Cycling of Sulfur in the Anoka Sand Plain Aquifer and Its Relation to Denitrification

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The fate and transport of agricultural nitrate is of major concern in the Midwest cornbelt, especially where farms are underlain by surficial glacial deposits. To better understand this problem, a multiscale study focused on an agricultural-management system and its impact on ground water. As part of this study, we investigated sources of dissolved sulfate, sulfate reduction, and pyrite oxidation coupled to nitrate reduction along a ground-water-flow path in the Anoka Sand Plain aquifer, Battle Brook drainage basin near Princeton, Minnesota. A sampling transect was designed to parallel the ground-water-flow path and a nitrate plume in the upper surficial aquifer. Ground-water samples were collected from single- and multi-level wells beneath the Management Systems Evaluation Area (MSEA) and from sites further downgradient in an adjoining wetland. Sediment samples were collected from two cores, one beneath the MSEA field and one beneath the wetland. In addition, water samples were collected from domestic wells and streams throughout the drainage basin to provide a regional geochemical datum.

This study identified high amounts of nitrate [up to 80 parts per million (ppm) NO_3] in domestic wells throughout the Battle Brook drainage basin. Most surface waters, however, are relatively uncontaminated. In oxygenated waters beneath the MSEA field, sulfate concentrations and $\delta^{34}S_{SO4}$ values versus depth are related linearly. Because the ground water is stratified, this relation likely reflects the evolution of meteoric recharge water (3 ppm SO_4 and $\delta^{34}S$ value of 8 per mil (‰) sourced from precipitation, fertilizer, and irrigation water) along the flow path. The deepest ground water has 15 ppm SO_4 and a $\delta^{34}S_{SO4}$ value of –3‰. A decrease in nitrate concentrations with depth (60 to 14 ppm NO_3), together with the increase in sulfate concentrations and decrease in $\delta^{34}S_{SO4}$ values, indicate that denitrification occurs along the flow path.

In waters beneath the oxygenated interval, in wetland samples below the nitrate plume, and in wetland samples from the well closest to Battle Brook, redox conditions are sufficiently anoxic (O_2 <1 ppm) to support sulfate reduction. With increasing depth, sulfate is progressively reduced with an isotope enrichment factor of –4.5‰ (estimate of $\Delta_{SO4\text{-}H2S}$). The calculated $\delta^{34}S$ value for the initial sulfate is –2.6‰, similar to that in deeper ground water.

In wetland sediment at the distal end of the nitrate plume, an active denitrification zone has been identified. Within this zone, NO_3 concentrations range from 14 to 55 ppm and are inversely related to dissolved SO_4 concentrations that are greater than 15 ppm (up to 80 ppm). The isotopic composition of the dissolved sulfate ranges from –8‰ to -14‰. Sediment in the denitrification zone contains between 0.17 and 0.60 wt% pyrite that similarly is depleted in ^{34}S ($\delta^{34}S$ -4‰ to –10‰). The pyrite occurs as <2 micrometer (µm) euhedral crystals, 1-2 µm grains aggregated into framboids that are 10-20 µm across, and detrital grains up to 400 µm across. These data and their relations show that sedimentary pyrite, most likely that in the 1-2 µm grains, is an important electron donor in the denitrification process.

Our results and those from collaborative studies on the MSEA nitrate plume show that denitrification coupled to pyrite oxidation occurs along the ground-water flow path and in wetland sediments prior to ground water discharging to the surface. Pyrite oxidation releases sulfate to the ground water. In anoxic ground water, bacterially mediated sulfate reduction further modifies sulfate concentration and isotopic composition. Our understanding of sulfur cycling in the Anoka Sand Plain aquifer and how it relates to the fate and transport of agricultural nitrate in the Battle Brook drainage basin provide a foundation for studying denitrification in other glacial deposits having similar geochemical and hydrologic characteristics.

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