Report for 2004SD21B: Coupled Carbon-Nitrogen Geochemistry under Reducing Conditions in a Prairie Pothole

There are no reported publications resulting from this project.

Report Follows

Progress Report
SOUTH DAKOTA STATE WATER RESOURCES RESEARCH INSTITUTE PROGRAM

Coupled Carbon-Nitrogen Geochemistry under Reducing Conditions in a Prairie Pothole

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Introduction

The physical geography of the northern Great Plains region is dominated by small, often transient, wetlands called "potholes". This area is often called the "prairie pot-hole" region. In eastern South Dakota, the potholes are underlain by the Big Sioux Aquifer and are part of the Big Sioux hydrologic basin. The Big Sioux aquifer is a shallow groundwater system that supplies water to many municipalities and rural, domestic wells. The aquifer has large storage capacity and very rapid recharge characteristics (1) primarily through surface water percolation into the aquifer.

There is an extensive literature on the habitat in and surrounding the potholes (2, 3) but relatively little on the chemical and geochemical processes taking place in them. These bodies of water are relatively shallow, well-mixed by wind and as a result, oxic. In the winter, an ice cap forms and the potholes quickly become anoxic. Thus a pothole represents an ideal, closed-system chemical reactor to study the effect of the oxidation/reduction (redox) potential on the geochemistry of an aquatic environment. There is a significant literature that the microbial and abiotic processes taking place differ significantly based on the amount of oxygen available (eg, 4).

Problem and Objectives

The initial hypothesis that will be considered is that more nitrogen is incorporated into organic matter as heterocyclic nitrogen under anoxic conditions that under oxic conditions. The nature and amount of this form of organic nitrogen is an unanswered question, and examining it will represent a significant contribution that this work could make, particularly since we can perform the reactions in a natural, closed environmental chemical reactor. This study will utilize ^{15}N solid-state NMR and gas chromatography and electrospray ionization mass spectrometry to study the differences in nitrogen incorporation into the organic under oxic or anoxic conditions. While these are not easy measurements, they can be done at natural abundances levels on natural organic matter. Nitrogen-15 and carbon-13 isotope ratio mass spectrometry will be used to study nitrogen incorporation into the organic matter using ^{15}N-labeled and ^{13}C-labeled model compounds. In this case, the ^{15}N and ^{13}C isotopes would be very effective, and environmentally safe, tracers to monitor the actual transformations and incorporations of nitrogen into the organic matter.

As originally proposed, this was to be a three-year project. Only the first year was funded. The objectives of the first year of the project are to:

1. determine the annual variation in the redox potential of the pothole.
2. create a nitrogen and carbon mass balance for the pothole.

Methodology

Water samples were collected every other week. An ice auger was used to open the pothole as needed. Samples were collected in 1L glass containers and sealed. The pH and redox potential (Eh) were measured at the time each sample was collected.

Upon return to the laboratory analyzed immediately for total dissolved organic nitrogen (DON) content, ammonia nitrogen, total organic carbon content (TOC). Separate aliquots were used to fractionate into the sample's TOC into hydrophobic and hydrophilic acids, bases and neutrals using the XAD-8/XAD-4 resin procedure (6). Samples were freeze-dried and weighed to construct a mass balance of the TOC among the various fractions.

Solid-state ^{13}C DPMAS NMR spectra were acquired as described by Mao *et al.* (7).

Principal Findings

Figure 1 shows the temporal variation of the pothole water's redox potential (Eh). The Eh rapidly becomes strongly reducing (~-350 mV) (December 29, 2004) when the pothole freezes over. During the course of the following months the ice cover melted and then refroze which explains the increase in Eh and the second minima.

In conjunction with the decrease in Eh, the dissolved organic nitrogen content (DON) increases once the water becomes anoxic (Figure 2).

The water's dissolved organic carbon (DOC) content (Figure 3) tracks the changes in DON with ice-over and transition from oxygen rich to oxygen-depleted conditions. This is not surprising since decomposition generally slows under anoxic conditions.

The ^{13}C DPMAS spectra of the water's DOC fractions (Figure 4) show chemical characteristics typical of these materials (8). ^{15}N CPMAS spectra of the whole DON and the hydrophobic and hydrophilic acid, base and neutral fractions is currently in progress.

Student Support

This project has provided support for field expenses and laboratory supplies for a female graduate student pursuing a MS (December 2004 –present) and a female undergraduate research assistant (summer 2004).

Notable Awards and Achievements

The Eh and DON analyses have shown the rapid transition of the water from oxic to anoxic condition after the pothole freezes. A spike in DON content of the water is observed immediately after the water becomes anoxic.

References

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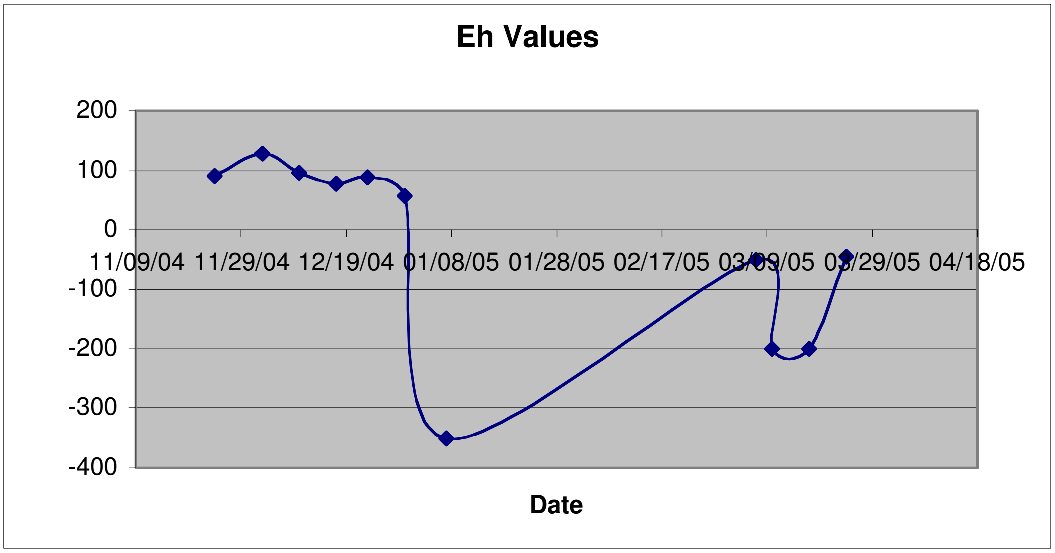

Figure 1. Temporal variation in the pothole water's redox potential (Eh). The pothole was ice covered on December 29, 2004 and during March 2005.

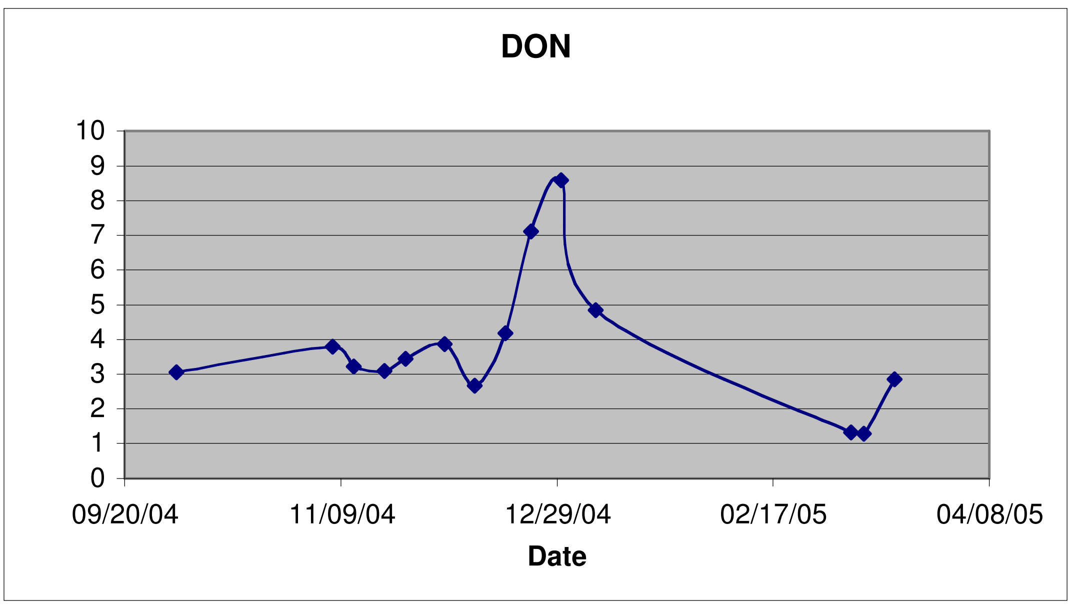

Figure 2. Temporal variation in the pothole water's dissolved organic nitrogen content (DON). The pothole was ice covered on December 29, 2004 and during March 2005.

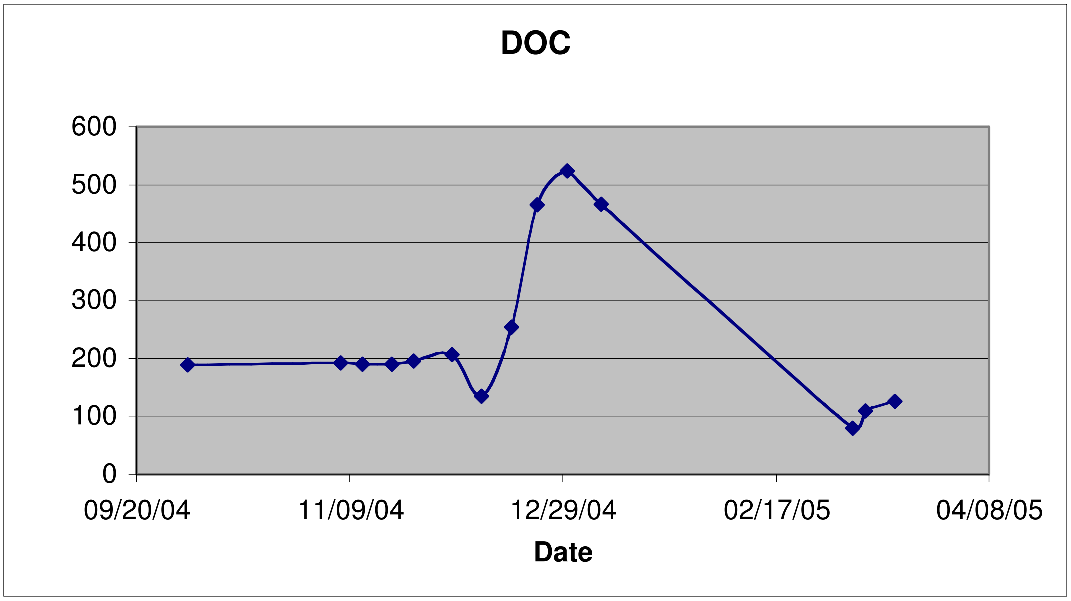

Figure 3. Temporal variation in the pothole water's dissolved organic carbon content (DOC). The pothole was ice covered on December 29, 2004 and during March 2005

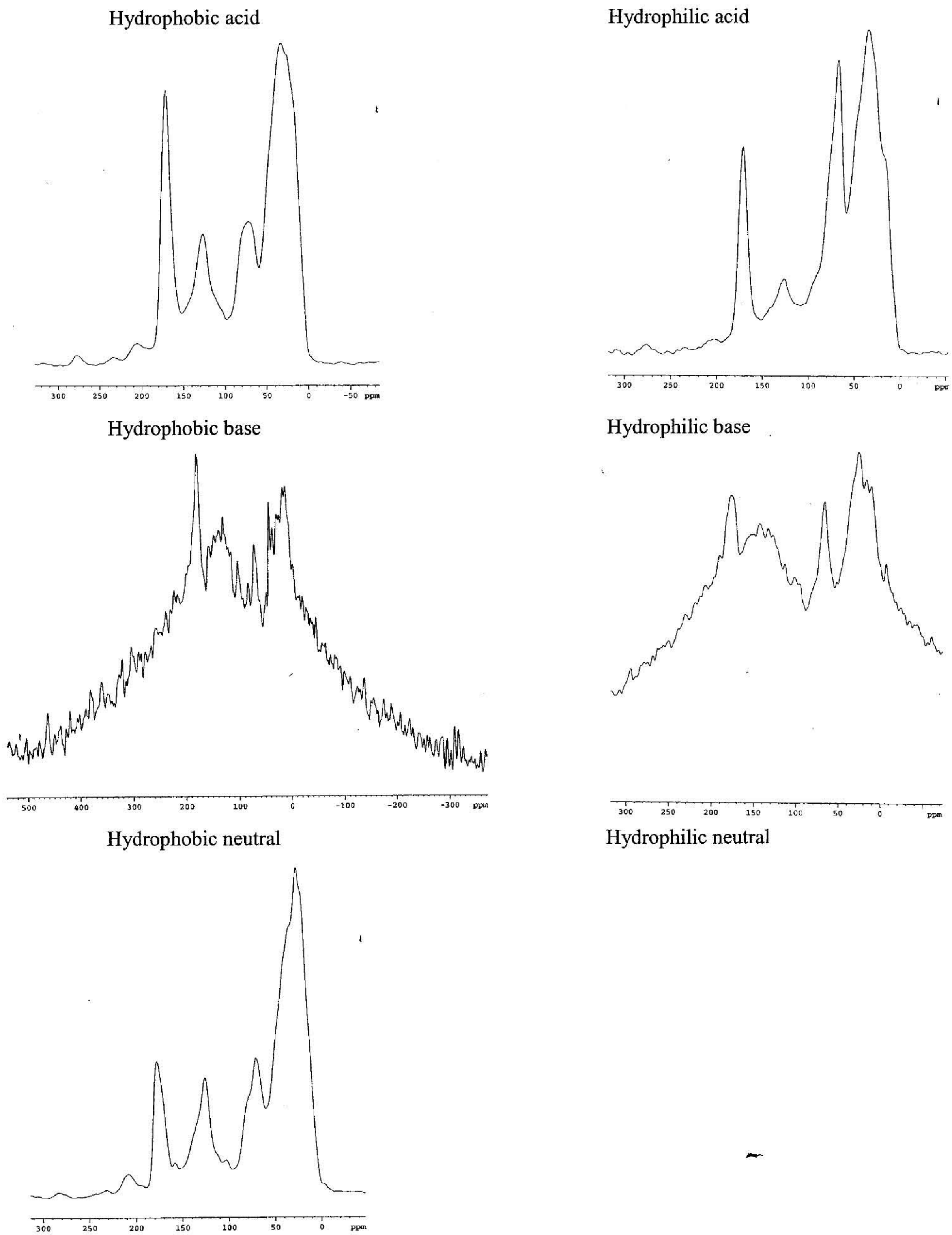

Figure 4. Solid-state ^{13}C DMPAS spectra of the waters hydrophobic and hydrophilic acid fractions. The hydrophilic neutral fraction has not been characterized yet.