

# **Report as of FY2006 for 2003ND27B: "Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC"**

## **Publications**

- Water Resources Research Institute Reports:
  - Tesfay, Tedros and Scott Korom, 2006, "Modeling Groundwater Denitrification by Ferrous Iron Using PHREEQC", Technical Report No: ND 06-03, North Dakota Water Resources Research Institute, Fargo, North Dakota.
- Conference Proceedings:
  - Tesfay, T. and S. F. KOROM, 2006, "The relative roles of electron donors in aquifer denitrification reactions: insights from geochemical modeling", 40th annual meeting, North-Central section, the Geological Society of America, University of Akron, Akron, Ohio, April 20-21.
  - Korom, S., 2007, "Denitrification in the Red River Basin and Beyond: How Aquifer Sediments Influence Water Quality", Third International Water Conference, International Water Institute, Grand Forks, March 13-15.
- Dissertations:
  - Tesfay, Tedros, 2006, "Modeling Groundwater Denitrification by Ferrous Iron using PHREEQC", Ph.D Dissertation, Department of Geology and Geological Engineering, University of North Dakota, Grand Forks, North Dakota.

## **Report Follows**

# MODELING GROUNDWATER DENITRIFICATION

## BY FERROUS IRON WITH PHREEQC

### DESCRIPTION OF THE PROBLEM

Studies made by members of the University of North Dakota (UND) denitrification research team show that organic carbon and sulfides are active electron donors in North Dakota and Minnesota aquifers (Korom et al. 2005). However, the role of Fe(II) was overlooked because the geochemical evidence for ferrous iron is more difficult to decipher as Fe(III) precipitates out from the aqueous solution. Thus far, little was known about the significance of solid phase ferrous iron. My research complements the previous works by investigating the two inseparable issues, abundance of biologically available ferrous iron and its role in the denitrification processes. Geochemical modeling, PHREEQC, is employed to gain insight into the *in situ* denitrification processes that take place via all possible electron donors.

### LITERATURE REVIEW AND PRIOR WORK

UND denitrification team's efforts, including the latest geochemical modeling work (Skubinna, 2004), have shown evidently the role of pyrite ( $\text{FeS}_2$ ) in reducing nitrates (Skubinna, 2004; Schlag, 1999). The remaining nitrate sinks were entirely attributed to organic carbon with the assumption that inorganic carbon has been produced but latter lost from solution via precipitation of  $\text{Ca-Mg-CO}_3$ . The bases of these arguments are the decline of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the N-ISM, but not in C-ISM, as well as XRD measurement of precipitates collected from sampling bottles (Schlag, 1999). However, this accounts for only a small portion of the remaining nitrate. For example in the Elk Valley aquifer about 7 % (first tracer test) of the denitrification can be explained by the precipitation of magnesian calcite (Schlag, 1999; Skubinna, 2004). The rest of the nitrate sink was explained by a similar argument but with the assumption that enough  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have been desorbed from mineral surfaces and latter on co-precipitated with C(+4) from solution (Korom et al. 2005). Nevertheless, the amount of cations that can be released from solid surfaces into the solution is limited. Commonly, the laboratory measured cation exchange capacity (CEC) and that of the CEC value used in geochemical modeling are significantly different (personal communication with Parkhurst; Skubinna, 2004). Barton and Karathanasis (1997) discovered, from the study of eight morphologically and physicochemically different pair of intact and disturbed soils that routine CEC measurements overestimates ion-exchange processes by about 49.1 %. The above assumption was probably the main reason for the ignorance of the possible role of reduced metals, such as Fe(II), in the previously studied aquifers of our region (Schlag, 1999). PHREEQC, based on the database and Gaines-Thomas convention, provides important information once the exchanger value and solution are defined in the input file (Parkhurst and Appelo, 1999). For practical modeling proposes, therefore, the exchanger (X-), presented in PHREEQC (mol/l), is determined by trial and error (Skubinna, 2004; personal communication with Parkhurst). Numerous runs are performed using different values for the exchanger (X-) until a good match is achieved between the modeled and the actual concentrations of cations in the ISM. That means the sample collected first after tracer injection is compared closely with the pre-injection cation composition of the native water to estimate the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (meq/l) desorbed from the mineral surfaces into solution. If all these cations are thought to be co-precipitated with bicarbonate, then the maximum amount of bicarbonate that could be produced by organic-carbon-

supported-denitrification can be determined. For example, using the  $X^-$  value of 3.5 mmole determined by Skubinna (2004) the maximum  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that can be exchanged for  $\text{K}^+$  are about 0.501 mmol/l. This in turn can boost the role of organic carbon by only 17 % (for the Time = 589 days with a net nitrate amount of 2.42 mmol/l). This confirms that there should be another possible electron donor, presumably Fe(II).

## **SCOPE AND OBJECTIVES**

Mixing of oxidized (nitrate polluted) water and reduced waters at depth trigger important multiphase aquifer hydrogeochemical reactions (Appelo and Postma, 1996). These reactions can be reproduced by injecting oxidants like nitrate along with a conservative anion that has similar physicochemical properties to that of the oxidant. Some of the common aquifer geochemical reactions are ion exchange, reversible reactions (dissolution and/or precipitation of dominant minerals), and redox reactions (Tesoriero et al., 2000). The latter reaction is naturally slow but when microbially catalyzed it has enormous environmental significance. The disequilibrium in the redox state between the two mixing waters instigates environmentally important reactions that change the fate of redox sensitive contaminants such as  $\text{NO}_3^-$  (Kehew, 2001).

## **METHODS, PROCEDURES AND FACILITIES**

Aquifer denitrification reactions are complex natural processes that require consideration of the role of bacteria along with the thermodynamic and kinetic principles (Appelo and Postma, 1996). In a classic sense, complete equilibrium of any given system is achieved when it occupies a specific region of space without any spontaneous tendency for a change (Bethke, 1996). In a more practical sense equilibrium to groundwater environments is assumed when the rate of geochemical reaction is greater than that of the flow of groundwater (Postma et al. 1991, and references therein). However, in most natural geochemical environments equilibrium cannot be developed fully among all interacting multiphases and the inference of local or partial equilibrium makes more sense.

For local equilibrium, a portion of the system develops equilibrium but as the fluid traverses the aquifer, it encounters fresh minerals, and the reaction progresses in discrete time steps (Bethke, 1996). A partial equilibrium geochemical modeling that included ion exchange, reversible reaction and redox reactions is used in this project (Figure 1). These modeling scenarios produced a series of potential recovered water qualities and the last in the sequence expected to reflect the target solution for that particular sampling date.

## **ANTICIPATED RESULTS**

Solutions of four sampling dates from each site were selected for modeling proposes and each solution was allowed to pass through sequential reaction steps, and then finally compared with the target solution. After the net nitrate was determined, for each time step, the role of each electron donor was investigated starting with pyrite. Next, the maximum amount of organic carbon that can be calculated back from the directly measured and concealed inorganic carbon is considered. The concealed amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  represents not only that in solution but also the fraction that may have been released from the sorbent and latter coprecipitated together with inorganic carbon. Finally, the remaining net nitrate unaccounted by these two major electron donors is attributed to Fe(II).

Table 1. Relative roles of the three common electron donors in natural denitrification reactions of North Dakota and Minnesota Aquifers.

| <b>Research Site</b> | <b>Electron Donors</b> | <b>OC %</b>   | <b>FeS<sub>2</sub> %</b> | <b>Fe(II) %</b> |
|----------------------|------------------------|---------------|--------------------------|-----------------|
| Akeley (MN)          | Range/Average in %     | 46 – 60/51.2  | 3.0 – 14/7.47            | 27 – 50/41.3    |
| Perham-M (MN)        | Range/Average in %     | 1.0 – 21/9.31 | 59 – 83/71.3             | 7.0 – 40/19.4   |
| Perham-W (MN)        | Range/Average in %     | 19 – 32/25.9  | 0.0 - 1.0/0.44           | 68 – 80/73.6    |
| Luverne (MN)         | Range/Average in %     | 28 – 36/32.9  | 25 – 41/30.5             | 32 – 39/36.5    |
| Robinson (ND)        | Range/Average in %     | 0.0 – 23/7.81 | 1.0 - 5.0/2.31           | 75 – 99/89.9    |
| Karlsruhe-S (ND)     | Range/Average in %     | 23 – 27/25.1  | 14 – 28/21.4             | 46 – 63/53.5    |
| Larimore-2TT (ND)    | Range/Average in %     | 19 – 30/24.7  | 22 – 48/37.7             | 27 – 48/37.5    |

## **PROGRESS TO DATE**

All aqueous analytical data, mineralogy and chemistry of sediments and geochemical modeling works are evidently showing the proportional role of all electron donors (Figure 2) and Fe(II) supported denitrification has a significant role as a natural remediation tool. For example, the diagrams of Akeley (MN) research site demonstrate that CEC and reversible reactions are responsible for the geochemical evolution observed in the N-ISM and that redox reactions are not important for the C-ISM (See figures in Appendix). Unlike the C-ISM, the nitrate chamber is expected to duplicate the redox disequilibrium observed in natural aquifers. Then, the initial solution was forced to react with the three electron donors, based on the methodology explained earlier. That means the net nitrate was reduced by the proportional role of the three major electron donors. The role of each electron donor varies for the solutions of the modeled sampling dates, however, the following ranges were deduced from the “REDOX REACTION” modeling exercise: - OC 46-60 %, FeS<sub>2</sub> 3-14 % and Fe(II) 27-50 % for Akeley (MN) (Figure 2).

## Local Equilibrium Reaction Model

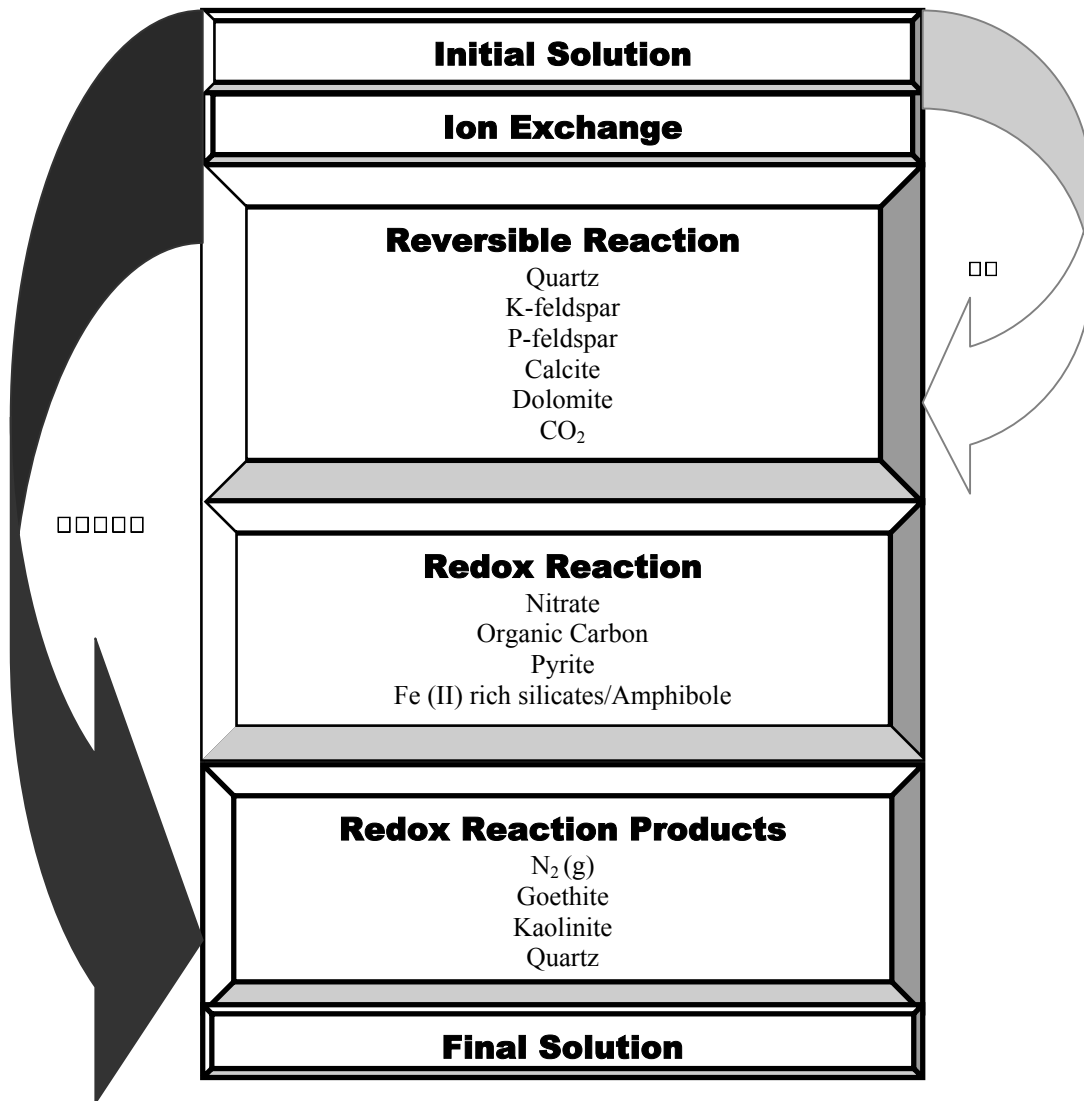


Figure 1. Partial equilibrium modeling conceptual representation; note that control chamber (C-ISM) and nitrate chamber (N-ISM) acquire different steps in the modeling sequence.

Electron Donor's Contribution in Minnesota and North Dakota Aquifer Denitrification Processes

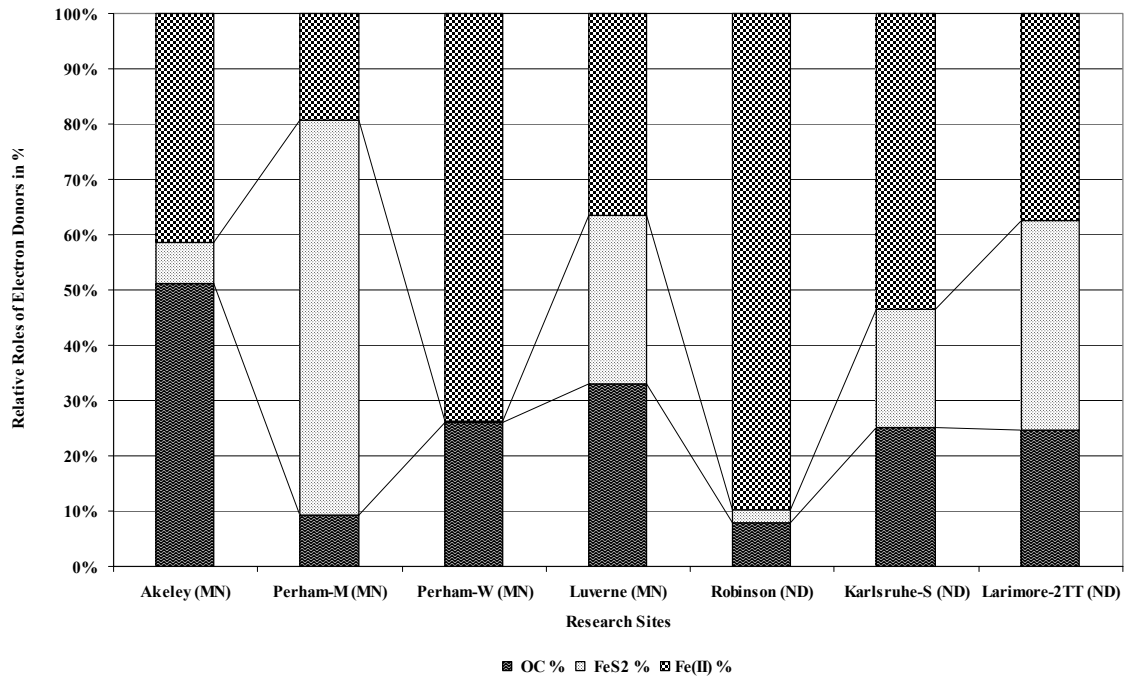
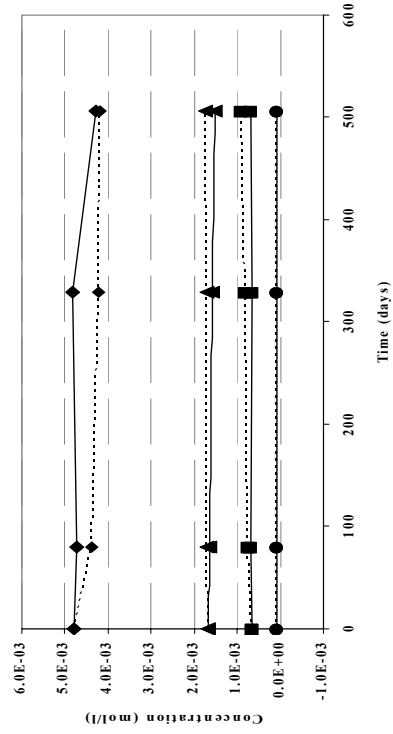


Figure 2. Average contribution of each electron donor in the natural denitrification reactions of North Dakota and Minnesota aquifers, as computed via advanced geochemical modeling, PHREEQC, employing the concept of partial geochemical modeling.

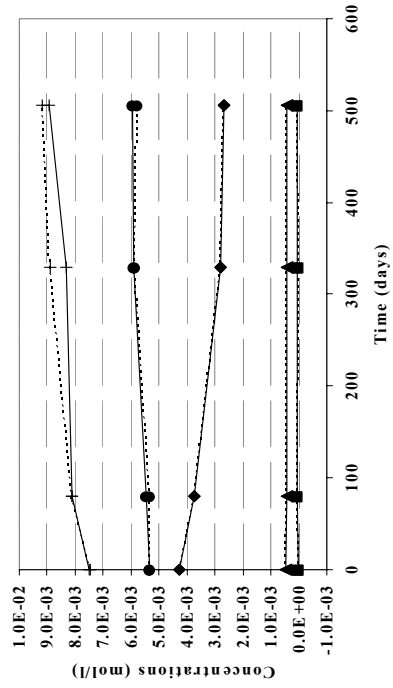
Appendix. Additional data comparing the modeled ("M") with dashed lines) vs. measured ions at the Akeley site.

Akeley N-ISM Modeling Results: Modeled vs. Measured Cations



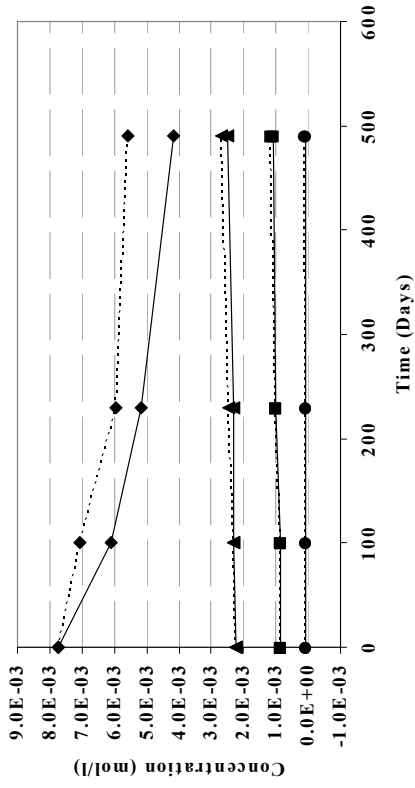
◆ Na —■ Mg —● K —▲ Ca ...◆ Na-M ...■ Mg-M ...● K-M ...▲ Ca-M

Akeley N-ISM Modeling Results: Modeled vs. Measured Anions



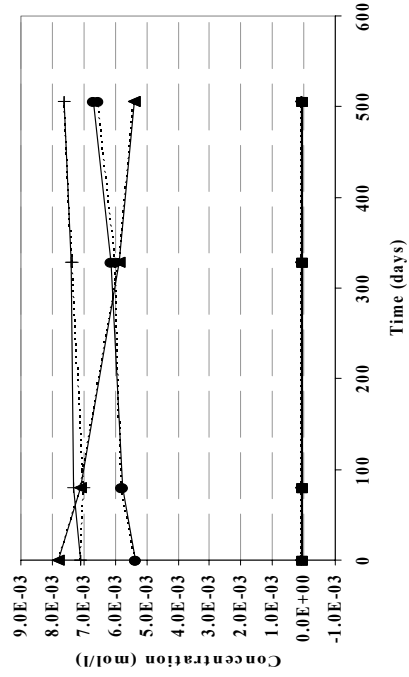
■ S(6) ...◆ N(5)M ...▲ Br-M ...● C(4)M ...■ S(6)M ...◆ N(5)M ...▲ Br-M ...● C(4)M ...+ pH-M

Akeley-C-ISM Modeling Results: Modeled vs. Measured Cations



◆ Na —■ Mg —● K —▲ Ca ...◆ Na-M ...■ Mg-M ...● K-M ...▲ Ca-M

Akeley-C-ISM Modeling Results: Modeled vs. Measured Anions



■ S(6) ...◆ N(5)M ...▲ Br-M ...● C(4)M ...■ S(6)M ...◆ N(5)M ...▲ Br-M ...● C(4)M ...+ pH-M

## REFERENCES

- Appelo, C.A.J., and D. Postma, 1996. *Geochemistry, groundwater and pollution*. A.A.Balkema, Rotterdam. p. 275
- Asmerom, Y., Tesfai, T., and Beirman, B., 2000b, The plume component in continental basalts: *EOS (Am. Geophys. Union Trans)*, 81.
- Barton, C.D., and Karathanasis, A.D. Measuring cation exchange capacity and total exchangeable bases in batch and flow experiments. *Soil Technology* 11 (1997) 153-162.
- Bethke, C.M., 1996, *Geochemical Reaction Modeling*, Oxford U.P., New York.
- Canfield, D.E., R. Raiswell, J.T. Westrich, C.M. Reaves, and R.A. Berner, 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales, *Chemical Geology*, 54(1/2), 149-155.
- Clynne, M.A., Duffield, W.A., Fournier, R.O., Giorgis, L., Janik, C.J., Kahsai, G., Lowenstern, J., Mariam, K., Smith, J.G., Tesfai, T. (1996a) Geothermal Potential of the Alid Volcanic Center, Danakil Depression, Eritrea. USGS Final Report to U.S. Agency for International Development under the terms of PASA Number AOT-0002-P-00-5033-00, 46p.
- Clynne, M.A., Duffield, W.A., Fournier, R.O., Giorgis, L., Janik, C.J., Kahsai, G., Lowenstern, J., Mariam, K., Smith, J.G., and Tesfai, T., 1996, Geology and Geothermal Potential of Alid Volcanic Center, Eritrea, Africa: *Transactions of the Geothermal Resources Council*, v. 20, p. 279-286.
- Duffield, W.A., Bullen, T., D., Clynne, M. A., Fournier, R.O., Janik, C.J., Lanphere, M.A., Lowenstern, J., Smith, J.G., W/Giorgis, L., Kahsai, G., W/Mariam, K. and Tesfai, T., 1997, Geothermal Potential of the Alid Volcanic Center, Danakil Depression, Eritrea. U.S. Geological Survey [Open File Report 97-291](#), p. 62
- Heron, G. Crouzet, C., Bourg, A.C.M., Christensen, 1994b. Speciation of Fe (II) and Fe (III) in contaminated aquifer sediments using chemical extraction techniques. *Environm. Sci. Technol.* 28, 1698-1705.
- Kehew, A.E., 2001, *Applied Chemical Hydrogeology*. Prentice-Hall, Inc., 368p.
- Kennedy, L.G., Everett, J. W., Ware, K. J., Parsons, R., Green, V., 1998. Iron and sulfur mineral analyses methods for natural attenuation assessments. *Biorem. J.* 2, 259-276.
- Korom, S. F., and T. Tesfay. 2004. Regional network of in-situ mesocosms for monitoring denitrification, part 2: Improving aquifer nitrate vulnerability assessments: 16th Annual Environmental and Ground Water Quality Conference, Pierre, South Dakota, March 17-18.
- Korom, Scott F., Schlag, Allen J., Schuh, William M. & Kammer Schlag, Alison (2005). In situ mesocosms: Denitrification in the Elk Valley aquifer. *Ground Water Monitoring & Remediation* 25 (1), 79-89.
- Lowenstern, J., Janik, J., Fournier, R. O., Tesfay, T., Duffield, W. A., Clynne, M. A., Smith, J. G., Woldegiorgis, L., Weldemariam, K., Kahsai, G., 1999. A geochemical reconnaissance of the Alid volcanic center and geothermal system, Danakil Depression, Eritrea. *Geothermics*, V. 28, P. 161-187.
- Parkhurst, D.L. and Appelo, C.A.J., 1999, User's guide to PHREEQC (version 2)--A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- Postma, D., C. Boesen, H. Kristiansen, and F. Larsen, 1991. Nitrate reduction in an unconfined aquifer: water chemistry, reduction processes, and geochemical. *Water Resour. Res.* 27: 2027-2045.
- Schlag, A. J., 1999. In-site measurements of denitrification in the Elk Valley aquifer, M.S. thesis, 104 pp., University of North Dakota, Grand Forks, ND.
- Skubinna, P. A., 2004. Modeling the hydrogeochemistry of denitrification in the Elk Valley M.S. thesis, 145 pp., University of North Dakota, Grand Forks, ND.
- Tesfay, T., and S. F. Korom. 2004. Aquifer denitrification and the concentration of electron donors in aquifer sediments: 16th Annual Environmental and Ground Water Quality Conference, Pierre, South Dakota, March 17-18.
- Tesfay, T., and S. F. Korom. 2004. Aquifer denitrification and the concentration of electron donors in aquifer sediments: 16th Annual Environmental and Ground Water Quality Conference, Pierre, South Dakota, March 17-18.
- Tesfay, T., Bolles, A.B., Korom, F. S., 2001. Laboratory study of denitrification by recently formed sulfides. American Geophysical Union, Spring Conference 2001, AN: H31C-07.
- Tesfay, T., Durbin, H., Korom, F. S., 2002. Predicting denitrification capabilities of Karlsruhe aquifer sediments based on data provided from a Network of In-situ Mesocosms. Midwest Groundwater conference.
- Tesoriero, A.J., H. Liebscher, and S.E. Cox. 2000. The mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along ground water flow paths. *Water Resour. Res.* 36:1545-1559.