Report as of FY2009 for 2006ND126G: "Collaborative Research on In Situ Denitrification and Glyphosate Transformation in Ground Water: NAWQA Eastern Iowa Basins Study Unit"

Publications

- Conference Proceedings:
  - Korom, S. F., and R. J. S. Klapperich, Electron donor concentrations in eastern North Dakota shale formations. 53rd Annual Midwest Ground Water Conference, September 29 October 2, 2008, Dubuque, Iowa.
  - Korom, S. F., and R. J. S. Klapperich, Why are the sediments of some regional aquifers more reactive than others? 21st Annual Environmental and Ground Water Quality Conference, March 18 19, 2009, Fort Pierre, South Dakota.
- Water Resources Research Institute Reports:
  - Maharjan, B., and S. F. Korom. (2009) Correlation of electron donor concentrations in sediments with sediment properties: New Providence, Iowa. Technical Report No. ND09-01, North Dakota Water Resources Research Institute, North Dakota State University.

Report Follows

1. Synopsis. Contamination of ground water by nitrate and pesticides is widespread in some areas of the country and can threaten drinking water supplies. It is well known that the most important removal mechanism of nitrate and most pesticides from ground water is biodegradation, but the *in situ* transformation rates are largely unknown. In this study, two 180-L stainless steel chambers forming *in situ* mesocosms (ISMs) of aquifer sediments will be installed below the water table at the NAWQA agricultural chemicals study sites in the glaciated region of Iowa. This work will extend the use of this technique to examine denitrification in an area characterized by high dissolved iron concentrations and to measure the transformation rate of the extensively-used herbicide, glyphosate. The objectives for the research are the following:

1. Measure the denitrification and glyphosate transformation rates in the two ISMs.
2. Determine whether the denitrification is better fit by zero-order or first-order reaction rates.
3. Determine what donors are contributing electrons for the denitrification and their relative amounts.
4. Incorporate the results of the two ISMs into the existing databank of nine other ISM sites in glacial outwash aquifers in the Upper Midwest.
5. Update the available data of the apparent isotopic enrichment factor for ^{15}N in nitrate versus denitrification rate among of ISM sites.
6. Update the nitrate vulnerability index and extrapolate the findings to similar, unmonitored agricultural and environmental settings.

Aquifer sediment samples were collected from the Iowa site and analyzed for grain-size distributions, mineralogy, and major e^- donors (organic carbon, inorganic sulfide, organic sulfur, and ferrous iron). These data were used to determine optimum locations for installation of the ISMs, provide insights on the types and heterogeneity of e^- donors at the site, and provide the e^- donor supply data at the Iowa site that can be compared to previous ISM studies in the Upper Midwest. Two ISM chambers were installed, purged, and amended with nitrate and bromide, which serves as a tracer for nitrate. The tracer test in the deep ISM ("D-ISM") went from November, 2007, through September, 2009. Two tracer tests were performed in the shallow ISM ("S-ISM"); the first went from November, 2007, through October, 2008; the second went from October, 2008, through November, 2009, and was amended with nitrate, bromide, and glyphosate. Modeling of the evolution of the geochemistry in the ISMs will provide insights into what e^- donors contributed electrons to the denitrification and their relative amounts. The results of this study will provide site-specific transformation rates for nitrate and glyphosate and extend the aquifer nitrate vulnerability index that was developed in earlier studies and continues to be expanded to other aquifers. This information is vital for the development of tools and quantitative methods to characterize the transport and fate of agricultural chemicals in the Eastern Iowa Basins Study Unit, the Upper Midwest, and beyond.

2. Progress. The starting date for the grant was August 1, 2006, and the ending date was July 31, 2009; however, the ISMs were sampled through November, 2009. The previous progress report was written in July, 2009. This is the final progress report.

Denitrification measured in D-ISM had a zero-order rate (that is, independent of concentration) of 0.018 mg/L/day ($R^2 = 0.98$) and a first-order rate (concentration-dependent) of

0.00060/day (R^2 = 0.95). Denitrification for the first tracer test in S-ISM had a zero-order rate of (0.0070 mg/L/day (R^2 = 0.84) and a first-order rate of 0.00015/day (R^2 = 0.72). These rates are at the low end of the range for the ISM network we have in Iowa, Minnesota, and North Dakota. Nitrate concentrations in the second tracer test for the S-ISM increased slightly, which indicates that native groundwater diluting the amended water during the test apparently had nitrate in it. Unfortunately, for this reason, the data from the second tracer test for the S-ISM are not helpful.

For the tests that showed denitrification, sulfate concentrations did not increase, which indicates that sulfide (as pyrite) did not serve as an electron donor. Therefore, organic carbon and/or ferrous-iron minerals are the likely source of electrons for the reactions. However, at these low denitrification rates, it is not yet known if there is enough of a denitrification "signature" in the water for geochemical modeling to indicate the likely mix of electron donors contributing to the nitrate reduction.

Analysis of the core samples showed low concentrations of organic carbon (0.13% ± 0.31%, ± 1 standard deviation used throughout), inorganic sulfide (0.033% ±0.046%), and ferrous iron (0.24% ± 0.19%). A subset of 14 samples measured for organic sulfur were all < 0.01%, which was the detection limit. With respect to the electron donor concentrations in the sediments, the nonparametric Spearman rank coefficient test showed the following correlations:

1) Organic C was positively correlated to silt and clay (both at $\alpha = 0.01$).
2) Inorganic S was positively correlated to clay ($\alpha = 0.05$).
3) Fe(II) was positively correlated to silt and clay (both at $\alpha = 0.05$).

Therefore, electron donors tend to be more available in the finer sediment textures. Coupling this finding with others that showed that finer-grained sediments are more reactive suggests that finer-grained sediments at the Iowa site would have a greater denitrification capacity both because of their smaller sizes and because of their greater contents of electron donors.

Incorporation of the results of the two ISMs from the Eastern Iowa Basin Study Unit into the databank of other ISM sites in glacial outwash aquifers in the Upper Midwest is ongoing because more ISM sites continue to be added to the denitrification network. The objective is to correlate dentrification rates with amounts of electron donors in aquifer sediments and to correlate the apparent isotopic enrichment factor for ^{15}N in nitrate versus denitrification rate among of ISM sites. The goal is to develop a nitrate vulnerability index for the Upper Midwest that may be used to extrapolate the findings to similar, unmonitored agricultural and environmental settings.

3. Information transfer. At the project level, communication has been effective; activities have been coordinated with Dr. Paul Capel, Agricultural Contaminants Team Leader. At the regional level, several presentations have been given that included data from the current project. At the national level, Dr. Paul Capel is reviewing a manuscript of our work for review and possible publication in the professional literature, including the possible publication as a USGS paper.

4. Students supported and level of support under the project. Mr. Bijesh Maharjan started on the project on January 1, 2007, as a half-time research assistant with a salary of $1,318/month. Bijesh completed an M.S. in Environmental Engineering in December, 2008. Currently he is a PhD student in Land and Atmospheric Science at the University of Minnesota.