matter (CH_2O) oxidized:

$$Fe(OH)_{3(s)} + \tfrac{1}{4}\, CH_2O_{(s/aq)} + 2H^+_{(aq)} + \tfrac{1}{4}\, H_2O_{(l)} \rightarrow Fe^{2+}_{(aq,ad)} + \tfrac{1}{4}\, CO_{2(aq)} + 3H_2O_{(l)} \quad (5)$$

then, H_2S produced by sulfate reduction:

$$\tfrac{1}{8}\, SO_4^{=} + CH_2O_{(s)} + \tfrac{1}{4}\, H^+_{(aq)} + \tfrac{1}{4}\, H_2O_{(l)} \rightarrow \tfrac{1}{8}\, H_2S + \tfrac{1}{4}\, CO_{2(aq)} + \tfrac{1}{4}\, H_2O_{(l)} \quad (6)$$

In other words, iron reduction produces 32 times more Fe^{2+} per mole of CH_2O oxidized than H_2S produced by sulfate reduction. Because much of the Fe^{2+} generated by iron reduction becomes sorbed on aquifer material or forms iron-bearing minerals, only about 2% of the Fe^{2+} generated enters solution (Lovley and Phillips 1988). Thus, the amount of Fe^{2+} available for reaction with H_2S is uncertain. Nevertheless, if conditions shift from iron to sulfate reduction along a given flowpath, excess Fe^{2+} must first be consumed (Equation 1) before the Fe^{2+}/H_2S ratio will fall below 0.3. This means that while Fe^{2+}/H_2S ratios of less than 0.3 are compelling evidence of dominant sulfate reduction, Fe^{2+}/H_2S ratios greater than 10 are more equivocal and encompass dominantly iron-reducing conditions as well as the shift from iron- to sulfate-reducing conditions with incomplete removal of Fe^{2+}. The shift from iron- to sulfate-reducing conditions has been observed under field conditions (Chapelle et al. 2002; Figure 2; Thomas et al. 2008) and can be identified if additional indicators of redox processes (such as sulfate concentrations declining along a defined flowpath or H_2 concentrations) are available.

Conclusions

Relative concentrations of dissolved Fe^{2+} and H_2S can provide useful information concerning the distribution of iron and sulfate reduction in ground water systems. However, because of the ecological and stoichiometric constraints discussed earlier, it is appropriate to use this information in conjunction with other available redox data rather than as a stand-alone redox diagnostic tool. Table 1 shows the framework for identifying redox processes proposed by McMahon and Chapelle (2008) as modified to distinguish dominant iron reduction from dominant sulfate reduction using Fe^{2+}/H_2S ratios. An Excel spreadsheet program that uses the logic of Table 1 (Jurgens et al. 2009), which is designed to assist in the assignment of redox conditions based on water-chemistry data, is available at http://oh.water.usgs.gov/tanc/NAWQATANCTools.htm. This modified framework may allow more precise assessment of redox processes in ground water systems when measurements of Fe^{2+} and H_2S are available.

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