Report for 2001SD1381B: Lipid Geochemistry of Waters and Sediments in a Prairie Pothole Hydrologic System

There are no reported publications resulting from this project.

Report Follows:

Problem and Research Objectives

The Big Sioux aquifer is a shallow groundwater system that supplies water to many municipalities and rural, domestic wells in eastern South Dakota. The aquifer has large storage capacity and very rapid recharge characteristics (1).

Until recently, water quality studies of the Big Sioux aquifer, and the Big Sioux Basin, have focused on the inorganic constituents of the waters. We have conducted a geochemical baseline survey of the aquifer's organic constituents that has shown that dissolved organic carbon (DOC) levels within the aquifer are low, averaging 7.7 mg DOC/L (2). However, we have found that DOC levels in wetlands, lakes and rivers that are hydrologically connected to the aquifer can be as much as 30 times higher. The relatively low levels of DOC in the system suggest that it may be a sensitive indicator of the groundwater's quality. Thus it is vital that the organic geochemistry of this system be understood and modeled.

While we are currently investigating the nature of the humic component of the DOC in the aquifer, and the flux of organic carbon between hydrologic domains (e.g., between surface water and the groundwater, or between soil water and the ground water), the effect of selective sorption of the lipid component (compounds such as fatty acids, fatty alcohols, hydrocarbons, etc.) on the chemical characteristics of the groundwater's DOC to subsurface and aquifer material as it moves from one hydrologic domain to the other, is unknown. This is particularly important since we have shown that natural sorbents such as sand, aluminum oxides and clay minerals can selectively sorb different chemical components of a water's DOC (3, 4, 5).

This proposal addresses two major priorities identified by the Water Resources Research Institute's Regional Competitive Grants Program in their solicitation. First, this study addresses the issue of ground and surface water quality. It fills a significant gap in the knowledge of the water quality of the Big Sioux aquifer by quantifying the DOC flux through the system and identifying sorptive reactions with subsurface materials that control lipid concentrations and geochemistry in the aquifer system. Second, it will investigate the relationship and connections between surface water and groundwater DOC and how the lipid components of the DOC contribute to the movement of organic carbon through each hydrologic domain. Since many organic contaminants (such as pesticides, herbicides, PCBs, or PAHs) rapidly and intimately associate with the organic coatings on mineral surfaces, knowledge of the lipid geochemistry will provide information that may be important in predicting organic contaminant fate and transport in this system. This study will provide a missing portion of the geochemical understanding of organic carbon movement that is necessary to manage this resource, protect the groundwater's quality from degradation from anthropogenic organic substances, and if one day needed, facilitate its remediation.

The comprehensive objectives of this project are to: 1) identify the solvent extractable organic compounds (ie, lipids) present in the water and sorbed to the sediments and aquifer materials using gas chromatography mass spectrometry; 2) perform sorption/desorption experiments using representative lipids (natural and model compounds) and sediment and aquifer materials (minerals isolated from cores and reference mineral specimens) to quantify the binding of lipids to mineral surfaces; 4) assess the importance of sorption to mineral surfaces as mechanism for controlling lipids in the aquifer, and; 5) identify the nature and mechanism of lipid binding to the sediment and aquifer material particle-surfaces suing solid-state NMR and small-angle x-ray and light scattering.

This report covers the first year of what has been proposed as a three-year study whose goal is a comprehensive understanding of the lipid geochemistry of the Big Sioux Aquifer. Completing Objective 1 was the focus of this project year.

Methodology

This site consists of self-contained, permanent/semi-permanent pothole wetland around which we have installed a field of 17 nested groundwater wells. We have recently developed a hydrologic model for this site using MODFLOW (6). The site's geology and hydrology are described in detail by Sumption (6). Sediment cores were collected from the pothole using a stainless-steel corer. Organic-matter-free mineral components was isolated from the sediments using a sequential removal procedure described Malekani *et al.* (7). They have shown that their procedure does not alter the mineral structure or surface.

Portions of the cores will extracted with chloroform. The extract will be concentrated by rotary evaporation. All solvents will be capillary GC grade. Lipid identification was performed using GCMS.

Principal Findings and Significance

A number of interesting lipid compounds were identified (such as saturated and unsaturated fatty acids, and ether-based lipids) in the extracts of the sediment cores. These compounds are potential candidates for use as sorbates in the objectives in the second project year (project Objectives 2 and 3).

It was also observed that the sediment environment is highly reducing; and becomes so within a few millimeters of the sediment water interface. The redox potential is so negative that elemental sulfur was observed in the GC mass-spectra that were recorded. The reducing conditions are almost certainly due to the high organic matter content of the sediment

Student Support

	2001/2002	Total
Undergraduate	1	1
Masters	1	1

References

1. The Big Sioux Aquifer Water Quality Study, State of South Dakota, Pierre, SD, 1987, 338 p.

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3. Vander Vorste, E.*; Rice, J. A., Selective sorption of natural organic matter by mineral surfaces II. Clay minerals, 34th Midwest Regional Mtg., Am. Chem. Soc., October 1999, Quincy, IL, abstract no. 150.

4. Williams, M.*; Rice, J. A., Selective sorption of natural organic matter by mineral surfaces I. Silica and alumina, 34th Midwest Regional Mtg., Am. Chem. Soc., October 1999, Quincy, IL, abstract no. 148.

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6. Sumption, A., 2000, MS Thesis, South Dakota State University.

7. Malekani, K.; Lin, J. S.; Rice, J. A., 1997, The effect of sequential organic matter removal on the surface morphology of humin, Soil Science, 162: 333-342.