

Report for 2003ND27B: Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC

- Other Publications:
 - Presentation: Tesfay, Tedros and Scott Korom, Sept. 23, 2003, Network of in-situ Mesocosms for Monitoring Denitrification in Selected Aquifers of Minnesota and North Dakota, ND WRI Advisory Committee, Bismarck, North Dakota.
 - Poster Presentation: Tesfay, Tedros and Scott Korom, 2004, Regional Network of in-situ Mesocosms for Monitoring Denitrification Part I: Improving Aquifer Nitrate Vulnerability Assessments, South Dakota 16th Annual Environmental and Groundwater Quality Conference, Pierre, South Dakota.

Report Follows

MODELING GROUNDWATER DENITRIFICATION BY FERROUS IRON USING PHREEQC

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PROBLEM DESCRIPTION

Nitrate is one of the most common groundwater contaminants (Freeze and Cherry, 1979). Nitrate concentrations may be reduced by denitrification, which is a natural process that converts nitrate irreversibly into harmless nitrogen gas (Korom, 1992). Denitrification requires an anaerobic environment, denitrifying bacteria, and sufficient and reactive electron donating species (Firestone, 1982). Korom (1992) indicated that the three common electron donors for denitrification in aquifers are organic carbon, sulfide (usually as pyrite), and ferrous iron. Numerous researchers show that the availability of electron donors within aquifer sediments limits the denitrification potential of aquifers (e.g., Trudell et al., 1986; Robertson et al., 1996). Efforts by members of the UND denitrification research team show organic carbon and sulfide are active electron donors for denitrification in aquifers in North Dakota and Minnesota. We also believe ferrous iron is an active electron donor; however, the geochemical evidence for ferrous iron is more difficult to interpret. To do so requires advanced computational techniques, such as incorporated in the computer code PHREEQC (Parkhurst and Appelo, 1999) produced by the U.S. Geological Survey.

SCOPE AND OBJECTIVES

Denitrification in aquifers involves numerous hydrogeochemical processes with both the water and sediment phases. These include dilution, ion exchange, dissolution, precipitation, and oxidation-reduction reactions (Tesoriero et al., 2000). Knowledge of the above reactions will enable us to decipher the denitrification capacity of aquifers, particularly when ferrous iron minerals are involved. Therefore, our objective is to use PHREEQC in order to gain a more comprehensive understanding of the hydrogeochemical environment that governs denitrification by ferrous iron and associated aquifer reactions.

KEY LITERATURE AND PRIOR WORK

Figure 1 shows the seven sites in North Dakota and Minnesota currently being studied by the UND Denitrification Research Team. At each site stainless



Figure 1. The seven in situ denitrification sites (indicated by stars) in North Dakota and Minnesota.

steel chambers partially isolate a portion of saturated aquifer sediments, thereby forming in situ mesocosms (ISMs) of the sediments. Tracer tests are performed in the ISMs and the resulting changes in the groundwater geochemistry provide evidence for denitrification rates and the electron donors involved. Schlag (1999) described how these sites are installed and how the tracer tests are performed. Results from the first tracer test done at the Larimore site (Schlag, 1999) illustrate how results from an ISM tracer test are interpreted.

Figure 2 shows the trends of several major anions during the first tracer test at the Larimore site. Note that the nitrate concentrations decreased at a faster rate than the bromide concentrations. The latter decreased due to dilution with native groundwater during the tracer test. Only the nitrate lost beyond that explained by dilution of bromide is attributed to denitrification. The steep increase in sulfate indicates that sulfide was an electron donor for denitrification. Schlag (1999) showed that about 60% of the denitrification could be explained by the oxidation of sulfide (as pyrite).

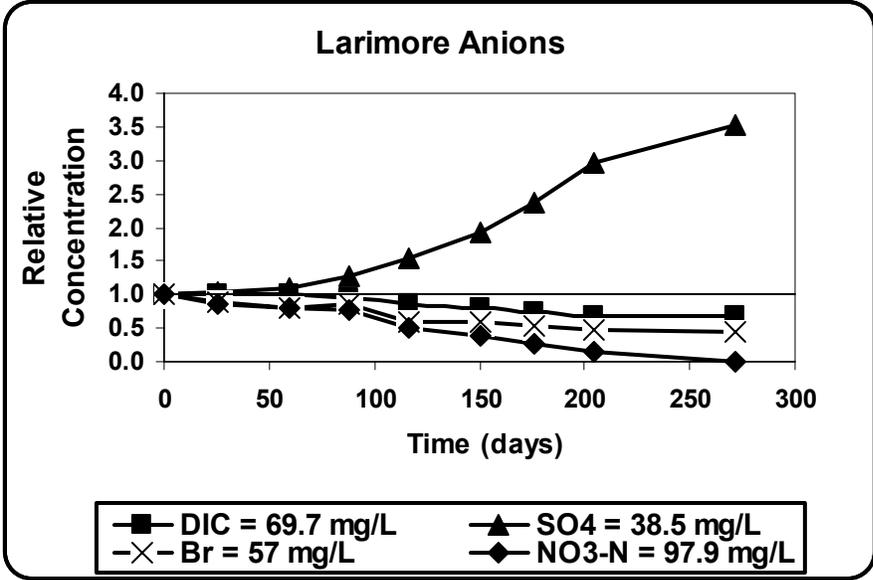


Figure 2. Anion concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

Schlag (1999) also showed that organic carbon was likely responsible for most of the remaining denitrification observed. This process is illustrated by noting the decreasing dissolved inorganic carbon (DIC) concentrations in Figure 2 and the steep loss of calcium and magnesium in Figure 3.

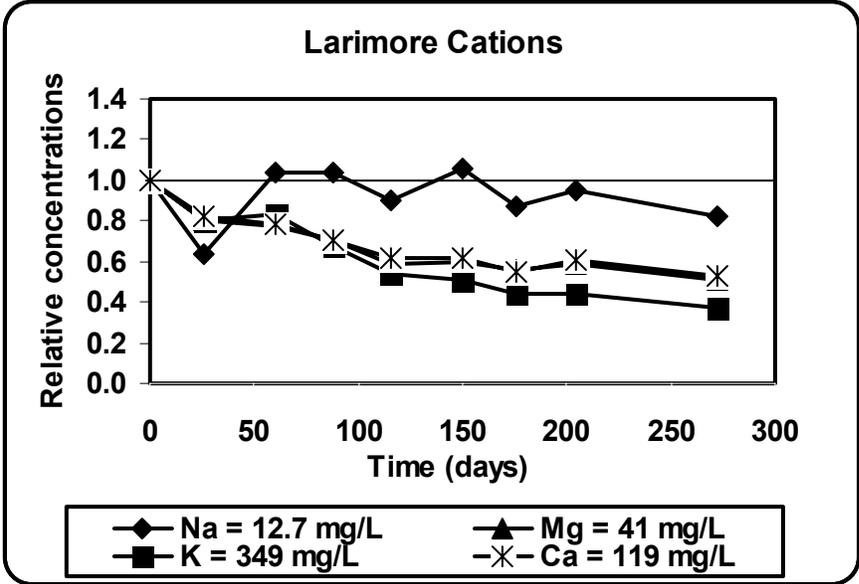


Figure 3. Cation concentrations during the first tracer test at the Larimore site. Initial concentrations are given in the box at the bottom of the figure.

The calcium and magnesium concentrations in Figure 3 should have behaved like the sodium concentrations, that is, they should have stayed near a relative concentration of 1. However, calcium and magnesium dropped much like potassium. The latter should have dropped because the nitrate and bromide added to the groundwater for the tracer test were added as potassium species, so the potassium should have decreased by dilution, as did the nitrate and bromide concentrations. Some other process is responsible for the loss of calcium and magnesium.

Denitrification by organic carbon produces inorganic carbon. We expected DIC to increase in Figure 2. It would have, except the increase in inorganic carbon was masked by the precipitation of a magnesium-rich calcite (CaCO_3). Therefore, we have these two patterns for denitrification by organic carbon:

1. an increase in DIC, or
2. a decrease in divalent cations (calcium or calcium and magnesium) and a decrease in DIC.

Previously, we showed that denitrification by sulfide causes an increase in sulfate.

We see these patterns at five of the seven ISM sites. Therefore, organic carbon and inorganic sulfides play a major role in the denitrification at these sites. However, these electron donors do not account for all the nitrate lost at some of the five sites. Furthermore, the reaction products for denitrification at the remaining two sites (Robinson, ND and Akeley, MN) do not reflect the involvement of organic carbon and sulfides at all. Our hypothesis is that ferrous iron is the major electron donor causing reduction of nitrates in the latter two aquifers and may also be involved to a lesser extent at some of the other five sites, as well.

METHODS, PROCEDURES AND FACILITIES

Denitrification reactions may involve many complex geochemical processes. Interpreting and understanding the processes may require computer models that incorporate multiple parameters for the participating processes and are able to solve the resulting nonlinear equations (Appelo and Postma, 1996). PHREEQC (Parkhurst and Appelo, 1999), which is one of the most advanced geochemical computer codes, will be used for the research. This code calculates the composition of a water sample at thermodynamic equilibrium by solving the mass balance and mass action equations.

To understand the controlling geochemical reactions that account for the observed denitrification results, batch-reactions that incorporate both equilibrium and kinetic reactions and inverse modeling will be invoked. Input files for the modeling will incorporate geochemical data of the native groundwater and the amended water from the tracer tests, as well as mineralogical data of the aquifers. Fortunately, substantial amounts of aqueous geochemical data for the tracer test have already been collected. These include major anions, major cations, pH, temperature, dissolved organic and inorganic carbon concentrations, and many tracer elements. Sediment data collected include inorganic sulfide and organic carbon

concentrations. Additional water and sediment analyses are planned, particularly to quantify ferrous iron contents of the sediments. Analytical instruments at the UND Water Resources Research Laboratory and the x-ray diffraction machine in Geology & Geological Engineering will be used for the analyses. Finally, modeling output will be compared with the field and laboratory results in order to validate both the numerical procedures as well as the hydrogeochemical reaction schemes.

RESULTS AND CONCLUSIONS

This research will provide insights into denitrification by ferrous iron. It is expected that the modeling results will support our hypothesis that ferrous iron is the major electron donor for denitrification at the Robinson and Akeley sites. We also expect to show that ferrous iron is also involved to lesser extents at some of the other ISM sites where sulfide and organic carbon are known to be the major electron donors for denitrification.

Funding has been secured to repeat the tracer tests at the ND sites. A proposal is in review to repeat the tracer tests in the MN ISMs. In total, over \$500,000 in funding and in-kind match has already been provided for our denitrification research. All data will be available to us for further investigation. Preliminary interpretations of all the completed tracer tests have been done. In addition, PHREEQC has been shown to be effective in interpreting the denitrification reactions in the ISMs during the tracer tests

NO_3^- lost unaccounted by the common e- donors, OC and IS, range from ~ 40 to 95 %.

Data collected already include:

- Analytical data of all the sites (from previous studies)
- Texture analyses of some of the samples
- TOC analyses of some of the samples
- IS analyses of some of the samples

Data to be analyzed in the near future

- Ferrous and total iron analyses
- Mineralogy (XRD) and CEC measurements of aquifer sediments

Fe (II) that participates in the reduction of NO_3^- is Fe (II) dissolved and ion-exchangeable (*digested in 1 M neutral salt, CaCl₂*)

Fe (II) in amorphous form (*digested in 0.5 M HCl*)

Fe (II) in crystalline forms (*digested in hot 5 M HCl*)

Fe (II) and total iron will be analyzed in Hach DR2010 spectrophotometer using the required reagents

Finally, modeling output will be compared with the mineralogical data (XRD) and analytical results in order to verify both the numerical procedures as well as the hydrogeochemical reaction schemes.

ACKNOWLEDGMENTS

MN Agriculture Department
 MN Department of Health
 MN Pollution Control Agency
 ND Department of Health
 ND State Water Commission
 ND Rural Water User System Association
 ND Water Resources Research Institute (USGS)
 University of North Dakota
 US EPA Section 319 Grants through MN & ND

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