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**MECHANISMS CONTROLLING THE PRODUCTION AND TRANSPORT OF
METHANE, CARBON DIOXIDE, AND DISSOLVED SOLUTES WITHIN A
BOREAL PEATLAND**

Progress Report

For Period July 15, 1992 to July 14, 1993

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June 24, 1993

Prepared for

**THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-90ER61013**

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Introduction

The role of freshwater peatlands in the global methane cycle remains uncertain. Most global budgets assume that peatlands are a major source for atmospheric methane although the estimated magnitude of this source varies by a factor of 4 from 40 to 160 Tg CH₄ yr⁻¹ (Mathews & Fung 1987; Cicerone & Oremland, 1988 Aselman & Crutzen 1989; Moore *et al.* 1990). Attempts to refine these estimates face several types of problems. Field measurements of methane emissions tend to be highly variable across a peatland and exhibit sharp seasonal fluctuations. The process of extrapolating these variable measurements to regional estimates is further complicated by rudimentary knowledge of the environmental controls on the production and emissions of methane from peat. In some peatlands the bulk of production is limited to the horizons just below the water table where root exudates are available for methanogenesis. However, in raised bogs significant concentrations of methane have been reported throughout the anoxic portions of the profile (Dinel *et al.* 1988; Brown 1989; Moore *et al.* 1990; Siegel *et al.* 1990; Romanowicz *et al.* in press). . The distribution of methanogenesis within the peat profile will strongly influence the response of methane emissions to potential climatic changes.

The effect of climatic drivers on the carbon balance of peatlands have been particularly difficult to discern. A global rise in air temperatures should elevate temperatures throughout the peat column producing a corresponding rise in the metabolic activity of the methanogens. A warmer drier climate, however, should also lower the water table creating a thicker aerobic zone in which methane may be oxidized to carbon dioxide. Climatic change may also alter the interplay between local and regional components of the groundwater flow-system producing significant changes in the storage and transport of methane within large peat basins. Experimental manipulations of small

peatlands are too limited in scope to detect such perturbations, which may be crucial for understanding the regional linkages among climate, groundwater hydrology, and the carbon balance of large peat basins.

The Glacial Lake Agassiz peatlands of northwestern Minnesota has provided an important opportunity for determining these relationships. These peatlands are situated at the extreme southern edge of the large boreal peat basins that extend across the continental interior of Canada and Alaska. At this southerly location, peatlands are subject to a relatively dry, warm climate with only a slight moisture surplus (Glaser 1987). The regional climate is also punctuated by seasonal and yearly droughts that provide an analog to the impacts of global warming.

During the summers of 1990 and 1991 we conducted a study on the mechanisms for the production, transport, and storage of methane within this peatland region as the regional climate shifted from extreme drought to a period of normal rainfall. This natural experiment provided unexpected insights on the linkages among climate, hydrology, and the methane cycle in large peat basins.

Results of Project Previous Work

In 1990 and 1991 we completed two week expeditions to the Glacial Lake Agassiz peatlands in northern Minnesota to assess the response of the groundwater flow-fields and subsurface-methane pool to climatic fluctuations. After 4 years of extreme drought, the region experienced normal rainfall in June and July of 1991, which significantly raised the water table. We were therefore able to compare data collected under both drought and moist conditions and detect a distinct climatic control on the storage and transport of methane. During the 1991 season, we returned to all the sites we sampled in 1990 and in addition were able to extend our work to several large patterned fens in the northwest and a large bog complex to the northeast. Nests of piezometers were established at each site to determine hydraulic head gradients and to collect samples of pore waters at 50 cm depth intervals. Surface emissions of methane, carbon dioxide, and other gases were

determined at these sites using Plexiglas chambers. In addition, long cores to the mineral substratum were collected using a 10 cm diameter peat sampler. The field expedition was led by Dr. Paul Glaser and Dr. Donald Siegel. Dr. Alan Lazrus from NCAR, Professor J. Chanton from Florida State University, and Dr. Cheryl Kelley of University of North Carolina measured the trace gas emissions and collected gas samples for isotopic analysis by Dr. Stan Tyler of NCAR. Four graduate students (Edwin Romanowicz, Dan Ours, Nat Rutkowski, and Patrick Korths) and one undergraduate student (Michael Stone) worked on thesis-related research projects. The previous season we were assisted by two graduate students (Ed Romanowicz and James McNamara) and three undergraduate students (Daniel Nelson, Bruce Frederick, and Calvin Struck). Sandra Neuzel from the United States Geological Survey in Reston Virginia also assisted in the field work. During the winter and fall of 1992 we obtained seismic refraction profiles within the Lost River peatland under the supervision of Professor George Shaw of Union College.

Dr. Shaw developed new equipment for inserting the geophones into the glacial deposits under the basal peat and thus obtaining a clear signal for the interface between the basal till and bedrock. The profile from the Lost River peatland region indicated considerable topographic complexity that will be used to constrain the computer modelling of groundwater flow-fields and solute transport in the peatlands. In the Red Lake peatland, we confirmed the predictions of Boldt's (1985) that buried bedrock ridges controlled the location of discharge zones for groundwater

Major Results

We observed a dramatic decrease in the pore-water concentrations of methane during the 1991 sampling period compared to the exceptionally high values observed in 1990. Although all the pore waters sampled in 1991 contained significant concentrations of methane, the highest concentration seldom exceeded 30 mg l^{-1} . In contrast, methane exceeded 100 mg l^{-1} in the bog and water track pore waters in 1990. There are two possibilities for Apparently, storage processes predominate during periods of drought

and permit very high concentrations of methane to accumulate. The most likely mechanism is a collapse of the pores associated with the extreme drawdown of the water table during periods of drought. As the de-watered pores collapse under the weight of the overlying forest vegetation it produces a confining layer that traps the methane produced below. We also discovered significant concentrations of methane at depths of 80' within the subsurface till in wells at the periphery of the peatlands. The preliminary investigation of these samples indicate that it is of biogenic origin from its isotopic signature and the ratio of ethane to methane.

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8. Graduate Student Education

The following graduate students have participated in the initial project "Mechanisms controlling the production and transport of methane, carbon dioxide, and dissolved solutes within a large boreal peat basin (Grant No. DE-FG02-90ER61013)." Progress on most aspects of the project has been timely. All data has been collected and all students are in the interpretation and writing stages of the programs. It is anticipated that most of the students will finish their theses and dissertations by the end of the granted period. All the theses and dissertations are being written as papers or a series of papers ready for submission to appropriate journals.

Edwin Romanowicz (PhD), Dissertation title: Hydrogeology and methane transport in the Glacial Lake Agassiz Peatlands, northern Minnesota, anticipated completion date June 1993.

Romanowicz is a major contributor to all aspects of the project, including the field and analytical efforts of the research. He is developing analytical and numerical mathematical models to evaluate and simulate the rate of methane production and the mechanisms for methane transport in peat. He is designated for the Post Doctorate position in future because of his expertise and to maintain continuity in the project. He is author and co-author of numerous abstracts and has a major paper already in press (see list of publications).

Yiping Shen, (MS), Methane storage, vegetation communities and water quality, Lake Agassiz Peatlands, Northern Minnesota, anticipated completion date June 1993.

Shen is conducting extensive multivariate statistical tests to test the hypothesis that different vegetation landforms may be related to their methane pools in storage. Her work also includes calculation of the amounts of methane in storage during sampling times 1990 and 1991. Volume modeling of methane storage was done using GIS based approaches. She is senior author of a paper presented at a meeting of the American Geophysical Union (see list of publications).

Nan Rutkowski, (MS), Trace element geochemistry of bog peat, Glacial Lake Agassiz Peatlands, Northern Minnesota, anticipated completion date June 1993.

Rutkowski has extended Hill's work in the Lost River Peatland to four other bog-fen complexes. Her data will be used in conjunction with Pat Korth's work to regionally determine the hydrogeologic controls over whether the hydrogeologic system of major bogs is sensitive to drought conditions. She is coauthor of several abstracts of papers presented at AGU.

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Juho So, The geochemistry of peat pore water, Lake Agassiz Peatland, Northern Minnesota, anticipated completion date June 1993.

So is evaluating the chemical controls over pore-water chemistry in the peatlands, paying special attention to acid-base chemical reactions that occur when ground water mixes with organic-acid rich surface water. He will be using chemical equilibria modeling to evaluate mixing and water-peat-mineral reactions, especially involving the carbon and sulfur systems.

Mike Stone (BS), Relationship between sedimentological characteristics of mineral substrate under bogs and fens and their hydrogeologic function, BS These, completion June 1993.

Stone is a senior geology major who presented his initial results at the 1992 National Geological Society of America. His research, coupled with seismic stratigraphic work by Dr. George Shaw (Union College), is critical to determine the hydrogeologic controls over bog formation in the peatlands, and will be incorporated in numerical models by Romanowicz to evaluate methane transport in the peat.

Dan Ours (MS), The effects of ligands on the effective porosity, dispersivity and hydraulic conductivity of peat, anticipated completion date June 1993.

Ours has discovered that peat dilates as a function of the chloride concentration. His data on the effective porosity and dispersivity of peat are the first available. The dilation phenomenon is the first evidence that chemical processes can cause secondary porosity in peat, enhancing the transport of methane through the peat column.

9. Collaborative Studies

The results of the field season in 1990 were so unusual that we invited several other researchers to collaborate with us on certain aspects of the project.

Dr. George Shaw, Union College.

Dr. Shaw received NSF funding to conduct seismic geophysical surveys in parts of the peatland to determine the topography under raised bogs. This work, the first ever done in mires, was successful. His results set important bounding conditions on groundwater flow models that are being prepared.

Dr. Jeff Chanton (Florida State University)

Dr. Chanton, an internationally respected research in methane isotopic systematics, has collaborated with us and obtained isotopic data on dissolved methane and carbon dioxide and these gases in chamber experiments. These results will be integrated with calculations of gas flux based on modeling the gas profiles in the peat.

Dr. Stan Tyler and Dr. Alan Lazarus, National Center for Atmospheric Research.

Drs Tyler and Lazarus participated in obtaining gas flux data in 1991 from chamber experiments, and will be involved in the interpretation of the data with Chanton and the PIs.

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10. Major Research Accomplishments

10.1. Objectives

The objectives of the project "Mechanisms controlling the production and transport of methane, carbon dioxide, and dissolved solutes with a large boreal peat basin (DE-FG0290ER61013)" were to determine if

1. the production of methane and carbon dioxide in peat is related to the botanical composition of peat derived from different peat landforms, temperature, and pore-water chemistry.

2. the transport of solutes and gases within a peat profile may be controlled as much by ground water as by chemical diffusion

10.2. Results for Objective 1.

The approach of study that was proposed was based upon the fundamental understanding (e.g. Siegel, 1981, 1983) that bogs were local recharge areas for ground water flow (downward flow) and that adjacent fens were local discharge zones (upward flow). Where ground water moved downward, methane transport upward would be inhibited; where groundwater moved upward, methane transport would be enhanced.

During 1990, when we sampled the peatlands at the end of the worst drought in 100 years, the following observations were made that changed the paradigm for mire hydrogeology.

- 1. Water table mounds had dissipated and all bogs were sites were located over site of pronounced regional ground water discharge, or upwelling.** Furthermore, observations of hydraulic head showed that fens throughout the peatland were **not** areas where groundwater discharged upward, but rather areas where ground water moved horizontally away from the bogs. These observations are in direct conflict with the standard concept of peatland hydrology that raised bogs are virtually divorced from regional groundwater flow and that fens are sustained by direct groundwater discharge (e.g Ingram 1983). Indeed, raised bogs in the Glacial Lake Agassiz region appear to have formed *only* where groundwater discharge sustains deep peat saturation. Based on these

results, a new hypothesis for wetland succession in mires has been proposed wherein raised bogs must form over raised fens (McNamara et. al, in press; Glaser et. al, in prep.)

2. Concentrations of dissolved methane were highly supersaturated (relative to 1 atm pressure) deep in the peat column. Indeed, methane discharged from monitoring wells under pressure at most bog locations in August 1990 and September 1992. Calculations of the methane pressure in zones from 1-2 meters beneath the water table were over 2 atmospheres pressure. Ground water at depth was near freezing (about 5-6 degrees centigrade), and the large amounts of methane were anomalous. The hydraulic and methane observations suggested that neither vegetation landforms nor temperature may affect methane production at depth.

The highest concentrations of methane appear to be associated with a change in the pH of the pore water from less than 4.5 to greater than 5.5. This change is caused by the mixing of surface water recharge with the upwelling base-neutral water from the underlying mineral soils. Increasing $\delta^{13}\text{C}$ of dissolved inorganic carbon suggests that the methane is associated with the reduction of dissolved carbon dioxide contributed by the ground water. This hypothesis needs to be further tested by additional data.

3. The temperature and botanical properties of the peat were not significantly related to the observed pore-water concentrations of methane. Despite the reported temperature dependence of the methanogenic bacteria, we observed very high concentrations of methane in 1990 at depth where the temperature ranged from 10° to 5° C. The botanical properties of the peat seem to be more important in determining the efficiency of methane transport through the peat column rather than limiting the rate of methanogenesis. Very high concentrations of methane were observed from zones with both *Sphagnum* and sedge peat. We are now analyzing the C:N:P and lignin and organic chemistry of the peat to determine its suitability for anaerobic decomposition.

10.3. Results for Objective 2.

In 1991, we returned to resample the peatlands for methane to obtain additional isotopic data. After 4 years of extreme drought, normal rainfall during June and July of 1991 had re-established the water table mounds on the raised bogs. Hydraulic measurements showed that the direction of groundwater flow at most bogs was downward throughout the peat column to the underlying mineral soil (in accordance with predictions). However, all the overpressured zones of methane had dissipated. This observation is counter intuitive: the downward movement of groundwater should inhibit the rapid release of methane to the atmosphere.

Peat landforms are known to expand with increasing pore pressure, a process known as "mooratmung" or bog-breathing (Ingram 1983; Almendinger *et al.* 1986). Our observations suggest that the resaturation of the peat may also expand the peat pores increasing the effective porosity to the extent that methane bubbled out, probably fairly quickly. Preliminary experiments made to determine the material properties of peat (effective porosity and dispersivity) that govern mass transport showed that peat pores also expand when chloride enters the system--a chemical process previously unknown.

Future work on methane transport from the wetlands must include the effect of transient release of large amounts of methane stored in the peat. Subsequent observations a year later, in 1992, showed that in some places methane at 1-2 m depth again was over pressured. This indicates that episodic methane release from deep peat occurs, perhaps on a yearly basis. Mathematical modeling is being done to determine the rates of methane production, and methane transport by diffusive, advective, and bubble processes under both dry and wet conditions.

10.4. Pathways for Methanogenesis

Isotopic analysis of the methane indicates that it is mostly produced by biogenic processes. The $\delta^{13}\text{C}$ for most methane samples ranges from about -75 to -55 ‰ (PDB). In contrast, increasing values for the $\delta^{13}\text{C}$ of dissolved inorganic carbon with depth indicate that some of the methane is generated by carbon dioxide reduction at depth

where ground water is penetrating into the peat column. Most δD of the methane ranges from about -290 to -260 ‰ (SMOW), again consistent with that expected from biogenesis of methane (Figure 7). In 1991, twenty measurements of the isotopic content of methane and carbon dioxide were obtained from air samples collected from chambers placed over selected vegetation plots near the piezometer clusters located on the major bogs and adjacent fens landforms. These data are being analyzed in conjunction with the isotopic data from pore-water methane to quantify isotopic fractionation as methane is oxidized in the unsaturated zone and to determine how much deep methane is being released to the atmosphere.

10.5. Paleomarkers for Groundwater Flow

Peat cores from the major types of peat landforms have been analyzed for major and minor metal concentrations (Ca, Mg, Na, Fe, Mn, Sr, and Si) at 10 cm intervals. Preliminary results suggest that the metal content of the peat may be useful to determine the long-term hydrologic function of the bogs and the extent to which their water table mounds recharge dilute and acidic surface water into the peat and underlying mineral soil (Hill & Siegel 1990; Bennett *et al.* 1990). From this work, we anticipate being able to regionally evaluate where bog water table mounds persist during droughts and what factors govern the recharge-discharge function of the bogs. This information is critical to determine the extent to which methane is transported from the deeper peat of raised bogs by advective flow.

10.6. Physical Constraints on Methane Transport

The transport of methane and solutes through peat deposits is greatly influenced by several material properties of the peat, such as its vertical hydraulic conductivity, dispersivity, and effective porosity. All these properties explicitly are part of Darcy's Law, which governs advective transport and mixing (dispersion). We used the standard field methods described by Chason and Siegel (1987) to obtain values for the hydraulic

conductivity of peat at 50 cm intervals throughout the peat column at each piezometer site. Hydraulic conductivity is on the order of 10^{-5} to 10^{-4} cm/s.

Virtually no published data exists on either dispersivity, a measure of the three-dimensional structure of interconnected-pore spaces (tortuosity) and the effective porosity, the amount of interconnected pore spaces. During 1991-1992, laboratory experiments were conducted using Darcy-type permeameters (e.g. Freeze and Cherry, 1979) on 1 m peat cores to determine the dispersivity and effective porosity. In these experiments, water with known chloride concentration was passed through the peat column. How the chloride "front" reaches the bottom of the core (the "breakthrough" curve) is used to determine the effective porosity and dispersivity (Freeze and Cherry, 1979). The effective porosity of the humified peat (about 30 experiments) ranged from about 0.1 to 0.2, and the dispersivity was on the order of a few cms. These values are comparable to that for medium mineral sand. In contrast to sand, however, the hydraulic conductivity of the peat *increased* by as much as 300% as concentrations of chloride were changed from 100 ppb to several hundred ppm. Preliminary evaluation of this previous unknown phenomenon suggests that the pore spaces enlarge in the peat column because of a chemical interaction of Cl^- with the boundary-layer water sorbed to the peat and organic functional groups related to the decomposing peat fibers. The preliminary results of this work suggest that groundwater discharging into the base of peat can enhance the material properties of the peat as it passes through it.

10.8. Analytical Modelling of Methane Transport and Production

The observed CH_4 profiles were first modelled conservatively, assuming that methane is neither produced nor consumed within the peat column. This model is modified from Martens and Berner (1977) and is a 1-D analytical solution for diffusive transport accompanied by peat accumulation. It includes terms for the rate of peat accumulation and the diffusion coefficient for methane. The rate of peat accumulation at these sites will be independently determined by techniques described below, whereas

the diffusion coefficient for methane will be determined from the literature. The CH₄ profiles were also modelled with a zero-order reaction term. These production values were obtained by fitting the observed data to the mathematical expression using the production rate as a variable. The preliminary results for both years 1990 and 1991 are shown in Figure 8. The calculated methane production rates will be incorporated as source terms in analytical models for diffusive and advective methane and solute transport. Numerical models will be used to bracket the expected range in groundwater velocities that could occur in the complicated flow-systems that develop under these raised bogs.

10.9. Regional Scaling

The amount of methane in storage in 1990 and 1991 was calculated using GIS techniques and computerized volume average methods. The preliminary results suggest that from about 30 to 120 Gg of methane was stored in the peat column during the drought in 1990, while only about 30 Gg remained after the drought in 1991 (Siegel et. al, 1992). This difference reflects the magnitude of methane loss from the peat during the intervening time. It is hypothesized that as the upper peat resaturated with spring rains in 1992, it expanded. Because the peat is a fibrous, interconnected porous media, it is possible that the expansion of the upper part was translated deep within the peat column to open up the effective porosity and enable the methane to quickly ebullate from the system. This hypothesis is being tested as a major part of the renewal effort.

10.10a. Publications (journals)

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10.10b. Book Chapters

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- Glaser, P.H. 1992. Development of patterned peatlands. In H.E. Wright, Jr. and B.A. Coffin (eds.), *Patterned Peatlands of Northern Minnesota*, University of Minnesota Press, Minneapolis, pp. 27-42.
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10.10c. Manuscripts (submitted)

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10.10d. Abstracts

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