Seasonal Changes of Nitrate Levels on the Decorah Edge Shale

Eric Darsow and Marissa Knodel

Century High School
2525 Viola Road NE
Rochester, MN 55906

Grade 12, Century High School

Advisor: Cheryl Moertel, Environmental Science

Introduction

The research and data associated with this project were done in conjunction with two current studies being conducted by the United States Geological Survey (USGS) in association with Rochester Public Utilities (RPU) and the Olmsted County Environmental Services. This study is located in the Stone Hedge wetland and the purpose of this study was to investigate the behavior of dissolved nitrate contaminants in the groundwater flowing over a graded wetland on the Decorah shale (Lee 1). The USGS and RPU study takes place on one of the sites selected for the Olmsted County Environmental Services project.

The site location is a rare wetland called a calcareous fen, where a high water table causes groundwater to seep out of the aquifer and into the wetland (USGS 239). Beneath the layer of topsoil at this site lies a fifty-foot-thick layer of bedrock called the Decorah shale. The clay-like composition of the shale is impermeable to water, thus forcing water to flow over the surface of the rock rather than percolate deeper into underground geologic layers. This unique geological feature creates an apt environment for the growth of various plant species including black ash, wet meadows, and lowland hardwood forests (USGS 240). The Decorah shale is found in between the upper carbonate aquifer and the St. Peter, Praire du Chien, and Jordan aquifers. Because of the shale's geologic position, on flat ground the shale is not the first encountered bedrock layer beneath the topsoil. However, on gradients created by the bedrock irregularities, the impermeable shale is uncovered due to the angled nature of the geologic formation and becomes the first encountered underground rock formation. This occurrence means that surface water flowing over the shale recharges into deep underground aquifers without first being strained or filtered by the upper carbonate aquifer, as it is on flatter ground. Rochester and surrounding areas draw drinking water from these deep aquifers, making the quality of water on the Decorah shale of high concern to scientists. (Lee 2).

Nitrates are primarily deposited into the groundwater of the Decorah shale by two different processes. The first process involves runoff contaminated by fertilizers rich in nitrates flowing in to the hydro-geologic system of the Decorah wetland. The second means by which nitrates are created is found by examining a process known as the nitrogen cycle. In nature, inorganic nitrogen gas makes up eighty percent of the air we breathe (California Water Quality Control Board 17). Organic nitrogen exists as nitrites, nitrates, or ammonia, and makes up amino acids, the building blocks of protein and DNA (Corbin 1). Atmospheric nitrogen is fixed (changed from N_2 gas into ammonia) by bacteria in the soil. The ammonia is then absorbed up by green plants, which in turn are consumed by animals.

When these animals and plants die and decompose, ammonia is released, which is soon converted to nitrites and then back to nitrates by bacteria (Environmental Quality Board 1). Nitrates are a major health concern because they are common in many farm and household substances. Nitrates are a primary ingredient in fertilizers and other products used on crops and home lawns. High levels of nitrates consumed by humans react with the hemoglobin in blood in a condition called methemoglobinemia. This condition often dubbed "blue baby syndrome" inhibits the cell's ability to transport oxygen and, if left untreated, can lead to serious health problems. (California Water Quality Control Board 18).

The peculiar phenomena observed in previous studies done on the Decorah shale involve nitrate levels being reduced as the water flows over the down gradient (down hill). Nitrates on the up gradient were found to be near ten milligrams per liter, near the limit for drinking water, whereas the nitrate levels on the down gradient were approaching zero milligrams per liter ("Nitrogen Removal or Accumulation Processes" 1). This process of the Decorah shale acting as water quality buffer zone has been documented by several studies involving parties such as the United States Geological Survey and the Olmsted County Environmental Resources department. According to the nitrogen budget for Olmsted County "only about 41% of nitrogen applied each year in upland agricultural areas could be accounted for by agricultural harvests and product exports" (Lee 2). The remaining 59% of nitrates remain in the environment, possibly contained in the soil and in crop runoff. These studies which search for the path the remaining nitrate takes in the environment implicate that somehow along the 200 to 600 foot wooded gradients (slopes) of the Decorah shale, the nitrogen in the water is being removed. The processes taking place to remove the nitrates are unknown, but one of the questions that arose from this observation became the basis for this research project: will groundwater nitrate levels continue to decrease along the Decorah shale as seen during the summer months or will the trends reverse in the fall? (Pieters). Considering that biological processes like photosynthesis are dormant during the winter and decaying leaves could possibly release nitrogen onto the wetland floor, it was hypothesized that the phenomenon of nitrate levels being reduced along the gradient will cease (will remain constant at all sample points on the slope).

Materials and Methods

Water sampling procedures used were aimed at ensuring that each sample was of freshly recharged water and free of contaminants. Samples from October, 2004 were taken in conjunction with the United States Geological Survey. The most accurate samples are taken from water was which recently discharged from the surrounding soil into the test well. This fact required that each well, although filled with water, be pumped dry at least once before actual sample water was collected. The USGS supplied an automatic water pump which removed water from the well continuously through ½ inch tubing. Each well was pumped dry and allowed to recharge until enough water was present to collect the needed samples (2-6 hours). In cases where the well was replenished with groundwater faster than the pump could remove it, three well volumes of water were pumped and then samples were collected.

Samples taken in late November and early December, 2004, were collected using a pipe bailer. This method of retrieval involved dropping and retrieving the bailer, a 24-inch long PVC tube with a ball valve, into the well and pouring the test water from the bailer into the sample containers. After being flushed, wells were allowed to recharge for 24 hours before the final sample water was collected.

All equipment used on all sample dates was washed thoroughly with distilled water to reduce the risk of cross-contamination between sample wells. Each sample container was labeled with the sample location, date, time, and names of researchers collecting the sample. When rain occurred during sampling, care was taken to prevent the rainwater from entering the wells or the sample containers. Ideally approximately 0.6 liters of well water were obtained for testing. In cases where more the recharge time was greater than 24 hours, as much sample water was taken as possible, only allowing for one method of testing to be performed on the sample.

After test water was retrieved from the wells, two independent styles of tests were conducted on each sample. The Olmsted County public water quality lab using a percolation-based anion analyzer conducted the first method of testing. This device reported the levels of nitrate, nitrite, chloride, fluoride, and sulfate present in the sample. The machine measures the speed at which the given ions flow through an 8-inch long cylinder of sand and converts these measurements into concentrations using computer software. The Olmsted County labs held the samples to stringent quality control standards, such as testing several samples twice and comparing the difference between the two values. Results were deemed valid if the duplicate sample was within 5% of the first sample value.

Tests were also conduced in the Melda Scientific laboratory facility using color comparison-based test kits distributed by Hach Laboratory Supply Inc. Tests kits yielded information on the nitrate, reduced iron, dissolved oxygen, and pH levels present in the samples. Procedures used for performing the tests were written and distributed by Hach Inc. Various kinds of laboratory equipment were used in conducting these tests including Erlenmeyer flasks, wash bottles, magnetic stirrer, distilled water, beakers, and pipettes. Both of the testing methods yielded data on the nitrate levels present in the samples, allowing for a quality control comparisons to be made.

All data collected was scanned for obvious testing errors and were compared with data logged previously by the United States Geological Survey (USGS) to verify trends or to locate anomalies. All previously logged data was used with permission from the USGS.

Results

The wells tested were arranged into four transects, or lines, which extend down the face of the gradient as seen in figure 1 of appendix A. As was previously mentioned, this study was an extension of a research project initiated by the USGS. The USGS supplied nitrate data for the April – August tests and are shown in graphs 1-4 as solid, colored lines. This study collected the data for the October and December tests dates, seen on the four graphs as broken lines. Plans have been made to continue testing into late January.

Trends seen on transect one, illustrated in graph 1, are difficult to discern and rather erratic. The October tests showed a significant decrease in nitrate levels, but by December, nearly all the sampling points on the transect showed nitrate levels of zero. It should be noted that elevation change between the up gradient and the down gradient was significantly smaller than the other three transects.

Graph 2, showing nitrate levels observed on transect 2, displayed the nitrate reduction trend with startling precision. This data along with that of transect 4 strongly support our conclusion that the nitrate reduction phenomenon does indeed continue into the winter months. All of the sampling dates, April – December showed a significant decrease in nitrate levels.

Transect three showed similar trends during all sampling dates. The nitrate levels decreased rapidly and were reading zero on the middle of the gradient. The increase in nitrate levels on the down gradient is a peculiar anomaly and will require further study to explain.

The graph of transect four looks visually to be rather inconsistent but upon closer examination shows the nitrate reduction effect with more clarity than any other data set. Nitrate levels in all months except June began at approximately 9 mg/liter on the up gradient, very near the legal limit for nitrate levels in groundwater. On the bottom of the slope, levels were significantly reduced. It should be noted that transect 4 is unique because it begins geographically above the designated wetland and extends into marsh. All three of the remaining transects start and end within the boundary of the wetland. This feature may explain the surprisingly elevated nitrate levels on the up gradient.

Discussion

It was hypothesized that the nitrate reduction phenomenon would halt as temperatures decreased during the winter months. The results indicated that nitrate reduction continued to occur along the down gradient, therefore the hypothesis was not supported. Because biological processes are active above freezing temperatures, it can therefore be assumed that the nitrate reduction phenomenon is largely independent of photosynthetic and bacterial activities.

Data analysis leads to the investigation of other possible sources of nitrate reduction along the Decorah shale. Such sources include temporal (time) differences related to the interflow of water through the shale, seasonal differences and their relation to interflow, dilution or leakage of the groundwater through the shale, and geo-chemical processes such as chemical reactions with minerals or chemicals on the surface of the Decorah shale (Lee Personal Interview).

Interflow is defined by the USGS as the water "within the collluvium that is discharging from the Upper Carbonate Aquifer and recharging the underlying St. Peter, Prairie du Chien, and Jordan aquifers"(Lee 1). The exact time it takes for the groundwater to flow over the Decorah shale before recharging the underlying aquifers is unknown. Yet preliminary estimates leads to the assumption that the groundwater being tested on the down gradient came from the same sources as the groundwater on the up gradient. According to the Olmsted County Environmental Services, if the total flow rate of water over the shale is anything less than ten to twenty years, the groundwater can be assumed to originate from the same source (Lee Personal Interview). Current studies estimate the interflow rate as between several days to up to two years, therefore, temporal differences can be safely ruled out as responsible for the nitrate removal. Since no groundwater sampling has thus far taken place between January and April, it is suggested that the experiment should continue testing seasonal and temporal changes by extending the sampling period from January through April and into the following year.

The chloride and sulfate data corroborate previous USGS studies that so far have ruled out dilution and leakage as sources of nitrate reduction. Graph five shows the sulfate levels present in selected samples. The data fluctuates but does not decrease or increase with regularity. Comparing this data with selected nitrate data displayed in graph six supports the conclusion that rainwater dilution is not the primary reason for the nitrate reduction phenomenon. If dilution had occurred, the sulfate and the nitrate levels would both have showed a distinct decrease in concentration due to the fact that the rainwater would have increased the overall volume of the water containing both ions. Because sulfates are essentially inert in a living system, rainwater dilution would have created this visible decrease in its concentration.

The final source of theorized nitrate reduction is a possible chemical reaction taking place on the surface of the Decorah shale through geo-chemical processes (Lee Personal Interview). Currently, no data or studies are present or have been conducted to test this hypothesis. It is suggested that geo-chemical processes be further looked into as a possible source of nitrate reduction along the Decorah shale.

The fluoride, reduced iron, dissolved oxygen, and pH data did not yield any conclusive results. None of the listed parameters showed distinct trends along the gradient and all values were deemed to be the norm for groundwater within a wetland ecosystem.

In this experiment, two different methods of testing nitrate and other parameters were used. One was a percolation column located at the Olmsted County Public Health Lab, which tested for nitrates, chlorides, sulfates, fluorides, and nitrites. The other consisted of Hach test kits for nitrates, reduced iron, dissolved oxygen, and pH, conducted in the Melda Scientific Laboratories. The results obtained from the Hach test kits did not consistently correlate with the Public Health Lab results or the USGS data, whereas the Public Health Lab results did correlate with current USGS data. The concentrations displayed by the color comparison kits were difficult to discern with accuracy and the reading are subject to fluctuations with changes in lighting, cleanliness of equipment, and age of reagents. Thus the kits were not useful in drawing conclusions from the data.

A possible source of error included the change in sample collection methods from the USGS well pump to the manual pipe bailer. The concern with the change came primarily from the cleaning method used to clear the pipe bailer to prevent cross contamination between well sampling. Contamination of equipment between sampling sites due to weather, and water and dirt residue from previous wells was also a concern. Well recharge time allowed was also a source of error due to the chemical reactions that occur as the water remains stagnant in the well basin. When sampling with the USGS scientists, recharge time varied between two to four hours. During the sampling in December, the wells were given twenty-four hours to recharge. Allotted recharge time was extended in the December tests since less precipitation was occurring.

Conclusion

The hypothesis was that the nitrate reduction phenomenon would halt as the below freezing temperatures of the winter season decreased biological processes such as photosynthesis and other bacterial activity. The results showed that high nitrate levels continued on the up gradient with near to zero levels on the down gradient, thereby not supporting our hypothesis. It can be assumed, therefore, that biological processes are not involved in nitrate reduction along the Decorah shale. A further analysis of other possible nitrate reducing sources produced the hypothesis for future study that geo-chemical processes are somehow involved in removing the nitrate along the down gradient.

Works Cited

Corbin, Katie. "The Nitrogen Cycle: Denitrification." Biogeochemical Cycles. 1 May 1998. 27 September 2004. <http://soils1.cses.vt.edu/ch/biol_4684/Cycles/Denit.html>.

Lee, Terry. "Decorah Edge Groundwater Recharge Area Study Proposal Draft." Olmsted County Environmental Services. 2001.

Lee, Terry. Personal Interview. 11 Dec. 2004.

"Nitrogen Removal or Accumulation Processes." Distributed by Olmsted County Health Department. 26 January 1995.

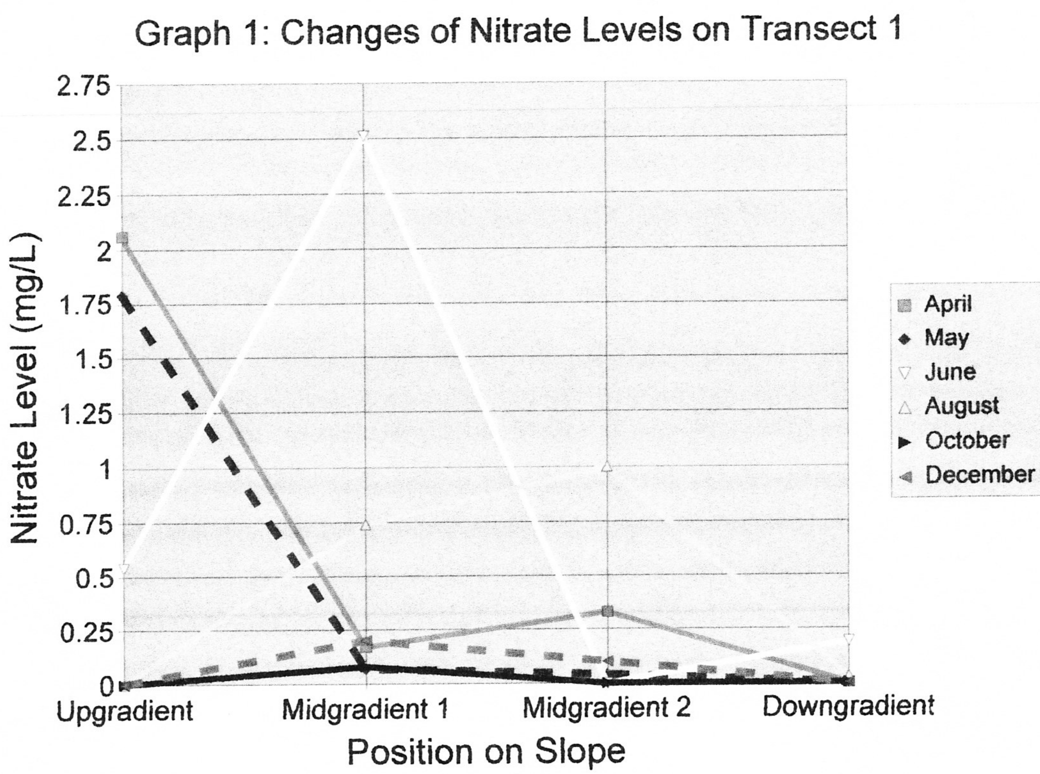
Pieters, Jeffrey. "Decorah Edge testing yields data, questions." Post-Bulletin. 2 October 2004.

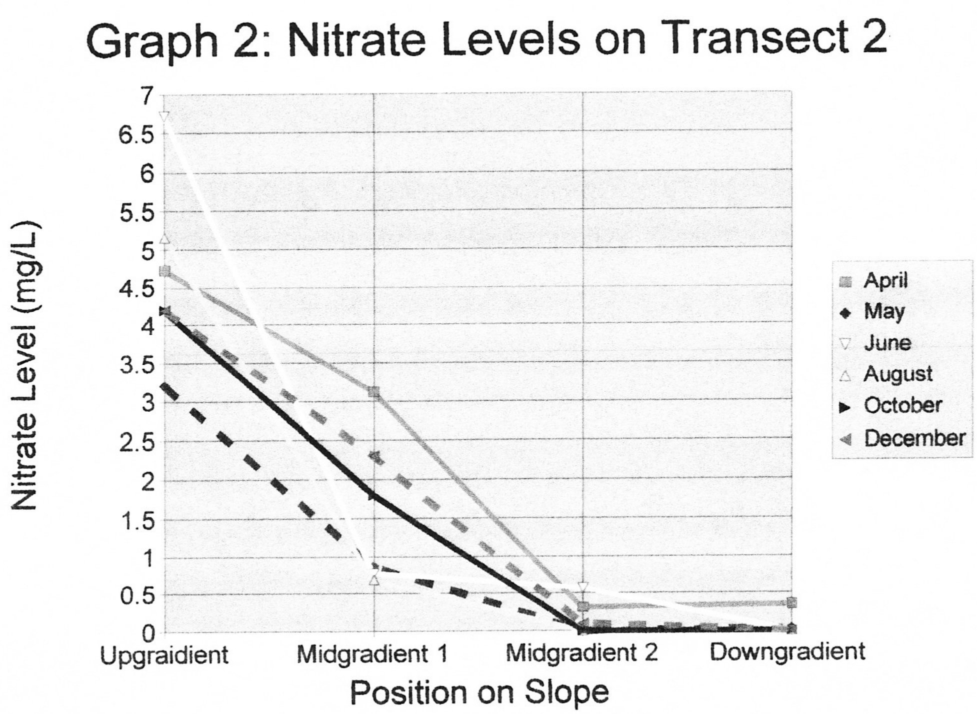
U.S. Geological Survey. Minnesota Wetland Resources.

Water Quality Criteria. Environmental Studies Board, National Academy of Sciences. Washington, D.C., 1972.

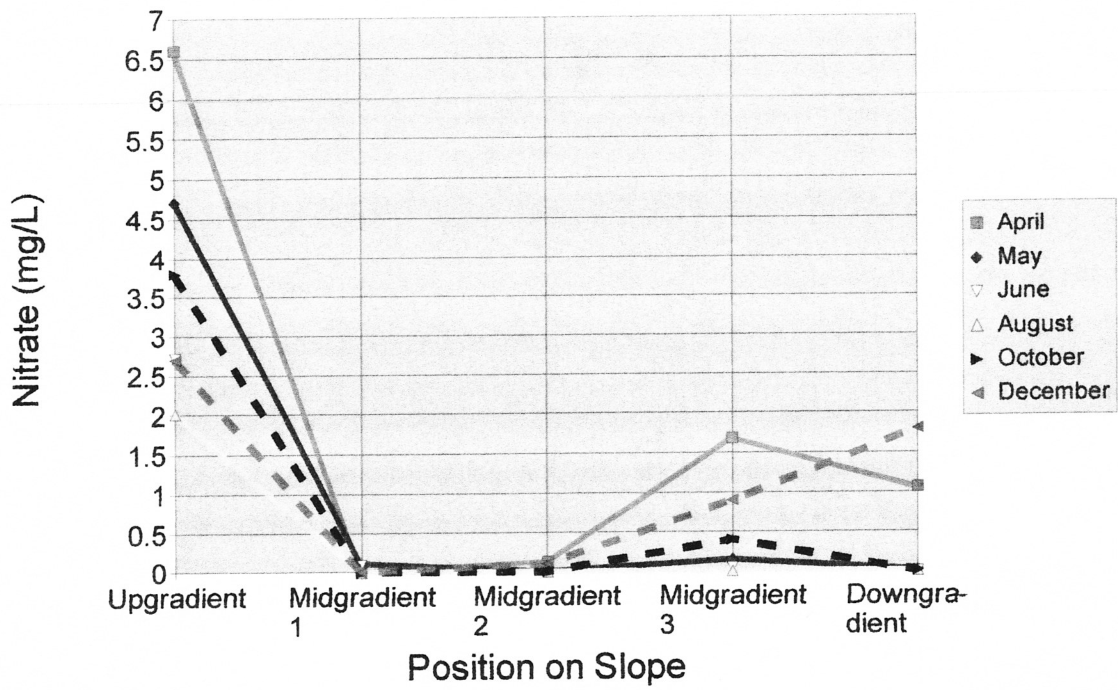
Water Quality Criteria. The Resources Agency of California, State Water Quality Control Board. Publication No. 3-A. 1963.

Appendix A: Graphs of Trends in Groundwater Contaminants





Graph 3: Nitrate Levels on Transect 3



Graph 4: Nitrate Levels on Transect 4