



WATER RESOURCES RESEARCH GRANT PROPOSAL

Title: In Situ Gibbs Free Energies for Hydrogen Oxidizing Terminal Electron-Accepting Processes in Contaminated Subarctic Groundwater

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Background Information

Identifying the predominant terminal electron-accepting processes (TEAPs) is important when determining redox conditions in contaminated ground water. Degradation of environmental contaminants is largely due to microbial activity, and the end products of those reactions are highly dependent upon redox conditions. For example, biological degradation of trichloroethene (TCE), one of the most common ground-water contaminants in the US (U.S. EPA, 1982), generally results in the accumulation of dichloroethenes (DCEs) under Fe(III)- to sulfate-reducing conditions. However, under methanogenic conditions, vinyl chloride (VC), a known carcinogen, may accumulate (DiStefano, et al., 1991). Under aerobic or weakly anaerobic conditions, these intermediates of TCE degradation may be completely mineralized to carbon dioxide and water (Bradley and Chapelle, 1996, 1997, 1998; Bradley, et al., 1998). Clearly, deducing the distribution of TEAPs is very important when predicting the fate of ground-water contaminants.

Historically, the use of platinum electrode probes has been the method of choice for determining redox conditions in ground water. However, this method has been criticized because redox electrodes do not respond to many important redox couples and most

environments are not at equilibrium (Berner, 1981; Stumm and Morgan, 1981; Thorstenson, 1984; Lovely and Goodwin, 1988).

More recently, the consumption of electron acceptors (e.g., nitrate, Mn(IV), Fe(III), sulfate, and carbon dioxide) and the accumulation of end products (e.g., nitrite, Mn(II), Fe(II), sulfide, and methane) have been used to delineate various microbially-mediated redox zones (Baedecker and Back, 1979; Bulger et al., 1989; Langmuir, 1969; Chapelle and Lovely, 1992; Thorstenson, et al., 1979; Jackson and Patterson, 1982; Baedecker, et al., 1988). However, results that rely entirely upon the distribution of electron acceptors and end products may be unreliable because many of these constituents may be replenished from mineral sources (Plummer et al., 1990) or confining bed pore water (Chapelle and McMahon, 1991). For example, depletion of sulfate may not be observed in pore waters of sulfate-bearing aquifer minerals even if sulfate-reduction is the predominant TEAP. Similarly, a lack of sulfide accumulation does not rule out the possibility of active sulfate reduction because sulfide readily precipitates in the presence of metals. This particular situation has been observed in the Tanana Alluvial aquifer (Richmond and Braddock, 1999).

The most current method for determining the distribution of TEAPs has been to couple the measurement of available electron donors and acceptors with concentrations of dissolved hydrogen (Chapelle, et al., 1995). The measurement of dissolved hydrogen as an indicator of TEAPs was first proposed by Lovely and Goodwin (1988) and is based upon the knowledge that hydrogen is the most ubiquitous intermediate of anaerobic microbial metabolism. Hydrogen produced by fermentative microorganisms is very quickly consumed by respiratory microorganisms in a process known as interspecies hydrogen transfer (Ianotti et al., 1973). Because this process is so rapid, different TEAPs display characteristically different, steady-state hydrogen concentrations (Lovely and Goodwin, 1988) which can therefore be used to delineate zones of predominant TEAPs in ground water.

Although widely accepted, this procedure has recently been scrutinized. Early work was conducted in warm (ca. 20°C) ground water systems. It has only quite recently been shown that temperature may have a significant effect on steady-state concentrations of hydrogen (Jakobsen, et al., 1998) and that various TEAPs may not always be competitively exclusive (Jakobsen, et al., 1998; Richmond and Braddock, 1999; see table 1). In these studies, evidence of concomitant Fe(III)- and sulfate reduction in cold (5-10°C) ground water was reported and, in both cases, hydrogen concentrations suggested that Fe(III) was the predominant TEAP. As shown in Table 1., hydrogen concentrations at Fort Wainwright, Alaska indicated that Fe(III)-reduction was the primary TEAP (within the accepted 0.1 to 0.8 nM range), but the presence of sulfide at most wells suggests concomitant sulfate reduction. Because sulfide reacts very quickly with Fe(II), its presence in measurable quantities is strong evidence of active sulfate reduction. In addition, we would not expect to see depletion of sulfate at this site even if active sulfate reduction was occurring because the Tanana Alluvium contains sulfate-bearing minerals. Clearly, in this and other cold water systems, hydrogen data may not accurately reflect

redox conditions and, therefore, may not allow investigators to accurately predict the fate of some environmental contaminants.

Objective

The objective of this study is to calculate DGr values of hydrogen oxidizing TEAPs in contaminated ground water near Fairbanks, AK. We will use activities of dissolved hydrogen, available electron donors, and final end products of microbially mediated redox reactions for our calculations. Calculated data will be used to identify which TEAP may predominate and which TEAPs may occur concomitantly with the predominant TEAP at the sites examined. This information is essential when predicting the fate of contaminants in ground water.