

# Preliminary observations of hydrogeological, microbiological and geochemical processes that influence groundwater redox zonation

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The fundamental hypothesis driving this research is that patterns of redox zonation, although similar in many aquatic environments, vary dramatically in scale due to solute transport processes. These processes control the availability of organic matter, nutrients, and electron donors and acceptors (Vroblesky and Chapelle, 1994). In marine and freshwater sediments vertical solute transport is dominated by diffusion, thus the entire sequence of

redox processes (e.g. aerobic respiration to methanogenesis) occurs in the top 50 cm of the sediment column (Baedecker and Back, 1979). Along a groundwater flow path closed to the atmosphere, uncontaminated groundwater biogeochemically evolves through a similar sequence of processes (Chapelle, 1993). The path length over which these sequences occur is much larger (10+ km) due to advection. Thus, a fundamental issue in aquifer

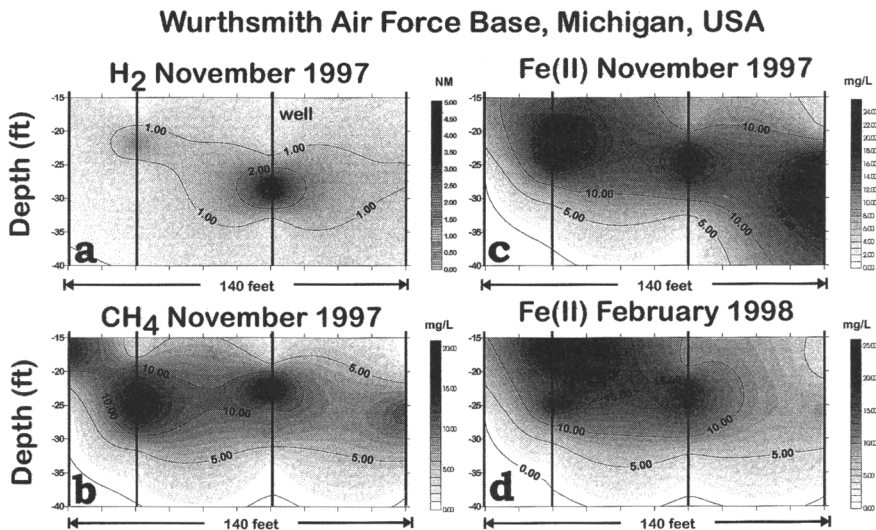


FIG. 1.

biogeochemistry is the means by which solute transport and geochemical processes interact with microbiological activity to influence spatial and temporal variations in redox zonation.

A shallow sandy aquifer contaminated with petroleum hydrocarbons and chlorinated solvents (Wurtsmith Air Force Base, Michigan, USA) provides an excellent opportunity to examine processes that influence redox dynamics. The most reduced conditions occur nearest the contaminant source, with less reducing conditions down gradient from the source. The redox zonation is reversed from those developed in closed groundwater systems, but is typical for contaminated groundwater systems (Baedecker *et al.*, 1993).

Seasonal measurements of hydrogeological, microbiological, and geochemical parameters have begun at the site and builds on previous work conducted at the site (e.g. Chapelle *et al.*, 1996). Here we report preliminary results and interpretations of the field and laboratory measurements. Spatial and temporal biogeochemical measurements include Eh, pH, temperature, alkalinity, stable isotopes, DIC, DOC, H<sub>2</sub>, CH<sub>4</sub>, DO, Fe (II and III), NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, and major cations and anions. We are integrating H<sub>2</sub> gas concentrations with the other biogeochemical parameters to assess variations in microbial terminal electron-accepting processes (TEAP) (e.g. Lovley and Goodwin, 1988). Selected results are summarized below and in Fig. 1, which shows the vertical and horizontal distributions of selected TEAP parameters transverse to groundwater flow within the contaminant plume.

Dissolved H<sub>2</sub> concentrations appear to reflect TEAP gradients (Fig. 1a) that change from from methanogenic to sulphate- to iron- reduction to aerobic down gradient from the contaminant source. TEAP variables such as CH<sub>4</sub> and Fe(II) (Fig. 1b,c) also show concentration gradients in the system. Although the spatial distribution of high H<sub>2</sub> and CH<sub>4</sub> concentrations are similar (Fig. 1a,b), temporal changes in their concentrations are not always of equal magnitude. In fact, at times H<sub>2</sub> concentrations do not indicate methanogenesis is occurring, even in areas with high CH<sub>4</sub>. These results suggest that other processes (e.g. acetate cycling) may influence the relationship between H<sub>2</sub> and CH<sub>4</sub> concentrations as well as redox zonation at the site.

Redox zonation is very dynamic. Figures 1 c and d show that significant changes in the concentrations of Fe(II) occurred within a four-month period. Changes in the dimensions of the redox zones have been observed to be accompanied by changes in water table elevation as well as in temperature. For example, the shift from methanogenesis to more oxidizing conditions appears to be related to the seasonal increase in recharge flux, which brings oxygen into the system.

Two additional observations are that the inorganic (e.g. Ca<sup>2+</sup>, K<sup>+</sup>) solution chemistry of the site appears to be indirectly influenced by redox reactions in predictable, but poorly understood ways. Secondly, geochemical modelling indicates that the minerals siderite (FeCO<sub>3</sub>) and iron sulphides (FeS<sub>x</sub>) and iron oxyhydroxides (FeOOH) are important in iron cycling in all redox zones.

These results indicate that redox zonation in groundwater is influenced by various interacting hydrological, microbiological, and geochemical processes. Although H<sub>2</sub> is an important tool in helping to identify redox zones, the complexity of processes that cause redox zonation necessitates the measurement of other biogeochemical variables to fully understand the spatial and temporal changes in zonation. The results support the hypothesis that the dimensions of H<sub>2</sub>-defined redox (TEAP) zones at the site are closely linked to the transport of chemicals (e.g. oxidants, nutrients) into the system.

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