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Can Denitrification Reduce NO_3 in Shallow Ground Water?

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CAN DENITRIFICATION REDUCE NO_3^- IN SHALLOW GROUND WATER?

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INTRODUCTION

Systematic sampling of springs, tiles, and wells in Kentucky, as part of a recent statewide program to assess agricultural impacts on water quality, showed that NO_3^- concentrations in these shallow ground water sources varied tremendously. The NO_3^- concentration could be correlated with flow rate; higher when ground water recharge flushed NO_3^- from soil in winter and spring, and lower or non detectable in summer and fall when less NO_3^- leaching occurred. Depending on the season, NO_3^- concentrations ranged from <1 to >10 ppm NO_3^--N in almost half of the sites. For example, the water in one site, a shallow well over a naturally occurring spring in Bourbon county, varied from 0 to 12 ppm NO_3^--N during the year (Figure 1).

There is an alternative explanation for this variability, an explanation that isn't based on ground water recharge events. An interaction between flow rate and biological activity could explain some of the variability of NO_3^- concentration in this and similar sites. Since the water percolated through a sediment layer in the Bourbon county well before it could be sampled, it seemed likely that biological denitrification (a microbial process in which bacteria convert NO_3^--N to N_2 gas) during low flow periods might account for the low NO_3^- concentrations. When water flow was high, NO_3^- movement through the sediment layer would be too rapid for complete biological removal. We tested this idea by recreating flow-dependent NO_3^- concentrations in a series of laboratory studies.

METHODS

We collected sediment from the spring-fed well in Bourbon county and used it to fill 7-inch-tall PVC cylinders about half full. During an experiment, a 10 ppm NO_3^--N solution was pumped into the bottom of the cylinders at either a fast, slow, or intermediate rate (10 ppm is the maximum allowable NO_3^--N concentration for drinking water in Kentucky). Outflow at the top of the cylinders was analyzed for NO_3^--N, nitrite N (NO_2^--N), and ammonium N (NH_4^+-N). We also used an inhibitor to stop the last step in denitrification, and measured the intermediates that accumulated. Two cylinders were used for each experiment to show that the results were reproducible. Multiple experiments were conducted, and multiple measurements were

taken within each experiment to demonstrate that the trends were consistent.

RESULTS AND DISCUSSION

The NO_3^- concentrations leaving the cylinders in the laboratory varied as they had in the spring-fed well; they were highest when flow rates were highest, lowest when flow rates were lowest, and of intermediate concentration when flow rates were intermediate (Figure 2). Since the NO_3^- concentration in the water supply was constant, something other than flow caused the changes in NO_3^- concentration in the sediment outflow. We assumed that by creating laboratory conditions which reproduced NO_3^--N variability in the spring-fed well, we could also reproduce mechanisms causing that variability.

When oxygen becomes deficient in waterlogged soils (because microbes can consume oxygen faster than it is supplied by flowing water) a biological process such as NO_3^- reduction can occur. The rate of NO_3^- reduction depends on the size and activity of the microbial population, and how long they have access to NO_3^-. If the rate of NO_3^- flowing into sediment was less than the rate at which it was reduced, then NO_3^- concentrations would decline. That's exactly what happened when flow rates decreased (Figure 2). If NO_3^- flow through the sediment exceeded the NO_3^- reduction rate, then NO_3^- concentration should rise; this also happened (Figure 2). As soon as the NO_3^- flow rose to an intermediate rate, the NO_3^- concentration in the sediment outflow increased. It didn't increase to its original level, which meant that some of the NO_3^- was still being reduced.

The NO_3^- could disappear by being converted to NH_4^+. If NO_3^- were reduced to NH_4^+, the NH_4^+-N concentration should have increased as flow rate decreased. However, the NH_4^+-N concentration in sediment didn't change much when flow rate changed (Figure 3) even though NO_3^- concentrations fluctuated.

The NO_3^- could disappear by being converted to N_2 (denitrification). We can't measure nitrogen gas (N_2), the final product of denitrification, as easily as NH_4^+. However, if we found nitrous oxide (N_2O), an intermediate of denitrification which can be detected easily with a gas chromatograph, it would be evidence that denitrification removed NO_3^-. Acetylene (C_2H_2) inhibits N_2O reduction to N_2 and causes N_2O to accumulate. So, if denitrification was the reason NO_3^- disappeared, N_2O would appear in the headspace of the cylinders once C_2H_2 was added, and flow was reduced. Just as we expected, N_2O appeared as soon as we added C_2H_2. Denitrification was clearly involved in NO_3^- reduction in this sediment, and based on the initial and final NO_3^--N concentrations we observed during these experiments, it removed between 60 and 68% of the added NO_3^-.

CONCLUSION

Assessing agriculture's contribution to NO_3^- contamination of ground water has been difficult because of varying NO_3^- concentrations. In addition to fluctuating NO_3^- concentrations due to ground water recharge, some of the variability of NO_3^- concentrations in watersheds could be due to biological denitrification. Our results indicate that when conditions are right for denitrification (for example, low flow, long residence time, poor water recharge and oxygenation, and abundant carbon), NO_3^- in shallow ground water can be reduced if it percolates through saturated layers of sediment.

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Figure 1. Nitrate N concentrations measured in a spring-fed Bourbon County well for 1 year.

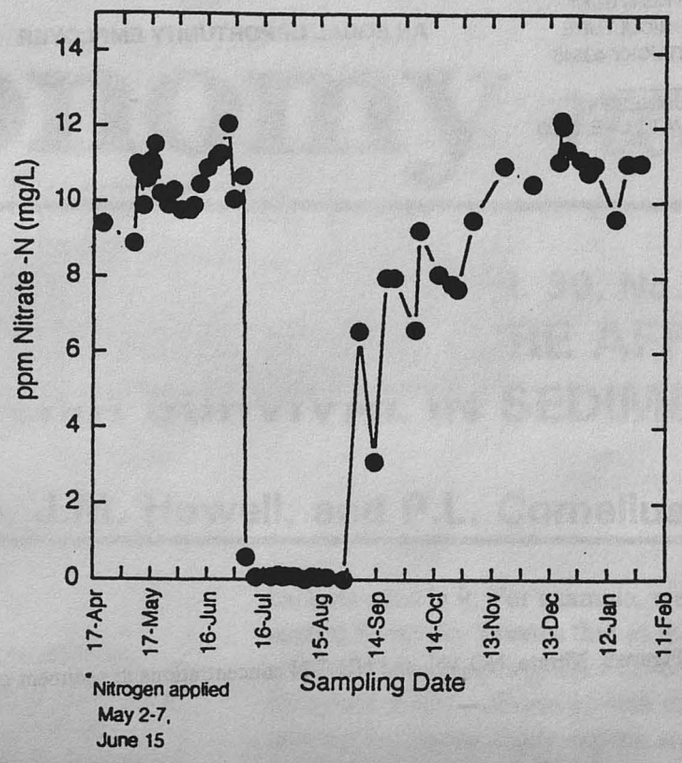

Figure 2. Ratio of NO_3^--N concentrations in outflow and inflow from a sediment with variable flow rates. Arrows indicate when flow rates were changed (fast ⌀_slow ⌀ intermediate) in two replicates (I & II).

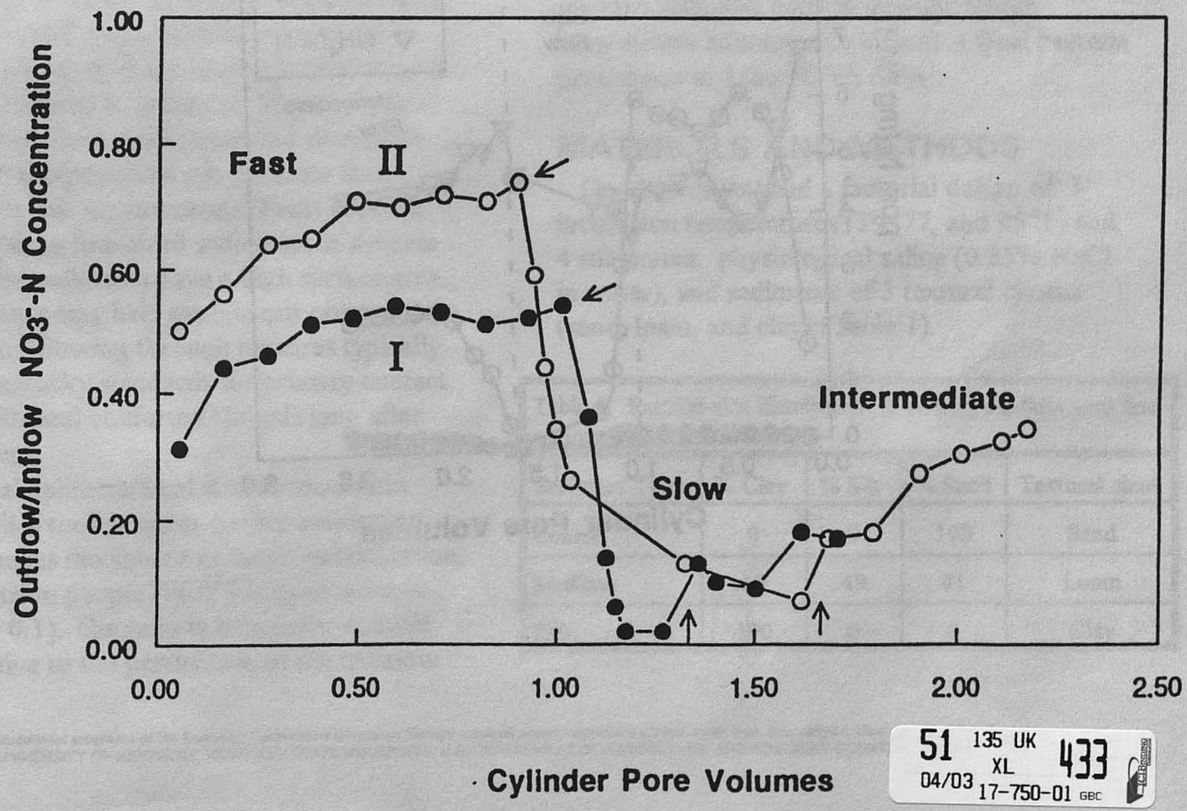

Figure 3. Nitrate, NO_2^--N, and NH_4^+-N concentrations in sediment subjected to variable flow.