Modeling soil climate controls on the exchange of trace gases between the terrestrial biosphere and the atmosphere

Stephen Edward Frolking
University of New Hampshire, Durham

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Modeling soil climate controls on the exchange of trace gases between the terrestrial biosphere and the atmosphere

Abstract
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Principal controls of biological denitrification in mineral soils are the availability of carbon and nitrogen substrates and the soil anaerobic status. A process-oriented model of decomposition and denitrification in soils (DNDC) was modified to have a more detailed portrayal of these controls. In particular, a diffusive soil gas phase was added, along with a method for determining anaerobic and aerobic fractional volume within a soil profile. The model generally overestimated N2O fluxes when compared to field data from a sandy soil in Costa Rica, but captured the timing and shape of the brief flux episodes. Several modeling shortcomings are discussed, including the nature of the carbon substrates and the nature and dynamics of soil anaerobic fractional volume.

Methane flux from wetland soils is generally correlated with soil temperature and depth to water table. A model of peat soil climate was developed and applied to a small, poor fen in southern New Hampshire. Temperature profiles and ice depth are in good agreement with field data, but depth to water table is more problematic. Field-based flux correlations to soil temperature, depth to water table, and weighted recent precipitation were developed. When used with the wetland soil climate model, much of the seasonal and shorter period flux variability was captured. The model was then driven by local weather data for 1926-1986; flux variability was dependent on both summer season temperatures and summer precipitation patterns. It is estimated that a five-year field study would capture most of the inter-annual variability.

Sensitivity of northern peatland methane flux to climate variability was studied by combining data on flux rates, inundation areas, and summer temperature anomalies (1900-1986) for the eight major northern peatland regions. Spatial and temporal variability in summer temperature anomalies caused regional methane flux anomalies to be small, and not likely to provide a strong feedback to initial climate change.

Keywords
Biogeochemistry, Physics, Atmospheric Science

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Modeling soil climate controls on the exchange of trace gases between the terrestrial biosphere and the atmosphere

Frolking, Stephen Edward, Ph.D.
University of New Hampshire, 1993
MODELING SOIL CLIMATE CONTROLS ON THE EXCHANGE OF TRACE GASES BETWEEN THE TERRESTRIAL BIOSPHERE AND THE ATMOSPHERE

BY

STEPHEN E. FROLKING
B.S., University of New Hampshire, 1980
M.S., University of New Hampshire, 1983

DISSERTATION

Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy in
Earth Sciences

December, 1993
This dissertation has been examined and approved.

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Berrien Moore, III, Director, Institute for the Study of Earth, Oceans, and Space

Martin A. Lee, Professor of Physics

28 Oct 1993
Date
This dissertation is dedicated with admiration to

Bob Harriss and Changsheng Li

and with love and admiration to

Joanna Wicklein
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My apologies (and thanks) to anyone I've neglected to mention. Feel free to add your name below.
PREFACE

The overall theme of this dissertation is to examine the control that soil climate has on trace gas fluxes from the soil to the atmosphere, and to consider the potential for feedbacks between changes in the climate system and the terrestrial biosphere. The dissertation is in two sections, each focusing on a different gas and ecosystem. Both sections include models of soil climate driven by the weather at the ground surface. References are grouped at the end of each section.

Section One - Nitrous Oxide Flux From Tropical Upland Soils

Chapter 1 - A Review of Denitrification Models

The principal controls on denitrification are soil oxygen status and substrate (nitrate and soluble carbon) availability. This chapter reviews a number of recently published models of denitrification, and compares how they treat these primary controls.

Chapter 2 - A Revised DNDC Model: Description, Sensitivities, Calibration, and Validation

This chapter describes the revisions to the DNDC model. First, improvements to the soil climate component of the model are described and tested against field data from Costa Rica. Second, revisions to the biogeochemistry component of the model are described. These revisions are intended to improve the model's treatment of the soil's physical environment and its controls on denitrification. This revised model is then tested for its sensitivity to external (i.e., site specific) variables, and to its internal

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(i.e., model specific) parameters. The model is then calibrated against three field studies in temperate and sub-tropical grasslands, as well as against the original DNDC model. Finally, the revised model (and the original DNDC model) are used to simulate a detailed field study from an experimental plot in Costa Rica.

Chapter 3 - Summary and Conclusions

This chapter summarizes the results of Section 1, and makes some suggestions for future research.

Section Two - Methane Flux from Northern Wetlands

Chapter 4 - A Model of Northern Peatland Soil Climate and Methane Flux

This chapter describes a detailed model of peat soil climate (temperature profiles, depth to water table, unsaturated zone water content, and ice thickness). The model is validated against data from a small fen in southeastern New Hampshire. Using correlations between methane flux and peat climate for this same site, the model is used to predict daily methane flux from the fen. This tests the control of peat climate (and precipitation in this case) on the observed variability of methane fluxes—both the strong seasonality, and the high degree of variability within a season.

Chapter 5 - Modeling the Sensitivity of Methane Fluxes to Climate Variability in Both Space and Time

This chapter has two parts. In the first the model of the previous chapter is used with historical weather data from Durham, NH, to examine the sensitivity of methane flux from a single site to local climate variability. In the second part, a simpler model is used to examine the sensitivity of methane flux from all northern
peatlands to temperature variability, again using the historical record, but this time for the entire northern half of the northern hemisphere.

NOTE: Copies of the models used in this thesis are available upon request, either on disk or on paper. These models will be evolving over the next few years, but I will archive the versions used for the dissertation. The models are:

- Model of wetland peat soil climate (FORTRAN) [Chapter 4];
- Model of upland mineral soil climate (QuickBasic) [Chapter 2];
- Revised DNDC model (QuickBasic) [Chapter 2].
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temporal variability in summer temperature anomalies caused regional methane flux
anomalies to be small, and not likely to provide a strong feedback to initial climate
change.
CHAPTER 1

A REVIEW OF DENITRIFICATION MODELS

1.1. Introduction

The atmospheric concentration of nitrous oxide (N2O), a long-lived greenhouse gas, is increasing at a rate of about 0.3% per year (Prinn et al 1990). The soils of terrestrial ecosystems are the major known source of N2O to the atmosphere, and tropical soils dominate current budgets (Davidson 1991; Matson and Vitousek, 1990). Land conversion in developing, often accompanied by N-fertilizer use (about 50 Tg N/yr—Vitousek and Matson 1992) is considered to be a major contributor to the increased atmospheric N2O over the past 50 years (Prinn et al 1990; Matson and Vitousek 1990).

Global budgets of N2O flux to the atmosphere are only poorly known, and current estimates of sources and sinks are not in balance (e.g., Davidson 1991). Only a combination of modeling studies and extensive field work can improve these estimates. The insights and questions raised by process-oriented models can focus field campaigns on regions and seasons that are significant contributors, and on processes that are important controls of the magnitude of fluxes.

Nitrous oxide is an intermediate product in microbially mediated nitrogen transformations in soil—both during nitrification under aerobic conditions and during denitrification under anaerobic conditions (Firestone and Davidson 1989). The “leaky pipe” conceptual model of Firestone and Davidson (1989) shows two levels of control on the rate of gaseous N loss from soils (N2O, NO, and N2) during these processes: (1) the rate of nitrogen flow through the pipe—i.e., the rates of nitrification and denitrification; and (2) the size of the leaks in the pipes—i.e., the partitioning of
reacting N-species into dinitrogen (N2), nitric oxide (NO), and N2O, and their efflux from the soil before further reactions occur. Numerous interacting factors affect both of these controls on N2O flux from the soil to the atmosphere (for a recent review see Williams et al. 1992).

It is generally agreed that the principal factors controlling biological denitrification and associated N2O flux from soils are: (1) oxygen status—if the soil solution in the vicinity of potential denitrifiers is sufficiently aerobic denitrification will not occur; (2) organic carbon substrate—an energy source for denitrifier metabolism; (3) nitrate (and nitrite and nitrous oxide)—electron acceptors or oxidants when oxygen is unavailable; and (4) denitrifying organisms (e.g., Firestone 1982). Unless these four factors are present, significant biological denitrification cannot occur. Denitrifiers are ubiquitous in soils, although their fraction of the total soil microbial biomass varies (Focht and Verstraete 1977). Although additional factors (temperature, pH, soil texture, land use/land cover) all affect the activity of denitrifiers and denitrification end products, they are of secondary importance except under extreme circumstances (e.g., Robertson, 1989).

Robertson (1989) has developed a more intricate conceptual model of the controls on denitrification (see Fig. 1.1). At the most proximal level (the microbial cellular level), oxygen status or degree/extent of anaerobiosis is the dominant control, with carbon and nitrate substrates of secondary importance. A level more distant, soil climate (H2O/temp in Fig. 1.1) is the most important control on all three of these immediate factors. To understand the dynamics of denitrification, one must understand the dynamics of soil climate and the nature of its controls on substrate availability and the anaerobic status of the soil.

Field measurements of denitrification (either as nitrate lost or N2O or N2 + N2O evolved) show it to be highly variable in both space and time. Folorunso and Rolston (1984) report high spatial variability in a single, apparently uniform field.
Figure 1.1 - Conceptual model of the factors and processes controlling denitrification in soils. Level of regulation is based on "distance" from the bacterial cell (horizontal axis). At each level, factors are ordered in a hierarchy of importance (vertical axis). From Robertson (1989).

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(coefficients of variation of 282 to 379%). A variety of time series measurements show N2O gas flux to have episodic peaks, generally associated with soil wetting, that appear to contribute a large fraction of the total N2O evolved from the soil (e.g., Brumme and Beese 1992; Mosier et al 1991, Johnsson et al 1991; Vitousek et al 1989; Grundmann and Rolston 1987, Sexstone et al 1985b). The challenge for process-oriented models of denitrification is to describe the dominant controlling factors and their dynamics in a general framework that will allow the model to be applied to a variety of sites or circumstances.

1.2. Modeling Approaches

Over the past decade a number of different denitrification models have been developed. Some are components of larger models of N (or C and N) cycling in soils; some are stand-alone models investigating particular details of the process or focusing primarily on trace gas emissions. All assume denitrifying bacteria are present in all cases.

1.2.1. Nitrogen Substrate.

Interest in denitrification stems from two concerns—ecosystem (and particularly agro-ecosystem) nitrogen budgets and trace gas (particularly N2O) emissions to the atmosphere. Denitrification is a key element in the biogeochemistry of nitrogen, returning N to the atmosphere and completing a loop begun by nitrogen fixation. Nonetheless, nitrogen substrate calculations are probably the least problematic of the three principal controls. Most important, there is a vast literature on nitrogen cycling in soils to form the foundation of any model development and parameterization (e.g., Stevenson 1982). In addition, inorganic N compounds (principally nitrate and ammonium) are simple ions that will be identical from one ecosystem to the next, and their behavior in the soil matrix, while complicated somewhat by adsorption and leaching, is comparatively straightforward. In fertilized
Table 1.1 - How recent denitrification models treat nitrogen substrate controls.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Treatment of Nitrogen Substrate Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li et al 1992a</td>
<td>N-mineralization and nitrification calculations supply nitrate. Denitrification sequence (nitrate -&gt; nitrite -&gt; nitrous oxide -&gt; dinitrogen) determines N2O and N2 production.</td>
</tr>
<tr>
<td>Smith 1980 and 1990; Arah 1990</td>
<td>Nitrate concentration supplied as initial condition. Total denitrification (N2O + N2) calculated as function of nitrate concentration.</td>
</tr>
<tr>
<td>Johnsson et al 1991</td>
<td>N-mineralization and nitrification calculations supply nitrate. Total denitrification (N2O + N2) calculated as function of nitrate concentration.</td>
</tr>
<tr>
<td>Grant 1991</td>
<td>N-mineralization and nitrification calculations supply nitrate. Total denitrification (N2O + N2) calculated as function of nitrate concentration.</td>
</tr>
<tr>
<td>Parton et al 1988; Mosier and Parton 1985</td>
<td>Soil nitrate concentration is an input variable.</td>
</tr>
<tr>
<td>Leffelaar and Wessel 1988</td>
<td>Denitrification sequence (nitrate -&gt; nitrite -&gt; nitrous oxide -&gt; dinitrogen) determines N2O and N2 production.</td>
</tr>
<tr>
<td>Molina et al 1983; Clay et al 1985</td>
<td>N-mineralization and nitrification calculations supply nitrate. Total denitrification (N2O + N2) calculated as function of nitrate concentration.</td>
</tr>
<tr>
<td>Refsgaard et al 1991</td>
<td>No treatment of nitrogen. The model actually simulates only denitrifying conditions (anaerobic fractional volume).</td>
</tr>
<tr>
<td>Scholefield et al 1991</td>
<td>N-mineralization and denitrification gaseous N losses determined as a function on N inputs, soil texture, and soil drainage.</td>
</tr>
<tr>
<td>McConnaughey and Bouldin, 1985</td>
<td>Nitrate concentration supplied as initial condition. Denitrification sequence (nitrate -&gt; nitrite -&gt; nitrous oxide -&gt; dinitrogen) determines N2O and N2 production.</td>
</tr>
</tbody>
</table>
agricultural soils, there is generally an abundance of inorganic N. Soil solution concentrations are relatively easy to measure (Keeney and Nelson 1986) on a sampling scale of centimeters. The microbiological details of nitrification (a principal source of nitrate in soils) are complex and not completely known. The net result—ammonium (NH$_4^+$) transformed to nitrate (NO$_3^-$)—which generally occurs both rapidly and completely (Schmidt 1982), is fairly constant across ecosystems (Firestone and Davidson 1989). Likewise, although the processes of mineralization and ammonification (Jansson and Persson 1982; Ladd and Jackson 1982) are complex, the resultant end product (NH$_4^+$ or NH$_3$) is constant across ecosystems. Finally, most field studies report some measure of soil inorganic nitrogen so model results can be tested.

Denitrification models take two basic approaches to modeling N-substrate availability (Table 1.1): (1) coupling to a model of aerobic soil decomposition and nitrification processes to generate inorganic N pools (e.g. Li et al 1992a; Johnsson et al 1991; Grant 1991; Molina et al 1983 and Clay et al 1985); and (2) supplying nitrate concentration as an input parameter (e.g. Smith 1980 & 1990; Arah 1990; Parton et al 1988 and Mosier and Parton 1985; and McConnaughey and Bouldin 1985).

1.2.2. Carbon Substrate.

As a microbially mediated process, denitrification requires an energy source to fuel denitrifier activity, and this is supplied by dissolved organic carbon compounds (Firestone 1982). The range of organic C compounds mineralizable under anaerobic conditions is enormous, from simple sugars like glucose to complex classes of large molecules like lignin (Beauchamp et al 1989). In a review, Beauchamp et al (1989) cited studies that have found denitrification potential to be best correlated with different measures of soil organic C: (1) C mineralizable under aerobic conditions (Davidson et al 1987); (2) biomass C (Germon et al 1981); (3) total organic C
(Burford and Bremner 1975); and (4) C mineralizable under anaerobic conditions (Bijay-Singh et al 1988). Beauchamp et al (1989) conclude that there is a “scarcity of information on the biodegradation of C compounds and natural substances in conjunction with denitrification under anaerobic conditions.”

This lack of understanding in carbon-nitrogen coupling is manifest in the many denitrification models (Table 1.2). Many models ignore C substrates completely. A few set denitrification activity as a proportion of decomposition activity, implicitly linking denitrification to C mineralizable under aerobic conditions (Grant 1991; Molina et al 1983 and Clay et al 1985; McConnaughey and Bouldin 1985). Two models (Leffelaar and Wessel 1988; Li et al 1992a) consider the C substrate to be a byproduct of decomposition and use it as an explicit substrate for denitrifier activity, again linking denitrification to C mineralizable under aerobic conditions. The detailed structural nature of the C substrate compounds is not considered in any of the models, and is rarely reported in field studies.

1.2.3. Oxygen Availability Control.

The enzymes responsible for the denitrification reduction sequence, while apparently synthesized under “semi-aerobic” conditions, seem to become active only as their “microenvironment” becomes “more anaerobic” (Firestone 1982). All terms in quotes are difficult to define, difficult to measure, and difficult to represent in a model. Nonetheless, for models that endeavor to capture the episodic nature of denitrification some resolution of this is necessary (Table 1.3).

Some models have focused on oxygen availability and anaerobic microsites. Smith (1980 & 1990), Arah (1990), and Refsgaard et al (1991) have developed models of anaerobic microsite volume, based on oxygen diffusion and consumption in saturated soil aggregates or anaerobic regions in structureless soils. They have not yet, though, incorporated their detailed treatment of oxygen controls into the broader framework of C and N substrate availability. McConnaughey and Bouldin (1985)
Table 1.2 - How recent denitrification models treat carbon substrate controls.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Treatment of Carbon Substrate Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li et al 1992a</td>
<td>For rain event denitrification, previous day's microbial C assimilation is assumed to represent the available C pool. This carbon used for denitrifier biomass growth and maintenance.</td>
</tr>
<tr>
<td>Johnsson et al 1991</td>
<td>No explicit soluble carbon control. Denitrification rate is based on potential rate for a site, which would implicitly include carbon effects.</td>
</tr>
<tr>
<td>Grant 1991</td>
<td>No explicit soluble carbon control; demand for electron acceptors under anaerobic conditions assumed to be 60% of demand under aerobic conditions.</td>
</tr>
<tr>
<td>Parton et al 1988; Mosier and Parton 1985</td>
<td>No explicit carbon factor. Denitrification related to a potential rate for a site, which would implicitly include carbon effects.</td>
</tr>
<tr>
<td>Leffelaar and Wessel 1988</td>
<td>C released by dying microbes assumed to be equivalent to glucose; denitrifiers consume this C for growth and maintenance. All soluble C assumed available. (Note: in model runs reported glucose concentrations given as input data).</td>
</tr>
<tr>
<td>Refsgaard et al 1991</td>
<td>No treatment of carbon. The model actually simulates only denitrifying conditions (anaerobic fractional volume).</td>
</tr>
<tr>
<td>McConnaughey and Bouldin, 1985</td>
<td>Soluble carbon availability factor assumed to be proportional to rate of O2 consumption by decomposition. This is used as a Michaelis-Menten type multiplier.</td>
</tr>
</tbody>
</table>
Table 1.3 - How recent denitrification models treat oxygen/water controls.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Treatment of Water Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li et al 1992a</td>
<td>Anaerobic zone determined by rainfall amount, soil saturated hydraulic conductivity, and soil porosity; WFPS &lt; 40% to stop denitrifiers, until then 100% anaerobic.</td>
</tr>
<tr>
<td>Smith 1980</td>
<td>Spherical soil crumbs with O2 diffusion and consumption. Anaerobic core volume determined. Integrate over log-normal distribution of crumb radii to get soil anaerobic fractional volume.</td>
</tr>
<tr>
<td>Johnsson et al 1991</td>
<td>Denitrifier activity reduced by WFPS function which is zero for WFPS &lt; 60%, rises slowly to about 0.15 at WFPS = 75%, and then rapidly to 1.0 at WFPS = 100%.</td>
</tr>
<tr>
<td>Grant 1991</td>
<td>O2 diffusion through vertical soil profile; spherical microsites, with O2 diffusion, delivers O2 to decomposers. Denitrification activity is function of decomposition activity not satisfied by O2 availability as an electron acceptor.</td>
</tr>
<tr>
<td>Parton et al 1988; Mosier and Parton 1985</td>
<td>Denitrifier activity reduced by WFPS function which has a parabolic shape, equal to 0.2 at WFPS = 40%, 0.33 at WFPS = 60 % and 1.0 at WFPS = 100%.</td>
</tr>
<tr>
<td>Leffelaar &amp; Wessel 1988</td>
<td>Complete anaerobiosis assumed; no WFPS effects.</td>
</tr>
<tr>
<td>Clay et al 1985</td>
<td>Denitrifier activity reduced by WFPS function which is zero for WFPS &lt; 60%, rises rapidly to 0.9 at WFPS = 80%, and then slowly to 1.0 at WFPS = 100%.</td>
</tr>
<tr>
<td>Scholefield et al 1991</td>
<td>Fraction of total N loss (denitrification and leaching) that is due to denitrification is constant function of site soil texture and drainage.</td>
</tr>
<tr>
<td>McConnaughey and Bouldin, 1985</td>
<td>Considers saturated soil layer exposed to surface concentration of gaseous O2. O2 liquid phase diffusion rate and O2 consumption rate determine depth of penetration, and thus anaerobic zone below this.</td>
</tr>
</tbody>
</table>
model O2 diffusion and consumption in a saturated soil slab and determine the location of a moving boundary between anaerobic and aerobic zones. N-oxide compounds are also in solution in the slab, subject to consumption, production, and diffusion. It is not clear, though, how this would be applied in field soils. In the most complete process-oriented model to date, Grant (1991) considers O2 diffusion into spherical microsites of aerobic decomposition, with demand based on microbial biomass. Microsite surface oxygen concentration is determined by vertical gas phase diffusion in the soil air-filled pores. If the oxygen supply is insufficient, unsatisfied demand is met by denitrifiers (implicit anaerobiosis). This model is within the framework of a broader model of soil C and N cycling. It does not, however, examine the reduction sequence of denitrification, and can only estimate total denitrification (N2O+N2).

Another class of models considers denitrifier activity to be regulated by soil water-filled pore space (WFPS), implicitly assuming that oxygen availability will decrease as WFPS increases (Johnsson et al 1991; Parton et al 1988 and Mosier and Parton 1985; Clay et al 1985). Operationally, this is a much simpler approach, but it requires a model of soil water dynamics to supply the controlling variable.

Li et al (1992a) greatly simplify oxygen controls on denitrification. They assume that while significant soil wetting (rainfall or irrigation > 0.5 cm) is essential to initiate denitrification and controls the volume of soil that actively denitrifies, soil moisture or oxygen status is rarely the limiting factor once the process has begun. The actively denitrifying soil is considered completely anaerobic until WFPS drops below 40%.

1.2.4. Temporal Variability.

Denitrification fluxes are highly variable in time, essentially on two scales—a seasonal scale (cold vs. warm in the temperate zone, wet vs. dry in the tropics) and a rain event scale. All field-scale, process-oriented models capture this variability by having climatic drivers control the soil climate, which, via temperature factors and

1.2.5. Spatial Variability.

There is a high degree of spatial variability in denitrification activity and gas flux. This variability occurs on large scales ($\approx 10^3$ m or more) due to broad variations in soils, climate, vegetation, and land use; on moderate scales ($\approx 1$-100 m) due to variations in soil texture and drainage, microtopography, and vegetation cover; and on small scales ($\approx 10^{-1}$ m or less—anaerobic microsites) due to variations in organic matter content, soil moisture, pore size distribution and drainage, and oxygen consumption at the scale of soil structural variability.

The anaerobic microsite models of Smith (1980, 1990), Arah (1990), and Refsgaard et al (1991) attempt to quantify this small scale variability. Nonetheless, all of the models are essentially point models that must be run for each set of field conditions (Table 1.4). The area scale that a single model run represents thus depends on the degree of spatial variability of the driving variables. Issues of macro-scale variability and scaling are discussed in Groffman (1991) for nitrification and denitrification in soil, and more generally in Ehleringer and Field (1993). They will not be discussed further in this dissertation.
Table 1.4 - How recent denitrification models treat soil heterogeneity.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Treatment of Single Site Soil Heterogeneity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li et al 1992a</td>
<td>Smooth variation in vertical profile.</td>
</tr>
<tr>
<td>Johnsson et al 1991</td>
<td>Distinct textural layers; vertical variability only.</td>
</tr>
<tr>
<td>Grant 1991</td>
<td>Smooth variation in vertical profile.</td>
</tr>
<tr>
<td>Parton et al 1988; Mosier and Parton 1985</td>
<td>None.</td>
</tr>
<tr>
<td>Leffelaar &amp; Wessel 1988</td>
<td>None.</td>
</tr>
<tr>
<td>Refsgaard et al 1991</td>
<td>Log-normal distribution of soil aggregate radii introduces two textural parameters.</td>
</tr>
<tr>
<td>Scholefield et al 1991</td>
<td>None.</td>
</tr>
<tr>
<td>McConnaughey and Bouldin, 1985</td>
<td>None.</td>
</tr>
</tbody>
</table>
CHAPTER 2

A REVISED DNDC MODEL: DESCRIPTION, SENSITIVITIES, CALIBRATION, AND VALIDATION

2.1. Introduction

The DNDC model (Li et al. 1992a,b; briefly summarized in Section 2.4.1 below) is a process oriented model of soil climate and carbon and nitrogen cycling in soils, which attempts to capture the dynamics of soil climate and its various influences on nitrogen and carbon cycling in soils. Both DNDC and a field campaign being currently conducted by Antonio Nobre (UNH doctoral project) in Costa Rica, are focused on understanding the unique role of rain events in denitrification. In order to collect a data set with which to rigorously test the model, Antonio Nobre measured key model parameters and variables on control and amended (water, nitrate fertilizer, nitrate fertilizer + glucose) plots at a site that was converted from humid tropical forest to agroforestry about 40 years ago (see Section 2.3.1). At the same time, the DNDC model was revised to give a more accurate portrayal of soil climate, and, in particular, a more detailed portrayal of soil climate controls on the denitrification process during and within a few days following a rain event. This chapter will describe the revised model, its sensitivities and calibration with other field data, and then test it with preliminary field data from Costa Rica.

2.2. Model of Soil Climate

The rates of many ecosystem processes that occur in the soil, such as microbi ally mediated cycling of carbon and nitrogen and trace gas generation, depend on the soil climate (soil temperature and soil moisture content). However, weather
stations generally only collect surface weather data (often just air temperature and precipitation). To use this widely available surface weather data to drive soil biogeochemistry models requires a model to derive soil climate conditions from surface weather data for a site. Both the original and revised DNDC models consist of two separate models: a soil climate model that generates soil temperature and moisture profiles, as well as soil water flow dynamics; and a biogeochemistry model that simulates the carbon and nitrogen dynamics of decomposition and denitrification.

A one-dimensional soil heat flux and moisture flow model (SCM) has been designed to calculate hourly average soil temperature and moisture profiles, as well as vertical soil water flow rates. The heat fluxes and moisture flows are modeled by gradient-driven diffusion (and gravity for water flow). These gradient driven equations are numerically modeled by explicit finite difference equations for a layered soil profile.

SCM characterizes soil physical properties based on texture, following the work of Clapp and Hornberger (1978). The modeled soil is divided into a series of horizontal layers. Each layer is assumed to have a uniform temperature \( T_j \) and moisture content \( W_j \), assigned to a point at the middle of the layer \( z_j \). For each time step, water fluxes and heat flows between layers are determined by the gradients of soil water head potential and soil temperature, respectively. All values are determined per unit area in the horizontal plane.

### 2.2.1. Soil Water Flow And Heat Flux Equations

The soil water flow equation (as a finite difference equation) is

\[
Q_{i,i-1} = -K_{i,i-1} (h_i - h_{i-1}) / (z_i - z_{i-1}) \quad (2.1)
\]

where \( Q_{i,i-1} \) is the Darcy flow of water per unit area (cm/s) from layer \( i-1 \) down to layer \( i \), \( K_{i,i-1} \) is the average hydraulic conductivity (cm/s) of layers \( i \) and \( i-1 \), \( h_i \) is the hydraulic head for level \( i \) (cm), and \( z_i \) is the depth of layer \( i \) (cm). The hydraulic
head is equal to the soil water potential ($\psi$) plus the gravitational head ($h = \psi - z$).

The top soil layer is layer 1. Similarly, the soil heat flux equation is

$$q_{i,i-1} = -k_{i,i-1}(T_i - T_{i-1})/(z_i - z_{i-1})$$

(2.2)

where $q_{i,i-1}$ is the heat flux (J/s) from layer $i-1$ down to layer $i$, $k_{i,i-1}$ is the average thermal conductivity (J cm/s °C) of layers $i$ and $i-1$, $T_i$ is the temperature for level $i$ (°C). Both the thermal and hydraulic conductivities are dependent on the soil moisture content. Since moisture content is variable through the soil profile, the thermal and hydraulic conductivities between two layers are taken to be the average of the conductivities of each of the two layers.

These flow/flux equations are solved for each time step of the simulation (typically about 15 minutes) using the temperature, head, and conductivity values at the beginning of the time step. At the end of the time step, the conservation equations for energy and water are applied to each layer, to update the soil temperature and moisture profiles

$$\frac{\delta W_i}{\delta t} = (Q_{i,i-1} - Q_{i+1,i})/(n_i l_i)$$

(2.3)

$$\frac{\delta T_i}{\delta t} = (q_{i,i-1} - q_{i+1,i})/(C_i l_i)$$

(2.4)

where $\delta W_i/\delta t$ is the change in the water content of soil layer $i$ as a fraction of the soil pore space ($0 \leq W_i \leq 1$), per model time step $\delta t$, $n$ is the soil porosity, $l_i$ is the thickness of layer $i$ (cm), $\delta T_i/\delta t$ is the change in temperature of soil layer $i$, and $C_i$ is the net volumetric heat capacity of layer $i$ (J/cm K), given by

$$C_i = (\rho_{\text{soil}} c_{\text{soil}}) + (n_i W_i \rho_{\text{water}} c_{\text{water}})$$

(2.5)

where $\rho$ is density (kg/m$^3$) and $c$ is specific heat (J/kg K).

Rainwater is added at the beginning of a time step, before the soil water potential is calculated, and evapotranspired water is removed at the end of the time step. The water flow and heat flux equations at the bottom of the soil profile are given by

$$Q_b = f K_b l_i$$

(2.6)
\[ q_b = k_{bl} \left( T_{bl} - T_{maat} \right) / (z_{bl} - z_{deep}) \]  
\hspace{1cm} (2.7)

where the subscript \( bl \) refers to properties of the bottom soil layer, \( f \) is a factor to simulate the relative permeability of the underlying soil layer (\( f \) is presently fixed at 1.0), \( T_{maat} \) is the mean annual air temperature, and \( z_{deep} \) is the soil depth at which temperature variation is assumed to be negligible throughout the year. This implies no change in moisture content between the bottom soil layer and the underlying soil (Van Bavel and Lascano, 1980) so that all water drainage is gravity driven, and a heat flux out of the bottom layer driven by a uniform temperature gradient between the bottom soil layer (at temperature \( T_{bl} \)) and the mean annual air temperature at depth (500 cm).

In order to be able to run the simulation with a minimum amount of meteorological input data, the heat flux at the soil surface is simplified to a gradient driven flux between the soil surface, which is assigned a temperature equal to the mean daily air temperature, and the top soil layer,

\[ q_s = -k_{1} \left( T_{1} - T_{air} \right) / (z_{1}) \]  
\hspace{1cm} (2.8)

2.2.2. The Surface Water Balance

The moisture boundary condition at the soil surface has two components, precipitation/irrigation and evaporation/transpiration. Precipitation (or irrigation) events are prescribed input events. SCM assumes that all rain events start at midnight, are of constant intensity (throughout a single storm, but potentially varying intensity from one storm to the next), and of variable duration. At the beginning of each timestep, the rainfall for that time step is added, usually to the surface soil layer. In some soils, due to the presence of macropores, some of the rainwater can effectively bypass the surface soil and be "directly and immediately" delivered to the deeper soil. Federer (1993) has developed a simple, two-parameter functional representation of this macropore-assisted bypass flow.
\[ \text{inf}_{1-2} = \text{inf} \cdot [(z_1/z_{\text{inf}})^{\text{exp}} - (z_1/z_{\text{inf}})^{\text{exp}}] \quad (2.9) \]

where \( \text{inf} \) is the total water infiltration, \( \text{inf}_{1-2} \) is the infiltration water delivered to the depth range between \( z_1 \) and \( z_2 \), \( z_{\text{inf}} \) is the maximum infiltration depth and \( \text{exp} \) is a parameter. If \( \text{exp} \) is 0.0, then all the water is delivered to the surface (no bypass flow). If \( \text{exp} \) is 1.0, then the water is distributed uniformly from the surface to \( z_{\text{inf}} \). Values for \( \text{exp} \) greater than 1.0 cause the distribution to be weighted towards the deeper soil; values less than 1.0 cause the distribution to be weighted towards the surface soil. If there is no site data to suggest otherwise, \( \text{exp} \) is set to 0.0 and no bypass flow occurs. This is the case in all studies presented here.

Vegetation interception of rainfall can significantly reduce a storm's impact on soil moisture, especially for light rains (Dunne and Leopold, 1978). Following Federer (1993), maximum rainwater storage on the canopy is set at \( 0.2 \times \text{LAI} \) mm water, where \( \text{LAI} \) is the canopy Leaf Area Index. The rainfall interception rate is

\[ \text{Int} = 0.1 \cdot \text{LAI} \cdot (\text{Rainfall Rate}) \quad (2.10) \]

so that a canopy with \( \text{LAI} = 5 \) will intercept half of the rainfall until it reaches its storage capacity of 1 mm water per unit ground area. There is no subsequent leaf drip—all intercepted water is lost from the leaves by evaporation.

Water loss by evaporation/transpiration is calculated in four steps. First the potential atmospheric demand for water (Potential Evapotranspiration or \( \text{PET} \)) is calculated from the surface weather data. \( \text{PET} \) is calculated as daily average values using the Thornthwaite formula (Dunne and Leopold, 1978). \( \text{PET} \) (cm/day) is given by

\[
\text{PET} = (1.6/NM) \cdot (10 \cdot T_{\text{air} / I})^a \quad (2.11)
\]

\[ I = \sigma_{i=1}^{12} (T_i^*/5)^{1.5} \quad (2.12) \]

\[ a = 0.49 + 0.079 \cdot I - 0.0000771 \cdot I^2 + 0.000000675 \cdot I^3 \quad (2.13) \]

where \( T^* \) is the mean monthly air temperature (°C), \( T_{\text{air}} \) is the mean daily air temperature (°C), and \( NM \) is the number of days in the month, and here the subscript \( i \)}}
refers to months of the year. This demand for water can be satisfied by three sources: intercepted water stored in the canopy, soil water evaporated from the soil surface, and soil water transpired through the vegetation. Intercepted water is evaporated first ($AE_{int}$), at the potential rate

$$AE_{int} = \min(PET, CAN_{wat})$$

(2.14)

where $CAN_{wat}$ is the canopy water content. If the intercepted water pool cannot meet the $PET$ demand, the remaining demand is partitioned between soil evaporation and transpiration, based on vegetation $LAI$. Data from Kristensen (1974, as reported in Rosenberg et al, 1983) show a near-linear increase in transpiration water loss as a function of $LAI$ as it increases from 0 to 3, at which point transpiration levels off. I interpret this as the canopy's ability to intercept incoming radiant energy (which drives both soil evaporation and transpiration) also rising linearly from zero to a maximum at $LAI = 3$. Energy for soil water evaporation thus falls linearly from a maximum to zero as $LAI$ increases from 0 to 3 (the effect of shading). Therefore, once intercepted water (if there is any) is evaporated, any remaining demand ($PET^* = PET - AE_{int}$) is partitioned into potential transpiration ($PT$) and potential soil evaporation ($PE_S$)

$$PT = PET^* \cdot \min(LAI/3, 1.0)$$

(2.15)

$$PE_S = PET^* \cdot \max(0.0, 1 - LAI/3)$$

(2.16)

Unless the soil is quite wet, soil evaporation is limited (often severely) by the rate at which the soil matrix can deliver water to the evaporating soil surface (Hillel, 1980b). Actual soil evaporation ($AE_S$) is taken as the minimum of $PE_S$ and the potential delivery rate ($PDR$). $PDR$ is calculated (Federer 1993) as the Darcian flow rate between a very dry soil surface ($\Psi_0 = 50,000$ kPa) and the soil at the bottom of the first model layer ($z_1$, generally 5 cm)

$$PDR = K^* (\Psi_0 - \Psi_1)/z_1$$

(2.17a)

$$K^* = (K_0 K_1)^{1/2}$$

(2.17b)
\[ K_0 = K(\Psi_0) \]  
\[ \Psi_1 = \Psi(z = z_1) \]  
\[ K_1 = K(z = z_1) \]

Plant transpiration occurs at the potential rate unless soil water is limiting.

SCM follows Feddes et al (1988) with a soil water limiting factor (SWLF)

\[ SWLF = \begin{cases} 
1; & \text{if } W > W_{lt} \\
\frac{(W-W_{wp})}{(W_{lt}-W_{wp})}; & \text{if } W_{lt} > W > W_{wp} \\
0; & \text{if } W < W_{wp} 
\end{cases} \]

where \( W_{lt} \) is the soil water content at which soil water content begins to limit transpiration (50 kPa), and \( W_{wp} \) is taken to be the soil water content at the plant wilting point (1500 kPa). Soil water transpiration loss as a function of depth is based on the plant root distribution in the soil. A soil layer's actual transpiration water loss is then given by

\[ AT = \min(1, \frac{LAI}{3}) \cdot PET \cdot SWLF \cdot FRBM \]

where \( FRBM \) is the fractional root biomass in the layer (see Section 2.2.3).

2.2.3 Vegetation

SCM can accept five vegetation classes: bare ground (fallow), grassland (or pasture), deciduous forest, evergreen forest, and crops. Grassland and evergreen forest are considered to have constant \( LAI \) and maximum root depths (input parameters). Deciduous forest has a constant maximum root depth but a seasonal \( LAI \), and crops have a seasonal \( LAI \) and maximum root depth. \( LAI \) is assumed to increase linearly from zero to \( LAI_{max} \) in a specified time interval (input parameter), and maximum root depth increases for crops from zero to its maximum as the \( LAI \) increases from zero to three. Root biomass is distributed as a function of actual root depth: 40% in the top quarter, 30% in the second quarter, 20% in the third quarter.
and 10% in the bottom quarter (Molz and Remson, 1970). This fractional
distribution holds constant as the root depth increases (for crops).

2.2.4. Soil Thermal And Hydraulic Conductivities

The soil thermal conductivity depends on soil water content and on the nature,
mineral or organic, of the soil. A representative thermal conductivity for mineral
soil, $k_{dry}$, is 4.0 W/m/K; the thermal conductivity of water, $k_{water}$, is 0.57
W/m/K; the thermal conductivity of organic matter in soil, $k_{om}$, is 0.25 W/m/K
(deVries, 1975). The soil layer thermal conductivity for a given moisture content,
$W_i$, is

$$k_i = (1 - n) \cdot k_{dry} + n \cdot W_i \cdot k_{water} \quad (2.20a)$$

or, for organic soil

$$k_i = (1 - n) \cdot k_{om} + n \cdot W_i \cdot k_{water} \quad (2.20b)$$

There are two related parameterizations for the soil hydraulic properties that
relate soil water tension ($\psi$), soil water content ($W$), and hydraulic conductivity ($K$).
The first, based on the work of Clapp and Hornberger (1978), relates these variables
to their values at “saturation”. The relative hydraulic conductivity ($K/K_{sat}$) is given
by

$$K/K_{sat} = W(2\beta + 3) \quad (21)$$

where $\beta$ is a parameter in the range of 4 to 11.4 and $K_{sat}$ is the saturated hydraulic
conductivity (see Table 2.1 below). The water retention relation is given by

$$\psi_i = \psi_{sat}(W_i)^{-\beta}, \quad \text{if } W_i < W^* \quad (2.22a)$$

$$\psi_i = -m_1 \cdot (W - m_2 \cdot (W - 1)^{-1}, \quad \text{if } W_i \geq W^* \quad (2.22b)$$

where $\psi_{sat}$ is a water tension parameter, $W^*$ is the water content at which the water
retention curve has an inflection point—taken to be 0.92 (Clapp and Hornberger,
1978), and

$$m_1 = \psi^*/(1-W^*)^2 - \psi^* \cdot \beta/[W^* \cdot (1-W^*)] \quad (2.23a)$$
where \( W^* \) is the soil water potential at the inflection point.

Federer (1993) has developed a related functional relationship which should be more appropriate for soils with lower bulk densities (higher porosities) than the soils used by Clapp and Hornberger to develop their parameterization. Federer's formulation relates the variables to their values at "field capacity".

\[
K = K_x \frac{W}{W_x} (2B + 3) \quad (2.24)
\]

where \( K_x \) is the hydraulic conductivity at "field capacity", always taken as 2 mm/d (Federer 1993; in effect, this is how Federer defines field capacity), \( W_x \) is the soil water content at field capacity, and \( B \) is the same parameter as above. The water retention relation is given by

\[
\psi_i = \psi_x \left( \frac{W_i}{W_x} \right)^B, \quad \text{if } W_i < W^* \quad (2.25a)
\]
\[
\psi_i = -m_1 \cdot (W-m_2) \cdot (W-1), \quad \text{if } W_i \geq W^* \quad (2.25b)
\]

where \( \psi_x \) is the water tension at field capacity, \( W^* \) is the water content at which the water retention curve has an inflection point—again taken to be 0.92, and \( m_1 \) and \( m_2 \) are the same as in Equations 2.23a,b.

SCM starts the simulation by assuming a soil profile with a uniform initial temperature and a uniform initial soil water tension (these are input variables). Model output is the hourly soil temperature profiles, hourly soil water content profiles, hourly average soil water flow rates between layers, and hourly infiltration rates.
2.3. Soil Model Results For La Selva, Costa Rica

2.3.1. The Vegas Site

The field site in Costa Rica, referred to as Vegas (previously called Finca Jack), is within the Las Vegas Annex of the La Selva Biological Station (10°26’ N, 83°58’ W, elevation about 40 m asl). The site is about 350 m upstream from the confluence of Rio Puerto Viejo and Rio Sarapiqui, and about 50 m in from Rio Sarapiqui. Annual climatic means are about 26°C and 3720 mm precipitation (Instituto Meteorologico National 1988). Air temperature varies by only a few degrees throughout the year. There is a drier season from roughly December through April. The soils of the La Selva region are all of volcanic origin (Sollins et al, 1992). The Vegas site is an alluvial terrace near the confluence of Rio Sarapiqui and Rio Puerto Viejo, about 20 m above the dry season river level. The site area, originally humid tropical forest, was cleared and planted to a cocoa plantation in the 1950s. The site area was re-cleared for an agroforestry experimental study in 1991 (Projecto Huertas). Antonio Nobre's Vegas site was an unused portion of the land cleared for this project. The vegetation (one year regrowth, mostly shrubs) was cleared of aboveground biomass one week before his experiment began. The soils near the site are described as mixed, isohyperthermic, oxic dystrandepts (A.F. Bouwman, unpublished field notes); typic dystrandepts (Sollins et al, 1992); and andic, isohyperthermic, “fluventic” dystropepts (R. Mata, unpublished field notes).

2.3.2. Model Parameterization

Unpublished field data from A. Nobre, A.F. Bouwman, and R. Mata was used to parameterize the soil for SCM, as well as two more general references (see Table 2.1). All three sets of field observations agree on three soil layers between the surface and 50 cm (model depth). Soil porosity \( n \) is calculated as (Federer 1993)

\[
n = 1.0 - \rho_b(F_{om}/\rho_{om} + (1-F_{om})/\rho_{min}) \tag{2.26}
\]
<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Layer #1</th>
<th>Layer #2</th>
<th>Layer #3</th>
<th>Source</th>
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</thead>
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<tr>
<td>depth</td>
<td>cm</td>
<td>0 to 10</td>
<td>10 to 25</td>
<td>25 to 50</td>
<td>1, 2, 3</td>
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<td>0.9</td>
<td>1.0</td>
<td>1</td>
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<tr>
<td>org. fraction</td>
<td></td>
<td>0.0596</td>
<td>0.0161</td>
<td>0.0054</td>
<td>2</td>
</tr>
<tr>
<td>porosity</td>
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<td>0.655</td>
<td>0.621</td>
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</tr>
<tr>
<td>sand frac.</td>
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<td>0.60</td>
<td>0.35</td>
<td>0.45</td>
<td>2</td>
</tr>
<tr>
<td>silt frac.</td>
<td></td>
<td>0.36</td>
<td>0.59</td>
<td>0.52</td>
<td>2</td>
</tr>
<tr>
<td>clay frac.</td>
<td></td>
<td>0.04</td>
<td>0.06</td>
<td>0.03</td>
<td>2</td>
</tr>
<tr>
<td>texture</td>
<td></td>
<td>sandy loam</td>
<td>silt loam</td>
<td>sandy loam</td>
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<tr>
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<td></td>
<td>4.9</td>
<td>5.0</td>
<td>4.0</td>
<td>1</td>
</tr>
<tr>
<td>$\psi_x$</td>
<td>kPa</td>
<td>16</td>
<td>16</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>$W_x$</td>
<td></td>
<td>0.37</td>
<td>0.45</td>
<td>0.4</td>
<td>1, 2</td>
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<td>°C</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>initial $\psi$</td>
<td>kPa</td>
<td>16</td>
<td>16</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

1 - Field notes and data of Antonio Nobre  
2 - Field notes of Rafael Mata  
3 - Field notes of A.F. Bouwman  
4 - Federer (1993)  
5 - Hillel (1980a)
where \( \rho_b \) is the soil bulk density (g/cm\(^3\)), \( F_{om} \) is the soil organic fraction by mass, \( \rho_{om} \) is the particle density of soil organic matter (1.3 g/cm\(^3\)), and \( \rho_{min} \) is the particle density of mineral soil (2.65 g/cm\(^3\)).

The parameters linking soil water tension, soil water content, and hydraulic conductivity (see Equations 2.24 and 2.25a,b) were chosen to fit data collected by A. Nobre. \( K_X \), the hydraulic conductivity at "field capacity" was taken as 2 mm d\(^{-1}\) for all three layers (Federer 1993). \( \psi_X \), the soil water tension at "field capacity", was determined from initial tensiometer data, as there had been several light rains during the few days preceding the field study. The parameter \( \beta \) was assumed to be within the range of 4 to 5.5 since all layers were quite sandy (Federer 1993). The final values for \( \beta \) and \( W_X \) (the WFPS at "field capacity") were determined so as to best fit the soil water tension vs. soil water content data collected during the field study. Soil water content data was collected with a TDR at several depths each time gas flux measurements were made; tensiometer readings were taken at the same time. Unfortunately, there appears to be a lot of scatter in the data (Figs 2.1.a, b, & c) and so the parameters (Table 2.1), although reasonable, are not well-determined.

### 2.3.3. Soil Water Results

Because of apparent problems with the TDR and gravimetric soil water data, the soil tensiometers gave the best time series results to test the model against. The field study had four treatments: (1) control (no additions), (2) water (three irrigations), (3) nitrogen (one nitrate fertilization in three irrigations), and (4) nitrogen + carbon (one nitrate + glucose fertilization in three irrigations). Treatments 2, 3, and 4 all had the same water additions and so serve as replicates for the soil water component of the study. There was no rainfall from the time of the first irrigation until three days after the third irrigation (Fig. 2.2).
Figure 2.1.a - Soil water content relationship to soil water tension for soil layer #1 (0-10 cm). Field data (hollow circles) for 5 and 10 cm TDR data; model relationship (solid circles) based on parameters in box.
Figure 2.1.b - Soil water content relationship to soil water tension for soil layer #1 (10-25 cm). Field data (hollow circles) for 10 and 20 cm TDR data; model relationship (solid circles) based on parameters in box.
Figure 2.1.c - Soil water content relationship to soil water tension for soil layer #1 (25-40 cm). Field data (hollow circles) for 20 and 40 cm TDR data; model relationship (solid circles) based on parameters in box.
Figure 2.2 - Weather data collected about 1 km from the Vegas site, plus irrigations applied to the plot.
Tensiometers were placed at 2 cm, 5 cm, 10 cm, 20 cm, and 40 cm for each treatment, and readings were taken at 0.5 h, 2 h, 4 h, 8 h, 24 h after each irrigation, and then every one to few days later. The model geometry was three 3.33 cm layers at the surface and eight 5 cm layers below this, to a total depth of 50 cm, with hourly output of soil moisture variables.

Soil water tension results (Fig. 2.3.a-c through 2.7.a-c) are plotted separately for each irrigation and each depth, with time on a logarithmic scale so that the data from the initial, intensive measurement period are more spread out. At each depth, the model and field results for the first irrigation (1 cm water on "field capacity" wet soils) are generally in good agreement (Figs. 2.3.a - 2.7.a). At 40 cm the model soil dries appreciably after about 4 days, while the field data do not show this (Fig. 2.7.a). Also, the model soil water tensions do not drop as low as the field data immediately following irrigation.

For the second irrigation (1 cm water on, by now, fairly dry soil) the upper model layers tend to be drier than the field data, although two points at 5 cm and 156 hours have such a range that the data are ambiguous (Fig. 2.4.b), and there is one data point at 156 hours at 2 cm depth in agreement with the model (Fig. 2.3.b). At 10 cm, the model responds more rapidly and more strongly to the second irrigation (Fig. 2.5.b), while at 20 cm and 40 cm the model remains drier and is more responsive than the field data (Fig. 2.6.b, 2.7.b).

The third irrigation (3 cm water on fairly dry soil) causes the field-measured tensions to drop quickly and dramatically at all depths (Figs. 2.3.c - 2.7.c). The model results tend to be somewhat drier (and, again, do not drop to near-zero tension), but capture the water dynamics of steep drop and slow increase in tension. Both field data and model results show the effects of three light (< 1 cm) and one moderate (~ 5 cm) rainfalls near the end of the field study.
Given the relatively soft parameterization, the model results seem to reasonably simulate field observations. The most troubling discrepancy is the inability of the model to capture the extremely low soil water tensions observed in the field in the hours immediately following an irrigation. However, for the model to achieve this, the soils would have to be near saturation—the specific water capacity, $\partial W/\partial \psi$, is very large at low tensions, so large changes in water content are required for significant changes in tension. Since soil porosities are about 70% and model soil field capacity is about WFPS = 40% (Table 2.1), to reach near-zero tension at 10 cm would require nearly 4 cm of water (10 cm x 0.7 x (1.0 - 0.4) = 4.2 cm for saturation). Thus, only for the third irrigation could the model be expected to reach low tension at 10 cm (it doesn't). In addition, having the soil hydraulic parameterization based on field capacity rather than saturation means that soils will have very high hydraulic conductivities at high water contents. A wetting event will only wet the soil to the point where hydraulic conductivity equals the rainfall rate; in this case that happens at relatively high tensions. At the drier times, the relatively large discrepancies in soil water tension will not necessarily mean a large discrepancy in soil water content. For example, for the surface soil layer, the difference in volumetric water content for $\psi = 450$ mbar versus $\psi = 350$ mbar is about 1% (corresponding to a change in WFPS of about 0.014). This same effect applies to the 40 cm tension data, where model tensions are higher by about 150 mbar and so would be about 7% drier. The impacts of these discrepancies on modeling denitrification will be discussed below (Section 2.8).
Figure 2.3 - (a) Soil water tension time series for week following irrigation #1. Field results at 2 cm for water, nitrogen, and nitrogen + carbon treatments (solid symbols). Model results for surface model layer (0 - 3.3 cm). Note logarithmic time scale. (b) Same as (a) but for week following irrigation #2. (c) Same as (a) but for week following irrigation #3.
Figure 2.4 - (a) Soil water tension time series for week following irrigation #1. Field results at 5 cm for water, nitrogen, and nitrogen + carbon treatments (solid symbols). Model results for surface model layer (3.3 - 6.7 cm). Note logarithmic time scale. (b) Same as (a) but for week following irrigation #2. (c) Same as (a) but for week following irrigation #3.
Figure 2.5 - (a) Soil water tension time series for week following irrigation #1. Field results at 10 cm for water, nitrogen, and nitrogen + carbon treatments (solid symbols). Model results for surface model layer (6.7 - 15 cm). Note logarithmic time scale. (b) Same as (a) but for week following irrigation #2. (c) Same as (a) but for week following irrigation #3.
Figure 2.6 - (a) Soil water tension time series for week following irrigation #1. Field results at 20 cm for water, nitrogen, and nitrogen + carbon treatments (solid symbols). Model results for surface model layer (15 - 25 cm). Note logarithmic time scale. (b) Same as (a) but for week following irrigation #2. (c) Same as (a) but for week following irrigation #3.
Figure 2.7 - (a) Soil water tension time series for week following irrigation #1. Field results at 40 cm for water, nitrogen, and nitrogen + carbon treatments (solid symbols). Model results for surface model layer (35 - 45 cm). Note logarithmic time scale. (b) Same as (a) but for week following irrigation #2. (c) Same as (a) but for week following irrigation #3.
2.4. The Revised DNDC Model

2.4.1. Classical DNDC (DNDC Version 1.0)

DNDC (Li et al, 1992a; see Fig. 2.8) is a model of soil carbon and nitrogen cycling with emphasis on soil C dynamics and denitrification. DNDC version 1.0 (as described in Li et al 1992a,b; it has evolved since then) has three submodels. A thermal-hydraulic submodel (an earlier version of the SCM model of Section 2 above), a decomposition submodel, and a denitrification submodel. DNDC has proven to be very successful at simulating N2O fluxes (Li et al 1992b; Li, Frolking, Harriss, and Terry, submitted; Li, unpublished results) and soil carbon dynamics (Li, Frolking, and Harriss, in prep.).

The basic paradigm of DNDC is that denitrification in the soil is not a continuous process, but is episodic, initiated by soil wetting (precipitation or irrigation). The model was therefore developed as a rain-event model. The decomposition submodel calculates daily decomposition of the several soil C pools, nitrification, plant N-uptake, clay adsorption of NH4+, and NH3 volatilization. When a rain event occurs, the decomposition submodel pauses and the denitrification submodel calculates denitrification activity for up to ten days, stopping only when WFPS drops below 40%. For many soils, especially clay-rich soils, this takes several days or longer, and, as a result, denitrification is generally limited by substrate availability (nitrate and/or soluble C). The substrates for the excursion into "denitrifier space" are the soil solution NO3- pool at the beginning of the rainy day, and the soluble carbon "pool", which is equal to the amount of C released by the decomposition of microbes and humads that is re-assimilated into microbial biomass on the day preceding the rainy day. During the denitrification period, there is no decomposition occurring so there can be no re-supply of substrates. After the denitrification period, decomposition resumes with the rainy day. Decomposition thus occurs every day, but the denitrification submodel considers only the initial supply of
Figure 2.8 - Core of DNDC model. Decomposition processes operate at one day timestep; denitrification at one hour timestep. Soil temperature and moisture affect all processes. All processes calculated for a series of soil layers. For clarity, plant uptake, adsorption, leaching processes omitted from figure.
substrate to be available to the denitrifiers.

During the denitrification event, the submodel calculates the active denitrifying zone by adding, each hour, a depth equal to the minimum of 1 cm divided by the soil porosity and the soil saturated hydraulic conductivity times one hour (e.g., for a loam soil with \( K_{\text{sat}} = 2.52 \ \text{cm h}^{-1} \), each hour of rain adds an additional 2.52 cm to the denitrifying profile). The thickness of the denitrifying zone is the product of the soil \( K_{\text{sat}} \) and the rain duration (all storms have a constant rainfall intensity of 0.5 cm \( h^{-1} \), so rainfall amount is determined by rainstorm duration). As a result, the simulated soil water content plays no role in controlling denitrification, other than as an "off-switch".

The revised DNDC model is an attempt to develop a more realistic treatment of soil moisture controls on denitrification, while maintaining the core processes of the classical DNDC model.

2.4.2 The Revised DNDC Model - Major Changes

**Motivation** - The primary goal of DX (the revised DNDC model) is to develop a control on denitrification and decomposition such that the two submodels can run simultaneously. The motivation for the approach I have taken comes from the work of Doran and colleagues on water-filled pore space (WFPS) as the best indicator of soil moisture control on soil microbial activity (Skopp et al 1990; Doran et al 1990; Linn and Doran 1984). Linn and Doran (1984) propose two basic controls on microbial decomposition activity in soils. For low soil water contents, thin water films on soil particles and large, air-filled voids restrict the liquid phase diffusion of substrates to microbes, and thus decomposition rates fall as soil water content drops. For high soil water contents, saturated soil pores restrict the gas phase diffusion of oxygen into the soil from the atmosphere, and thus decomposition rates fall as soil water content increases. Figure 2.9 shows their conceptualization of these two effects. Their
laboratory work indicates that, for most soils, the optimum WFPS for decomposition is
around 60%, somewhat higher for clayey soils and lower for sandy soils (Doran et al
1990). Since denitrification generally occurs in soils (or sites within soils) with
little or no available oxygen (Firestone and Davidson, 1989), it follows from this line
of reasoning that denitrification should begin to occur as oxygen diffusion becomes
limiting to decomposition. Doran et al (1990) observe this—low levels of
denitrification at 60% WFPS, none under drier conditions, and much higher levels at
90% WFPS.

The fundamental differences between the classical DNDC and DX are (1) the
establishment of aerobic and anaerobic zones in the soil so that decomposition and
denitrification can occur simultaneously, and (2) the addition of a soil gas phase (O2,
CO2, N2, N2O, NH3) and gas phase diffusion (Fig. 2.10).

**Aerobic and Anaerobic Zones** - Determining the anaerobic fractional volume in
soil is a very challenging problem, both in the field and in a model. Yet the size,
location, and duration of these anaerobic regions will have a strong control on overall
denitrification activity. In models that base denitrification activity on a fractional
anaerobic volume (as opposed to a direct WFPS control parameter), two approaches
have been taken. DNDC, in effect, compresses the anaerobic zone to the soil surface,
assuming there is a completely anaerobic layer from the surface to a depth roughly
equivalent to the thickness of soil the rainstorm would saturate if there were no
internal drainage. However, it does not take into account antecedent soil moisture
conditions, and it will create thicker zones in sandy and loamy soils (high $K_{sat}$) than
in clayey soils (low $K_{sat}$). A thicker zone implies that, potentially, more denitrifier
biomass and substrate are active. In addition, DNDC considers each model layer in this
anaerobic zone to remain totally anaerobic (actively denitrifying if substrates are
available) until its WFPS drops below 40%.

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Figure 2.9 - Conceptual model of water-filled pore space (WFPS) controls on microbial activity. Axis scales are arbitrary. Modified from Linn and Doran (1984).

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Gas and Solution Phase Movement of Constituents

Figure 2.10 - Features added to the revised model, DX. Production and consumption based on processes depicted in Figure 9. WFPS is water-filled pore space; AFPS is air-filled pore space; and AFV represents the anaerobic fractional volume.
A second, much more detailed approach, is to consider the oxygen status throughout the soil, and identify anaerobic regions. This work has been developed over the past 30 years (e.g., Currie 1961; Greenwood and Berry 1962; Smith 1977). I will focus on the work of Keith Smith and colleagues because of their particular emphasis on denitrification (Smith 1980 & 1990; Arah 1990). They consider the soil to consist of a collection of spherical aggregates or crumbs, although other regular geometric shapes are possible. Within an individual crumb, given an oxygen diffusivity (assumed constant throughout), an oxygen concentration at the aggregate surface, and an oxygen consumption rate (or decomposition rate, again usually assumed constant throughout), the diffusion equation in spherical coordinates can be solved analytically. A third order polynomial equation is derived for a critical radius-aggregates with a larger radius \( R_c \) will have anaerobic cores (of radius \( R_{an} \)) and for a calculable fractional anaerobic volume \( \left( R_{an}/R_c \right)^{3/2} \). This polynomial can be solved numerically. Then, assuming that the soil consists of a log-normal distribution of aggregate radii, one can numerically integrate the function for the aggregate fractional anaerobic volume over this distribution to determine the soil's total fractional anaerobic volume. This is a computationally intensive approach, which, considering its level of detail, requires some major assumptions, particularly uniform \( \text{O}_2 \) diffusivity and \( \text{O}_2 \) consumption rates throughout all of the aggregates.

DX considers the anaerobic fractional volume to be a function of WFPS above the value for peak decomposition \( (W_c) \). At WFPS values below this the soil is considered totally aerobic unless oxygen consumption is quite high—see Oxygen subsection below). As the WFPS increases above \( W_c \) the anaerobic fractional volume expands, engulfing microbial biomass (a fraction of which can denitrify under anaerobic conditions) and denitrifier substrates (nitrate and soluble C) from the aerobic zone. Denitrification (the reduction sequence \( \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \)) occurs only within the anaerobic zone; meanwhile decomposition is occurring in the
remaining aerobic zone. After the rain stops, the soil water content gradually decreases and the anaerobic zone contracts, losing denitrifier biomass and substrates back to the aerobic zone. Thus soluble C, NO3, and N2O have both anaerobic and aerobic pools. Decomposition and nitrification supply the soluble C and nitrate aerobic pools and denitrification consumes soluble C, nitrate and N2O from the anaerobic pools. Nitrite has only an anaerobic pool—in the model it is produced only by denitrifiers, and when it moves into the aerobic zone it is immediately oxidized to nitrate. N2, which is biogeochemically inert in this model, has only one pool. N2O in the aerobic pool is biogeochemically inert. To account for an uneven distribution of denitrifiers and substrates, a fixed parameter is introduced defining the fraction of the nitrate and soluble carbon in the anaerobic pool that is available to denitrifiers.

In all three modeling approaches, the anaerobic fractional volume represents a region (or regions) in the soil where there is not enough oxygen present to support aerobic decomposition, and where, if substrates are present, denitrifiers are active. DNDC places this region at the soil surface. The aggregate core model simulates anaerobic cores in the centers of all soil aggregates. DX does not specify the geometries or sizes of anaerobic and aerobic volumes, only their total fractional volume in the soil.

In DX there are two processes for transferring substrates between the aerobic and anaerobic pools—diffusion and changes in anaerobic fractional volume (AFV). AFV is calculated every hour based on soil WFPS and oxygen status (see Fig. 2.11),

\[
AFV = \max(0.0, (W - B)/(1.0 - B)) 
\]

\[
B = W_c \quad \text{if } [O_2]_g > 0.1 
\]

\[
B = W_c \{1.0 - ([O_2]_g - C_1)/(C_2 - C_1)\} \quad \text{if } [O_2]_g < 0.1 
\]

\[
C_1 = 0.1 
\]

\[
C_2 = 0.115 
\]
Figure 2.11 - Soil anaerobic fractional volume (AFV) as a function of both WFPS and gas phase oxygen deficit. Oxygen deficit rises linearly from zero, if the gas-phase oxygen concentration is equal to the atmospheric value (0.21), to one, if the gas-phase oxygen concentration is zero.
where $W_C$ is the critical value for initiating denitrification when air-filled pores are not oxygen deficient, and $[O2]_g$ is the gas phase oxygen mixing ratio (a discussion of the role of gas phase oxygen in this function is given below—Oxygen sub-section). As the AFV changes, substrates move from one pool to the other to reflect the volume changes; increasing AFV transfers substrates from the aerobic pool to the anaerobic pool, decreasing AFV transfers substrates from the anaerobic pool to the aerobic pool. If there were no consumption or production of nitrate, for example, then the model aerobic and anaerobic nitrate pools would simply be

$$\begin{align*}
(NO_3)^{aerobic} &= (1.0 - AFV) (NO_3)^{total} \\
(NO_3)^{anaerobic} &= (AFV) (NO_3)^{total}.
\end{align*}$$

The aerobic and anaerobic concentrations would be equal. Microbial activity, however, will produce nitrate in the aerobic zone and consume nitrate in the anaerobic zone, so a concentration gradient will be established. The magnitude of the gradient will depend on rates of production and consumption, relative fractional volumes, and an effective diffusion length. Diffusional transfer is then given by

$$TR_{diff} = D_{sol} ([C]_{ox} - [C]_{anox})/\lambda$$

where $TR_{diff}$ is the diffusional transfer (g/h), $D_{sol}$ is the solution phase diffusivity (2 x 10$^{-11}$ m$^2$/h; Jury et al 1991), $[C]_{ox}$ is the aerobic pool concentration (g/m$^3$), $[C]_{anox}$ is the aerobic pool concentration (g/m$^3$), and $\lambda$ is the effective diffusion length (a model parameter) combining two poorly known values, the actual average diffusion length and the aerobic zone/anaerobic zone contact area across which the transfer will take place.

The Gas Phase - DX includes a gas phase of O2, CO2, N2O, N2, and NH3. There are two primary questions that motivate this addition: (1) Will a more careful treatment of gas phase diffusion within the soil lead to an improved resolution of the N2O flux peak following a rain event? (2) Will the inclusion of O2 as a partial control on anaerobic fractional volume (and thus on denitrification) improve N2O flux. 

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results, particularly under conditions of low oxygen in relatively dry soil? Field measurements of N2O soil gas concentration profiles will allow this component of the revised model to be tested.

Species in the gas phase are assumed to always be in equilibrium with their dissolved counterparts in the soil solution (see Table 2.2 for solubility constants), based on the fact that the soil solution tends to have a very high surface-to-volume ratio (Radford and Greenwood 1970). This assumption will be weakest under very wet soil conditions. In the model, vertical movement in the gas phase occurs by two processes: basic concentration-gradient driven diffusion, and advection due to changing gas volume as the soil wets or dries (the gas phase is assumed to be incompressible).

Advection is modeled as simple mass balance. If AFPS (air-filled pore space; AFPS = 1.0 - WFPS) is increasing, the mass of a gas-phase constituent in a layer increases by an amount equal to its gas-phase concentration in the layer above times the change in AFPS. If AFPS is decreasing, the layer loses an amount equal to its gas-phase concentration times the decrease in AFPS. For decreasing AFPS (wetting of the soil) the gas is assumed to be driven upward.

Diffusion is modeled following Fick's Second Law (Jury et al. 1991)

$$\frac{\partial [X]}{\partial t} = D \frac{\partial^2 [X]}{\partial z^2}$$

(2.31)

where [X] is the gas phase concentration of a species X (g/m³), and D (m²/h) is the soil gas phase diffusivity, modified from the free air diffusivity (see below). The equation is solved using an implicit finite element model (e.g., Wang and Anderson, 1982). The boundary condition at the bottom of the soil profile is zero-flux (i.e., no downward concentration gradient). The surface node is set to the (constant) atmospheric concentration of the constituent (taken as zero for NH3 and N2—thus N2 is modeled as the difference from atmospheric, otherwise the 79% N2 in the atmosphere swamps any denitrification produced N2). D is given by

$$D = D_o \varepsilon(W,n)$$

(2.32)
where $D_0$ is the free air diffusivity (which varies slightly from one species to the next—Campbell, 1985) and $\epsilon(W,n)$ is a reduction factor depending on WFPS ($W$) and soil porosity ($n$). A variety of functions have been proposed for $\epsilon$; Jury et al (1991) recommend a formulation based on the work of Millington and Quirk (1961)

$$\epsilon(W,n) = \frac{(1.0 - W) \cdot n^{10/3}}{n^2}$$  \hspace{1cm} (2.33)

No gas phase chemistry occurs in the model.

**Oxygen** - Dissolved oxygen is consumed in the soil during the decomposition and nitrification processes; NH4 -> NO3 is assumed to consume 64 g oxygen per 14 g N nitrified (Schmidt 1982); each 12 g of soil organic carbon (SOC) oxidized to CO2 is assumed to consume 32 g oxygen (Glinksi and Stepniewski 1985). For each time step (one hour), if there is not enough oxygen in the solution phase to satisfy the predicted decomposition and nitrification processes, the rates of these processes are reduced to a level that the dissolved oxygen can support. After decomposition, nitrification and denitrification (if any) are calculated, dissolved and gas phase oxygen concentrations are re-equilibrated (along with the other gas phase species), and then gas phase diffusion is calculated.

Since the ultimate initiator of denitrification is not high soil water content but low dissolved oxygen concentrations (Firestone 1982), anaerobic fractional volume is a function of the spatial distribution of dissolved oxygen concentrations. This is what the aggregate diffusion models attempt to simulate (see Section 1.2.3 in Chapter 1 above). In DX the anaerobic fractional volume function depends on both WFPS and layer-average gas-phase oxygen concentration. Since gas phase diffusion is about $10^4$ times more rapid than liquid phase diffusion (Jury et al 1991), assuming a uniform gas phase concentration (at a given depth) seems a reasonable approximation.

Reported values for maximum soil gas-phase oxygen concentrations ($[O_2]_g$) at which denitrification occurs range from 4% to 17% (Firestone, 1982). Data from Smith and Arah (1990) show no abrupt cut-off, but a tendency for little or no
denitrification at a soil gas-phase oxygen mixing ratio of $[O_2]_g < 0.1$, and higher rates for lower concentrations. This implies that at least partial anaerobiosis occurs when $[O_2]_g < 0.1$ under most conditions, while it is rare for $[O_2]_g > 0.1$. In DX, if the gas phase $[O_2]_g$ is greater than 0.1, anaerobic fractional volume is a linear function of WFPS for values greater than the field capacity WFPS value plus an offset parameter ($W_C = W_x + dnxwfps$). At lower $[O_2]_g$, the critical WFPS to generate anaerobic fractional volume is less than $W_C$ (see Eq. 27 above and Fig. 2.11). With this relationship, lowering of pO2 will cause an onset of fractional anaerobiosis to occur in drier soils.
Table 2.2 - Gas solubility values at 25°C
(Sposito 1989; Warneck 1988)

<table>
<thead>
<tr>
<th>GAS</th>
<th>K [mol m⁻³ atm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>1.26</td>
</tr>
<tr>
<td>CO₂</td>
<td>34.1</td>
</tr>
<tr>
<td>N₂O</td>
<td>25.6</td>
</tr>
<tr>
<td>N₂</td>
<td>0.62</td>
</tr>
<tr>
<td>NH₃</td>
<td>1500†</td>
</tr>
</tbody>
</table>

† Sposito (1989) lists this as 57600, but model results for ammonia loss were too low.
2.4.3. The Revised DNDC Model - Minor Changes

WFPS Controls on Microbial Activity - DX uses a reduction factor based on the results of Doran et al (1990). The function has a parabolic shape, and is equal to 1.0 at the mean of 0.6 (the canonical value of Doran and colleagues) and \( W_x \) (the WFPS at field capacity for the particular soil). At WFPS values near that for maximum decomposition, the reduction factor is only slightly less than 1.0. Thus decomposition in DX is less sensitive to WFPS than DNDC (Fig. 2.12). If, as is the case at the Vegas site in La Selva (see Section 2.7 below), \( W_x \) is not 0.6 but instead about 0.4, decomposition at rates are enhanced in the revised versions for WFPS around field capacity (\( W_x \)).

Nitrification - DNDC models nitrate production via nitrification as a linear function of NH4 concentration, with soil temperature and soil moisture reduction factors. Its nitrification rate is generally quite high, so most ammonium is transferred to nitrate within a few days, except under extremely dry conditions. DX models nitrification via Michaelis-Menten kinetics, again with temperature and moisture rate reduction factors,

\[
N_{\text{trans}} = N_{\text{rate}} \cdot m_T \cdot m_M \cdot \frac{NH4}{(NH4 + K_{NH4})} \tag{2.34}
\]

where \( N_{\text{trans}} \) is the actual nitrification rate, \( NH4 \) is the free ammonium concentration in solution, \( m_T \) and \( m_M \) are the temperature and moisture reduction factors of DNDC. The maximum nitrification rate, \( N_{\text{rate}} \), is taken as 2 mg N/g dry soil/d (Davidson et al 1991; Robertson and Tiedje 1989) for mineral soils and 20 mg N/g dry soil/d for organic soils (parameter), and \( K_{NH4} \) is taken as 0.05 mg N/liter (Focht and Verstraete 1977). In DNDC, N2O production from nitrification is modeled as

\[
N2O = 0.0002 \cdot NH4 \cdot \left(0.54 + 0.51 \cdot T\right) / 15.8 \tag{2.35}
\]

where \( T \) is the soil temperature. Since nitrification occurs so rapidly in DNDC, and ammonium pools have short residence times, there is very little N2O produced by
Figure 2.12 - WFPS reduction factors for decomposition activity for DNDC and DX models. DNDC is more sensitive to WFPS at values near the optimum. Note that DNDC has fixed optimum at WFPS = 0.6, while optimum for DX is average of 0.6 and WFPS at soil field capacity ($W_x$). Two cases for DX are shown: $W_x = 0.6$ and $W_x = 0.4$. 

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nitrification (see Section 2.6 below). DX considers N2O production to be a small fraction (parameter) of nitrification; field values are generally less than 1% (Firestone and Davidson, 1989).

**Glucose** - Glucose has been added as a separate carbon pool in order to be able to simulate a particular field experiment (see Section 2.7 below). Glucose, in the model and probably in the field study, has three roles: (1) it is a soluble carbon substrate for denitrifiers and thus can enhance denitrification; (2) it is a carbon substrate for decomposers and will cause enhanced oxygen consumption and enhanced anaerobic conditions, and thus can enhance denitrification; and (3) since glucose contains no nitrogen, through assimilation into microbial biomass it will be a “sink” for inorganic nitrogen (ammonium and nitrate) (Craswell, 1978), and thus suppress denitrification. Carbon lost from the glucose pool on decomposition is either assimilated into microbial biomass (60%) or respired as CO2 (40%); the specific decomposition rate is taken as 0.021 h\(^{-1}\) (Paul and Clark, 1989). Like soluble carbon, glucose in the model has both an aerobic and an anaerobic pool, with a transfer determined by the anaerobic fractional volume. The anaerobic glucose pool is added to the anaerobic soluble carbon pool as denitrifier substrate. Glucose assimilated by denitrifiers is moved to the microbial biomass pool. Glucose is added to the model soil in the same way as a fertilizer supplement.

**Soluble Carbon** - Soluble, available, organic C compounds are a key substrate for denitrifier activity in soils. These compounds are an intermediate product and/or byproduct of decomposition processes. DNDC considers the soluble C available to denitrifiers to be that portion of the decomposition of microbial biomass and humads that is re-assimilated into microbial biomass. The daily “pool” of soluble C is thus a direct function of decomposition rates and humads and microbial biomass pool sizes. If a rain event occurs, denitrification is initiated and the available soluble C for the denitrification period is the “pool” representing the carbon re-assimilation
occurring the previous day. All of this soluble C (and no additional C) supplies the entire denitrification interval of up to ten days (or is depleted in the process).

Since DX has a much shorter decomposition timestep (1 hour), the soluble C "pool" (still the C re-assimilated during microbial biomass or humads decomposition) must accumulate of many timesteps, or denitrification is too limited by carbon availability. The new formulation has a soluble C "pool" that "accumulates" the re-assimilated C and "loses" 1/36 of itself every hour (a calibration parameter). Terms are in quotes because the soluble C "pool" does not have the same physical status as, say, the labile humads pool.

In effect, the difference between the two approaches amounts to a difference in residence time and availability of the carbon in this soluble state between mineralization and re-assimilation. DNDC considers this residence time to be shorter, but since active denitrifying layers are fully anaerobic, all soluble C is available to denitrifiers. DX considers soluble C to have a residence time on the order a couple of days, but, due to only fractional anaerobic volumes (generally < 50% and often < 10%), not all of the soluble C is available to denitrifiers. It is difficult to compare either soluble carbon approach to field studies because (1) field measurements (grab sample analysis) will yield values for pool size, but not residence time, and (2) what portion of the soluble C is actually available to denitrifiers depends on the distribution and size of anaerobic zones in the soil, and on which constituents of a soluble C pool denitrifiers actually utilize (e.g., Beauchamp et al 1989). The nature of the model soluble C "pool" is as a parameter linking the decomposition processes and the denitrification processes.

**Denitrification Electron Acceptors** - Both DNDC and DX simulate the reduction sequence NO3- -> NO2- -> N2O -> N2, with the rate of each step being a function of N-oxide concentration, denitrifier biomass, growth, yield, and maintenance coefficients, soluble C availability, soil temperature, and pH. DNDC assumes that both
the reduction and assimilation of \( \text{NxOy} \) to fuel the growth of denitrifiers is reduced by a factor \( \text{NxOy} / \Sigma \text{N} \), where \( \Sigma \text{N} \) is the total N-substrate concentration and \( \text{NxOy} \) is the concentration of the species being reduced. Thus each substrate contributes to denitrifier activity according to its relative abundance. For DX, with its much shorter total denitrification period and its rapid loss of denitrifier substrates due to a shrinking anaerobic zone once the rain stops, the formulation is modified so that, instead of relative abundances, the rate multipliers are \( 1/2 \) for NO3 reduction, \( 1/3 \) for NO2 reduction, and \( 1/6 \) for N2O reduction. This reflects a preference of denitrifiers for the more oxidized species; Focht and Verstraete (1977) report molar growth yields are greatest for nitrite, then nitrite, and lowest for nitrous oxide.
2.5. Model Sensitivity

A series of model runs tested its sensitivity to internal and external parameters. The standard case was a 30 day simulation of bare loam soil (clay = 19%), with constant air temperature (20°C), initial nitrate and ammonium each at 5 mg N/ g dry soil; pH at 6.5, and initial SOC at 0.03 g C/g dry soil. There were two rain events: 2 cm on day 10 and 5 cm on day 20. Model soil depth was 35 cm for these sensitivity runs.

2.5.1. External Parameters

The external parameters are those model parameters that will generally be available as input data from a field study (e.g., soil pH). These parameters reflect the specific climatic, soil physical, and soil chemical variables that define a site.

For each run a single parameter value was either increased or decreased relative to its standard value, with all other parameters held fixed (Table 2.3). The effect of changes in each of the external parameter on N2O and N2 gas flux can be compared to the standard run (Fig. 2.13; the standard run (#1) is on the left). The internal parameters were held constant (see Section 2.5.2). The results are generally consistent with field and lab observations (see, for example, reviews by Focht and Verstraete 1977; Firestone 1982; Sahrawat and Keeney 1986; Aulakh et al 1992):

- at low pH, N2O reduction to N2 is inhibited; at higher pH N2O reduction is enhanced (runs #2 & #3);
- increasing temperature increased denitrification (runs #4 & #5);
- low clay content enhanced denitrification (runs #6 & #7) because of enhanced decomposition and thus increased substrate levels (the effects of clay on soil water content were ignored in this simulation);
- very low SOC values suppress denitrification; at high SOC most gas flux is as fully reduced N2 (runs #8 - #10);
increasing initial nitrate (runs #11 - #14) caused a decline in both N2O and N2 fluxes. This result is counter-intuitive. As nitrate concentration increased from 1 to 10 mg N/kg soil, total N reduction was constant but a larger fraction of the reduced N stopped at nitrite and was not lost as N2O or N2 (Fig. 2.14). At higher nitrate concentrations total denitrification is reduced, probably because of rapid denitrifier growth consuming a large fraction of the soluble C very quickly, and sequestering much of it in biomass. If a grass cover is simulated, the results are very different (Fig. 2.14; Note that results in Fig. 2.13 for bare ground are different than runs 11 - 14 because a different value of $dnxwfps$ was used; it allowed denitrification to begin under drier conditions, and enhanced denitrification overall). Increasing nitrate concentration from 1 to 50 mg N/kg soil caused large increases in both total denitrification and N gas flux. In this case more soluble C is available (plant root effect) and less nitrogen (plant uptake). There are reports of high nitrate concentrations inhibiting N2O reduction to N2 (Blackmer and Bremner 1978); high nitrate concentration in the model inhibits both N2O and N2 production, and suggests that this might not be biochemical inhibition but just the complex dynamics of several interacting processes.

- increasing the initial ammonium concentration had little effect N gas flux, except that at high ammonium concentrations nitrification was enhanced so total N2O flux increased (runs #15 -#18).
- adding a grass cover (#19) suppressed total fluxes (even though there was increased soluble C) by both drying the soil (AET > soil evaporation) and by plant uptake consuming nitrogen;

- The precipitation pattern affected N gas fluxes:
  1. 50% less precipitation severely reduced fluxes, particularly N2 (#23);
  2. 200% more precipitation increased fluxes by about 80% (#24);
  3. One large storm (same total precipitation) slightly increased fluxes (#21);
Table 2.3 - Sensitivity to External Parameters

<table>
<thead>
<tr>
<th>Run</th>
<th>Parameter adjusted</th>
<th>Parameter Value (Standard)†</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none (standard run)</td>
<td>- - - -</td>
<td>N2O &amp; N2 fluxes ~ equal</td>
</tr>
<tr>
<td>2</td>
<td>pH</td>
<td>4.5 (6.5)</td>
<td>N2O enhanced; N2 near zero</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
<td>8.5 (6.5)</td>
<td>N2 enhanced; N2O reduced</td>
</tr>
<tr>
<td>4</td>
<td>air temp. (°C)</td>
<td>10 (20)</td>
<td>N2 &amp; N2O reduced</td>
</tr>
<tr>
<td>5</td>
<td>air temp. (°C)</td>
<td>30 (20)</td>
<td>N2 &amp; N2O enhanced</td>
</tr>
<tr>
<td>6</td>
<td>clay content (%)</td>
<td>5 (19)</td>
<td>N2 &amp; N2O enhanced</td>
</tr>
<tr>
<td>7</td>
<td>clay content (%)</td>
<td>50 (19)</td>
<td>N2 &amp; N2O reduced</td>
</tr>
<tr>
<td>8</td>
<td>init. SOC (%)</td>
<td>0.3 (3)</td>
<td>very low fluxes</td>
</tr>
<tr>
<td>9</td>
<td>init. SOC (%)</td>
<td>1.0 (3)</td>
<td>low fluxes</td>
</tr>
<tr>
<td>10</td>
<td>init. SOC (%)</td>
<td>10.0 (3)</td>
<td>N2 enhanced, N2O up slightly</td>
</tr>
<tr>
<td>11</td>
<td>init. nitrate (ppm)</td>
<td>1 (5)</td>
<td>slight increase in N2O &amp; N2¶</td>
</tr>
<tr>
<td>12</td>
<td>init. nitrate (ppm)</td>
<td>10 (5)</td>
<td>slight reduction in N2O &amp; N2¶</td>
</tr>
<tr>
<td>13</td>
<td>init. nitrate (ppm)</td>
<td>50 (5)</td>
<td>N2O &amp; N2 reduced¶</td>
</tr>
<tr>
<td>14</td>
<td>init. nitrate (ppm)</td>
<td>200 (5)</td>
<td>N2O &amp; N2 reduced¶</td>
</tr>
<tr>
<td>15</td>
<td>init. NH4 (ppm)</td>
<td>1 (5)</td>
<td>little change</td>
</tr>
<tr>
<td>16</td>
<td>init. NH4 (ppm)</td>
<td>10 (5)</td>
<td>little change</td>
</tr>
<tr>
<td>17</td>
<td>init. NH4 (ppm)</td>
<td>50 (5)</td>
<td>little change</td>
</tr>
<tr>
<td>18</td>
<td>init. NH4 (ppm)</td>
<td>200 (5)</td>
<td>N2O increased (nitrification)</td>
</tr>
<tr>
<td>19</td>
<td>vegetation cover</td>
<td>grass (bare)</td>
<td>N2 &amp; N2O reduced ~ 80%</td>
</tr>
<tr>
<td>20</td>
<td>precipitation</td>
<td>[5,10] &amp; [2,20]*</td>
<td>little change</td>
</tr>
<tr>
<td>21</td>
<td>precipitation</td>
<td>[7,10]</td>
<td>slight enhancement</td>
</tr>
<tr>
<td>22</td>
<td>precipitation</td>
<td>[1,5]&amp;[1,10]&amp;</td>
<td>20% reduction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[2.5,15]&amp;[2.5,20]</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>precipitation</td>
<td>[1,10] &amp; [2.5,20]</td>
<td>fluxes reduced by ~ 80%</td>
</tr>
<tr>
<td>24</td>
<td>precipitation</td>
<td>[6,10] &amp; [15,20]</td>
<td>fluxes increased by ~ 80%</td>
</tr>
</tbody>
</table>

† The standard run value is in parentheses.
¶ Very different results occur when there is grass cover (see Fig. 2.14).
* The notation is [rain amount (cm), day of rain];
  The standard scenario is [2,10] & [5,20]

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Figure 2.13 - Nitrous oxide and dinitrogen gas flux for series of runs varying external parameters (see Table 2.3). Gas flux is total for simulation of 30 days.
Figure 2.14 - For low initial concentrations in bare soil, increasing initial nitrate concentration reduces N2O and N2 gas flux but not total denitrifier activity. As nitrate concentration increases more of the soluble carbon is consumed converting nitrate to nitrite, and less N2O and N2 are produced. At higher nitrate levels denitrifier growth is enhanced enough to consume significant amounts of soluble C and total denitrification is reduced. With a grass cover, increasing nitrate causes enhanced denitrification until fairly high levels are reached. For low initial nitrate levels plant uptake has consumed much of it before the rain events initiate denitrification.
(4) Four small storms (same total precipitation) slightly reduced fluxes (#22);
(5) Reversing the order of the storms had no effect (#20).

2.5.2. Internal Parameters

The internal parameters (Table 2.4) are those model parameters that will not generally be available as input data from a field study (e.g., fraction of microbial biomass that are denitrifiers). These parameters reflect the specific nature of this particular model. Their values are determined by calibrating the model against a series of field studies (see Section 2.6 below).

For each run a single parameter value was either increased or decreased relative to its standard value, with all other parameters held fixed (Table 2.5). The effect of changes in each of the internal parameter on N20 and N2 gas flux can be compared to the standard run (Fig. 2.15; the standard run (#1) is on the left). The external parameters were held constant (see Section 1.5.1). Because the internal parameters reflect the internal structure of the model, they cannot readily be compared to field and lab results. Those parameters which have a strong effect on the model results are both the strongest “tuning knobs”, and also point to issues that need more attention in field research. Discussion of the influential parameters follows (a brief summary of all the results is in Table 2.5). The standard values are those arrived at during model calibration (Section 1.6).

The parameters controlling the use by denitrifiers of nitrate, nitrite, and nitrous oxide have a strong effect on gas flux results. If the nitrate-nitrite ratio is high (i.e., nitrate is a preferred oxidant over nitrite), more N reduction stops at nitrite and N20 flux is reduced, though N2 flux does not change much (run #10). For a low nitrate-nitrite ratio N20 flux nearly doubles, while N2 flux increases slightly (run #11). The N20 use fraction controls the ratio of N20 to N2 (runs #12 & #13). The classical formulation, with use of N-oxides based on relative abundance, had very
similar results to the standard case (#20), though when tested under conditions of higher carbon availability it did not.

The denitrifier biomass fraction determines what fraction of the total microbial biomass can denitrify. Gas flux in DX drops if a low values is used (run #6), but increases only slightly for much higher values, implying other limiting factors (run #7). Focht and Verstraete (1977) report values for this parameter ranging from <0.01 to 0.5. In DNDC, the results are insensitive to this value (fixed at 0.05), presumably because the ten day denitrification period allows the denitrifier population (biomass) to grow sufficiently, even if it is initialized at a much lower value. Their growth is limited more by soluble carbon availability than by the duration of the anaerobic event, and a smaller fractional denitrifier population will consume soluble C more slowly.

The available substrate fraction is a direct multiplier of substrate transfer (nitrate and soluble C) by expansion of anaerobic fractional volume. For example, if this parameter is set at 0.5, and if half the soil volume is anaerobic (AFV = 0.5), then 0.5 x 0.5 or 25% of the nitrate and soluble C pools are available to the denitrifiers. This factor is introduced to allow that not all substrate in a region of the soil is likely to be available to denitrifiers, due to uneven distributions and obstacles to transfer. It has surprisingly little effect (runs #14 & #15) over the range shown (10-50%).

The loss factor for soluble C controls the size of the soluble C “pool” by setting the fraction of that “pool” that is lost each hour. The standard value of 1/36 (roughly a 24 hour half-life, compared to a 24 hour complete turnover in DNDC). Following DNDC, this pool size is doubled for vegetated soils, in this case by setting the loss rate to 1/72 h⁻¹. Since soluble C is often a limiting factor for denitrification in this model, particularly on bare soils, model output is very sensitive to this factor (runs #4 & #5).
Solution diffusion length ($\lambda$) is a parameter to control the rate of solution phase diffusion of substrate (nitrate and soluble C) between the aerobic and anaerobic zones. Tripling $\lambda$ cuts gas flux in half (run #17); reducing $\lambda$ increases had little effect (run #16). A series of runs over four orders of magnitude ($\lambda = 0.00005$ m to 0.5 m) showed that the results are constant for all values of $\lambda$ less than 0.0005 m. If $\lambda$ is greater than 0.05 m the results are the same as if there is no diffusion ($\lambda$ effectively infinite). Within this range (0.05 m - 0.0005 m) though, the model is quite sensitive to $\lambda$. This should be especially true for heavy, wet soils where substrate depletion is likely to occur before re-oxygenation. It also had a strong effect on the grassland calibration runs (see next section).

The final internal parameter, $dnxwfps$, is the offset from field capacity ($W_f$) at which denitrification is initiated when oxygen is not limiting. Changing this value from +0.02 to +0.10 caused nearly a tripling of gas flux (runs #8 & #9). Given the difficulty of getting accurate field or model WFPS results, this is a troubling result. This is discussed further below (Section 2.8). This parameter is reserved to be set for each site; values for vegetated soils need to be lower than for bare soils because bare soils tend to be wetter.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O clay factor</td>
<td>Controls equilibrium partitioning between clay-adsorbed and dissolved N2O; both pools are available to denitrifiers, but only the dissolved N2O is in equilibrium with the gas phase.</td>
</tr>
<tr>
<td>rate of Csol loss</td>
<td>Controls the residence time in the soluble carbon pool, and thus controls the size of this pool.</td>
</tr>
<tr>
<td>denitrifier biomass</td>
<td>Fraction of microbial biomass that is also denitrifier biomass.</td>
</tr>
<tr>
<td>fraction</td>
<td></td>
</tr>
<tr>
<td>available substrate</td>
<td>Percent of substrate in anaerobic zone that is available to denitrifiers.</td>
</tr>
<tr>
<td>solution diffusion</td>
<td>Controls strength of solution phase diffusional transfer between aerobic and anaerobic pools.</td>
</tr>
<tr>
<td>length</td>
<td></td>
</tr>
<tr>
<td>dnxwfps</td>
<td>Controls offset from field capacity for initiation of denitrification when oxygen is not limiting.</td>
</tr>
<tr>
<td>o2c1</td>
<td>Gas phase oxygen deficiency (relative to atmospheric) at which anaerobic fractional volume can be exist in dry soils.</td>
</tr>
<tr>
<td>o2c2</td>
<td>Controls strength of oxygen deficiency control on anaerobic fractional volume.</td>
</tr>
<tr>
<td>NO3:NO2 use ratio</td>
<td>Controls relative use of nitrate and nitrite by denitrifiers</td>
</tr>
<tr>
<td>N2O use fraction</td>
<td>Controls relative use of nitrous oxide by denitrifiers</td>
</tr>
</tbody>
</table>
Table 2.5 - Sensitivity to Internal Parameters

<table>
<thead>
<tr>
<th>Run</th>
<th>Parameter adjusted</th>
<th>Parameter Value (Standard)</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none (standard run)</td>
<td>- - - - -</td>
<td>N2O &amp; N2 fluxes ~ equal</td>
</tr>
<tr>
<td>2</td>
<td>N2O clay factor</td>
<td>78 (15.6)</td>
<td>little change</td>
</tr>
<tr>
<td>3</td>
<td>N2O clay factor</td>
<td>3.16 (15.6)</td>
<td>little change</td>
</tr>
<tr>
<td>4</td>
<td>rate of Csol loss (1/h)</td>
<td>0.0416 (.0278)</td>
<td>N2O &amp; N2 reduced ~ 20%</td>
</tr>
<tr>
<td>5</td>
<td>rate of Csol loss (1/h)</td>
<td>0.0208 (.0278)</td>
<td>N2O &amp; N2 increased ~ 20%</td>
</tr>
<tr>
<td>6</td>
<td>denitr. biomass fraction</td>
<td>0.025 (.05)</td>
<td>N2O &amp; N2 increased ~ 20%</td>
</tr>
<tr>
<td>7</td>
<td>denitr. biomass fraction</td>
<td>0.01 (.05)</td>
<td>N2O &amp; N2 reduced ~ 60%</td>
</tr>
<tr>
<td>8</td>
<td>dnxwfps</td>
<td>0.10 (.06)</td>
<td>fluxes reduced by ~ 50%</td>
</tr>
<tr>
<td>9</td>
<td>dnxwfps</td>
<td>0.02 (.06)</td>
<td>fluxes increased by ~ 50%</td>
</tr>
<tr>
<td>10</td>
<td>no3:no2 use ratio</td>
<td>3.0 (1.5)</td>
<td>N2O reduced by ~ 40%</td>
</tr>
<tr>
<td>11</td>
<td>no3:no2 use ratio</td>
<td>0.75 (1.5)</td>
<td>N2O increased by ~ 80%</td>
</tr>
<tr>
<td>12</td>
<td>N2O use fraction</td>
<td>0.15 (.10)</td>
<td>N2O down 50%; N2 increases</td>
</tr>
<tr>
<td>13</td>
<td>N2O use fraction</td>
<td>0.05 (.10)</td>
<td>N2 down 50%; N2O increases</td>
</tr>
<tr>
<td>14</td>
<td>available substrate (%)</td>
<td>50 (33)</td>
<td>little change</td>
</tr>
<tr>
<td>15</td>
<td>available substrate (%)</td>
<td>10 (33)</td>
<td>little change</td>
</tr>
<tr>
<td>16</td>
<td>solute diff. length (m)</td>
<td>0.0005 (.0015)</td>
<td>little change</td>
</tr>
<tr>
<td>17</td>
<td>solute diff. length (m)</td>
<td>0.005 (.0015)</td>
<td>fluxes reduced by ~ 50%</td>
</tr>
<tr>
<td>18</td>
<td>gas diffusivity</td>
<td>times 5</td>
<td>little change</td>
</tr>
<tr>
<td>19</td>
<td>gas diffusivity</td>
<td>times 0.2</td>
<td>little change</td>
</tr>
<tr>
<td>20</td>
<td>DNDC N use ratios</td>
<td>- - - -</td>
<td>little change</td>
</tr>
<tr>
<td>21</td>
<td>Critical O2 deficit [%]</td>
<td>65(50)</td>
<td>little change</td>
</tr>
<tr>
<td>22</td>
<td>Critical O2 deficit [%]</td>
<td>35(50)</td>
<td>little change</td>
</tr>
<tr>
<td>23</td>
<td>Sensitivity to O2 deficit</td>
<td>0.25(.10)</td>
<td>little change</td>
</tr>
<tr>
<td>24</td>
<td>Sensitivity to O2 deficit</td>
<td>0.04(.10)</td>
<td>little change</td>
</tr>
</tbody>
</table>

† The standard run value is in parentheses.
Figure 2.15 - Nitrous oxide and dinitrogen gas flux for series of runs varying internal parameters (see Table 2.5). Gas flux is total for simulation of 30 days.
2.6 Model Calibration

The model's internal parameters were set during a series of calibration runs, including three field studies and a classical DNDC run. The three field studies are those DNDC was tested against (Li et al 1992b): (1) a one-month study of total denitrification (N2O+N2) from fertilized grassland in England (Ryden 1981); (2) a two-month study of N2O emissions from fertilized and unfertilized grassland in Colorado (Mosier et al 1981; Parton et al 1988); and (3) four months of a two-year study of N2O emissions from an unfertilized grassland on organic soil in Florida (Terry et al 1981). In addition, the results of the standard scenario of the sensitivity study (unfertilized bare loam, Section 2.5) were compared with DNDC results (no field data). DX internal parameters were adjusted to match, as well as possible, daily gas fluxes for the five cases; no other model output was considered.

The external parameters for each case are listed in Table 2.6. The final internal parameter values are listed in Table 2.7. Gas flux results for each case are shown in Figs. 2.16 - 2.19. All internal parameters except dnxwfps, the offset from field capacity at which anaerobic fractional volume is generated, are the same for all cases.

In order to achieve the sustained denitrification flux peaks observed at an English grassland (Fig. 2.16), it was necessary to allow substantial diffusional substrate transfer (λ = 0.0015 m). This had the effect of enhancing the second peak on the Case 4 (bare loam soil, Fig. 2.19). For the English grassland, since dnxwfps = -0.06 and the soil water content is initialized to field capacity, there is an initial pulse of denitrification without a rain event (days 1 and 2, Fig. 2.16).

Nitrous oxide emissions agree quite well with the data for the dry grassland in Colorado (Figs. 2.17.a&b). Since there was an extended dry period (days 6 to 32) the moderate rain on day 32 (1.8 cm) was not enough to wet the model soil significantly above field capacity, and so DX predicts only a very small N2O pulse related to this
Table 2.6 - Calibration External Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Colorado</th>
<th>England</th>
<th>Florida</th>
<th>Bare Loam</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7</td>
<td>6.3</td>
<td>5.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Init. SOC [g C/kg soil]</td>
<td>5.7</td>
<td>33.0</td>
<td>429.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Init. nitrate [mg N/kg soil]</td>
<td>1</td>
<td>2</td>
<td>100.0</td>
<td>5</td>
</tr>
<tr>
<td>Init. ammonium [mg N/kg soil]</td>
<td>2</td>
<td>1</td>
<td>20.0</td>
<td>5</td>
</tr>
<tr>
<td>Clay fraction</td>
<td>0.09</td>
<td>0.19</td>
<td>0.03</td>
<td>0.19</td>
</tr>
<tr>
<td>Soil texture</td>
<td>sandy loam</td>
<td>loam</td>
<td>muck</td>
<td>loam</td>
</tr>
<tr>
<td>Wfield capacity</td>
<td>0.58</td>
<td>0.57</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Fertilization</td>
<td>450</td>
<td>125</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>[kg N ha⁻¹]</td>
<td>(urea)</td>
<td>(NH₄NO₃)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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### Table 2.7 - Calibration Internal Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{2o}$ clay factor</td>
<td>15.8</td>
</tr>
<tr>
<td>soluble C loss rate (vegetation)</td>
<td>$1/72 \text{ h}^{-1}$</td>
</tr>
<tr>
<td>soluble C loss rate (bare soil)</td>
<td>$1/36 \text{ h}^{-1}$</td>
</tr>
<tr>
<td>denitrifier biomass fraction</td>
<td>0.05</td>
</tr>
<tr>
<td>$\text{no3no2ratio}$</td>
<td>1.5</td>
</tr>
<tr>
<td>fraction $n_{2o}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$o_{2c1}$</td>
<td>0.5</td>
</tr>
<tr>
<td>$o_{2c2}$</td>
<td>0.6</td>
</tr>
<tr>
<td>transfer factor</td>
<td>$1/3$</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.0015 m</td>
</tr>
<tr>
<td>$d_{nxwfps} - \text{Colorado}$</td>
<td>-0.01</td>
</tr>
<tr>
<td>$d_{nxwfps} - \text{England}$</td>
<td>-0.06</td>
</tr>
<tr>
<td>$d_{nxwfps} - \text{Florida}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$d_{nxwfps} - \text{Bare Loam}$</td>
<td>+0.06</td>
</tr>
</tbody>
</table>
storm, while the field data indicates a stronger response (Figs. 2.17.a&b). Likewise, the models peak on day 5 is higher than the field data, possibly because the model soil water content was initialized at field capacity, so the day 5 storm (2.5 cm) wet the soil significantly. The fertilizer (450 kg urea-N/ha on day 3) caused only a slight enhancement on day 5 because little of the nitrogen had been nitrified to nitrate before this storm.

The fraction of nitrified N emitted as N2O (0.3%) was set to match dry period data for the Colorado grassland (Figs. 2.17.a&b). The value is within the common range reported for field data (Firestone and Davidson, 1989). As a result, for the unfertilized case (2b), about 90% of the emitted N2O is from nitrification, while the classical DNDC predicted only 1.3% of N2O from nitrification for this case. For the fertilized case DX predicts 45% of N2O from nitrification, DNDC predicts 5.8% from nitrification, and Parton et al (1988) estimate that 60-80% of the N2O flux was due to nitrification. An important difference between DX and DNDC in this case is the residence time of the ammonium pool. For the urea fertilized plot, in DX after 40 days there is still about 100 mg NH4-N/kg soil present and so nitrification is still significant, while in DNDC the large, fertilizer-induced ammonium pool disappears within a week (Li et al 1992b) so nitrification-induced N2O is quite small.

The magnitude of N2O flux for rain events is about half that observed in the field in the Florida study (Figure 2.18). In addition, the model generates several strong events that were not observed in the field, and it misses at least one observed flux peak. Some of the model denitrifier activity may have been missed by the field sampling scheme (every 2 to 6 days), and perhaps the field site precipitation scenario was not the same as that measured at the meteorological station (and used to drive the model).

The bare loam test compares DX and DNDC N2O gas fluxes (Fig. 2.19 and Table 2.8). For each model, the first rain event (2 cm) causes about 8 hours of active
denitrification—in both DX and DNDC the soluble C is depleted within 10 hours. During those few hours, though, DNDC produces about 300% more N2O than DX. I believe this is due to the relatively larger anaerobic fractional volume (about 10 cm/unit area in DNDC vs. about 1 - 2 cm/unit area in DX). In the second rain event (5 cm rain in 10 hours), DNDC soluble C is depleted after 10 hours, and for hours 8 - 10 only the soluble C in the deepest layers (17.5 to 25 cm) is available; all soluble C above that is already gone. In DX, this rain event causes about 50 hours of active denitrification, although the anaerobic fractional volume is greater than 10% for only 29 hours and the surface (0 - 10 cm) soluble C is depleted within 10 hours. Below 10 cm, though, the denitrifiers are active for about 24 hours. For the final 24 hours only limited denitrification activity occurs at depth. This enhanced actual denitrification period in DX accounts for its overall higher gas flux. It is also apparent that the gas diffusion routine in DX releases the N2O much faster than DNDC. In both models, the majority of the denitrifier activity only reduces nitrate to nitrite (Table 2.8), which, in both models, is instantly re-converted to nitrate when aerobic conditions resume.
Figure 2.16 - Total denitrification (N₂O + N₂) for a fertilized grassland in England during June 1979. Field data from Ryden (1981). Model WFPS at initialization (field capacity) is high enough to cause denitrification that was not observed in the field.
Figure 2.17 - (a) N2O flux for an unfertilized grassland in Colorado during June and July 1979. Field data from Mosier et al (1981). (b) Same as (a) but plot was fertilized with urea (450 Kg N/ha).
Florida grassland - muck soil
Nitrous oxide flux

Figure 2.18 - N2O flux for an unfertilized grassland on organic (muck) soil in Florida during the summer of 1979. Field data from Terry et al (1979).

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Figure 2.19 - N2O flux for an unfertilized bare loam soil. Results are for DNDC model (bars) and DX model (solid line).
Table 2.8 - Comparison of DNDC and DX (for simulation in Figure 2.19)

<table>
<thead>
<tr>
<th>Variable (g N or C m(^{-2}))</th>
<th>DNDC</th>
<th>DX</th>
</tr>
</thead>
<tbody>
<tr>
<td>total N(_2)O flux</td>
<td>0.084</td>
<td>0.131</td>
</tr>
<tr>
<td>total N(_2) flux</td>
<td>0.056</td>
<td>0.111</td>
</tr>
<tr>
<td>Nitrite†</td>
<td>0.568</td>
<td>0.724</td>
</tr>
<tr>
<td>total NH(_3) flux</td>
<td>0.079</td>
<td>0.066</td>
</tr>
<tr>
<td>mineralized N</td>
<td>2.47</td>
<td>2.75</td>
</tr>
<tr>
<td>soil CO(_2) respiration</td>
<td>33.0</td>
<td>32.2</td>
</tr>
</tbody>
</table>

† Equals nitrate reduced to nitrite that is not further reduced to N\(_2\)O and/or N\(_2\).
2.7. Vegas Site Simulation

To investigate what are considered to be the principal controls on denitrification (oxygen, nitrate, and soluble C), four separate soil treatments were used at Antonio Nobre’s field Vegas site (Table 2.9). For each case, N2O gas flux, N2O soil gas profiles, and solution nitrate and ammonium concentrations were measured before each treatment, at 0.5h, 2h, 4h, 8h, 24h, and every one to few days following the treatment. DX was run for each of these cases (see Table 2.1, above, and Table 2.10, below, for initialization data). Model soil temperature and WFPS for the surface layer are shown in Fig. 2.20.

2.7.1. Nitrate and Ammonium Profiles

**Ammonium** - Model ammonium profiles for the water and nitrogen treatments are very similar—a gradual accumulation at the surface and about 20% of the surface pool leaching in each irrigation. There is little response in the ammonium pool to the nitrate addition (Fig. 2.21). Field data for the water treatment at 2 cm shows a stronger accumulation rate during dry periods and more pronounced leaching (Fig. 2.22). The nitrogen treatment field data shows a stronger response to the nitrate addition, with higher surface ammonium until the third irrigation. At 10 cm, field NH4 concentration appears to decline while the model slowly accumulates.

**Nitrate** - The water treatment field and model nitrate profiles are in good agreement, showing surface accumulation during dry periods (due to surface evaporation and capillary rise of soil water), and strong surface leaching at each irrigation (Fig. 2.23). For the nitrogen treatment (nitrate added at 50 Kg N/ha or roughly 20 mg N/ kg soil for the top 30 cm of the soil profile), the model surface layer shows very strong surface accumulation, drawing from the top 15 cm (Fig. 2.24). The field data rise to about 50 mg N/kg soil at the surface, 30 mg/kg at 5 cm,
and 10-15 mg/kg at 10 cm, and shows only slight leaching or accumulation. The model always has more nitrate in the profile than the field data.

Discussion - For the unfertilized case, agreement between field and model is quite good. The major discrepancy is in the variability in the surface ammonium pool—the model appears to have too much NH4 adsorbed onto clay (clay content about 4%). For the nitrate fertilized case, model and field agreement is not so good. The model wicking of nitrate to the surface is too large (there is vertical, water-phase diffusion in the model, but it cannot overcome the capillary rise). If model vertical diffusion rates are increased by 10 times in the nitrogen treatment, surface nitrate rose to about 100 mg N/kg soil and then dropped to about 60 mg/kg. This had very little impact on N2O fluxes, and it flattened out the nitrate results for the water treatment. Also, the field data implies that nitrate additions will increase the ammonium pool; the model has no real mechanism for this except for reduced NH4 assimilation/uptake. This cannot give the rapid response in the ammonium pool seen in the field.
Finca Jack Soil Temperature and Moisture
Model results for surface layer

Figure 2.20 - Soil climate model temperature and WFPS results for irrigated plots at the Vegas site (also called Finca Jack site), and control (unirrigated) plot WFPS. Surface layer is 0 - 3.3 cm.
### Table 2.9 - Vegas Site Plot Treatments

<table>
<thead>
<tr>
<th>Plot name</th>
<th>Treatment #1</th>
<th>Treatment #2</th>
<th>Treatment #3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(3/22/92)</td>
<td>(4/2/92)</td>
<td>(4/9/92)</td>
</tr>
<tr>
<td>control</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>water</td>
<td>1 cm water</td>
<td>1 cm water</td>
<td>3 cm water</td>
</tr>
<tr>
<td>nitrate</td>
<td>1 cm water +</td>
<td>1 cm water</td>
<td>3 cm water</td>
</tr>
<tr>
<td></td>
<td>50 kg NO3-N/ha</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nitrate + glucose</td>
<td>1 cm water +</td>
<td>1 cm water</td>
<td>3 cm water</td>
</tr>
<tr>
<td></td>
<td>50 kg NO3-N/ha +</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250 kg glucose C/ha</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.10 - Vegas Site Soil Properties (Model initial values)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Layer #1 (0 - 10)</th>
<th>Layer #2 (10 - 25)</th>
<th>Layer #3 (25 - 50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>depth (cm)</td>
<td>0 - 10</td>
<td>10 - 25</td>
<td>25 - 50</td>
</tr>
<tr>
<td>SOC (kg C/kg dry soil)</td>
<td>0.026</td>
<td>0.012</td>
<td>0.006</td>
</tr>
<tr>
<td>NO3 (mg NO3-N/kg dry soil)</td>
<td>15</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>NH4 (mg NH4-N/kg dry soil)</td>
<td>10</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>pH</td>
<td>6.4</td>
<td>6.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Figure 2.21 - (a) Field and model soil solution ammonium concentration profiles for 2 and 5 cm in the nitrogen treatment plot at the Vegas site (also called Finca Jack site). Results for the nitrogen + carbon treatment are very similar. (b). Same as (a) but for 10, 20, and 40 cm in the nitrogen treatment plot.
Figure 2.22 - (a) Field and model soil solution ammonium concentration profiles for 2 and 5 cm in the water treatment plot at the Vegas site (also called Finca Jack site). (b) Same as (a) but for 10, 20, and 40 cm in the water treatment plot.
Figure 2.23 - (a) Field and model soil solution nitrate concentration profiles for 2 and 5 cm in the water treatment plot at the Vegas site (also called Finca Jack site). (b) Same as (a) but for 10, 20, and 40 cm in the water treatment plot.

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Figure 2.24 - (a) Field and model soil solution nitrate concentration profiles for 2 and 5 cm in the nitrogen treatment plot at the Vegas site (also called Finca Jack site). Results for the nitrogen + carbon treatment are very similar. (b) Same as (a) but for 10, 20, and 40 cm in the nitrogen treatment plot.
2.7.2. N2O Gas Fluxes

**Control** - Model N2O fluxes (Fig. 2.25) in the control case are about 0.013 mg N/m²/h reflecting steady dry-period nitrification of about 4 mg N/m²/h, most of it occurring in the top 15 cm of the soil. The field data shows oscillations near this value.

**Water Treatment** - Model N2O fluxes for the first and third irrigations are about 5 and 10 times higher than field data; for the second irrigation model flux enhancement above background is only about 20% of field results (Fig. 2.26.a,b). Model flux peaks last about 24 hours, while field flux has dropped back to the background within 8 hours. DNDC was run with a silt loam soil texture because soil moisture results for this texture were closest to the DX soil moisture results; sandier textures were too dry. The first irrigation produced about the same total N2O as DX, though the peak is much broader. There was no denitrification for the second irrigation as the surface soil was too dry, decomposition rates were near zero, and there was no soluble C available when the soil wetted up. The third irrigation produced lower N2O flux than DX, probably because of much lower soluble C, though still higher than the field results. For the Vegas case, DNDC will generally have lower soluble C availability than DX because the soil is dry and decomposition rates are lower (see Fig. 2.12 above). N2 flux in DX is about half the N2O flux for each irrigation. In DNDC N2 flux is about 10% of N2O for the first irrigation and 1300% for the third irrigation (neither N2O nor N2 is produced in the second irrigation).

**Nitrogen Treatment** - In the field, the first irrigation peak is about twice as high as the water treatment, while the second and third are more equal for each treatment (Fig. 2.27a,b). Nitrate additions caused the fluxes to stay above background for at least 24 hours. DX model flux peaks for the nitrogen treatment are just slightly less than for the water treatment, and still much above the field results for irrigations one and three, and below for irrigation two. Nitrate fertilization causes the first irrigation peak to be suppressed by about 65% in DNDC, as high nitrate concentrations...
and relatively low soluble C concentrations cause most denitrifier activity to produce nitrite. Again, the second irrigation produces no N2O. In DNDC the third irrigation produces about the same flux as the water treatment, this time in closer agreement with the field data. Again, N2 flux is about half the N2O flux in DX, while in DNDC it is negligible for the first irrigation and about ten times the N2O flux for the third irrigation.

**Nitrogen + Carbon Treatment** - The addition of glucose and nitrate produced a dramatic pulse of N2O in the first irrigation, both in the field data and in the models (Fig. 2.28a,b). Field fluxes are enhanced above the nitrogen treatment by factors of about 100, 5, and 1.5 for the three irrigations, respectively. The model second irrigation peak is enhanced about three times above its low results for water or nitrogen treatments. By the third irrigation, the model flux is roughly the same as its results for water and nitrogen treatments, again much higher than field results. A glucose addition in the DNDC model enhances the soluble C pool for one rain/irrigation event— it is not treated in the decomposition routine. The integrated peak N2O flux for the first irrigation is comparable to both the field and DX results, though the peak is much broader. The third irrigation has lower flux than the water or nitrogen treatments. In DX, N2 flux is about equal to N2O flux for the first irrigation, and half the N2O flux for the third irrigation. In DNDC N2 flux is about 40 times larger than the N2O flux for the first irrigation, and 500 times larger for the third irrigation.

**Discussion** - The DX model cannot predict the second irrigation flux peak because the soil WFPS does not rise enough above the critical value ($W_x + dnxwfps$) to generate significant anaerobic fractional volume ($< 1\%$ of the surface 5 cm, and none below). Lowering the critical value will increase the flux for the second irrigation, but increase it even more for the first and third irrigations. DNDC cannot predict the second irrigation flux peak because the soil is too dry near the surface, so decomposition is very slow and the soluble carbon pool is very small.
Figure 2.25 - N2O gas flux for the control plot at the Vegas site (also called Finca Jack site). No irrigation events occurred. Model flux is due to nitrification.
Figure 2.26 - (a) Field, DX model, and DNDC model N2O fluxes for water treatment plot at Vegas site (also called Finca Jack site). DNDC model run using a silt loam soil. (b) As (a), but rescaled. DX model has very small enhancement for second irrigation.
Figure 2.27 - (a) Field, DX model, and DNDC model N2O fluxes for the nitrogen treatment plot at the Vegas site (also called Finca Jack site). DNDC model was run using a silt loam soil. (b) As (a), but rescaled. DX model has very small enhancement for second irrigation.
Figure 2.28 - (a) Field, DX model, and DNDC model N2O fluxes for the nitrogen + carbon treatment plot at the Vegas site (also called Finca Jack site). DNDC model was run using a silt loam soil. (b) As (a), but rescaled. DX model has very small enhancement for second irrigation.
The good agreement for the first irrigation in the nitrogen + carbon treatment implies that, when neither carbon nor nitrogen is limiting, the DX model can predict the magnitude and duration of anaerobic conditions reasonably well. Although the glucose amendment did enhance oxygen consumption, oxygen limitation due to rapid decomposition of glucose did not play a role in the model results. The soil has a very high porosity and (at least in the model) a relatively low WFPS at field capacity, so gas diffusion is quite rapid, and depleting the oxygen supply is difficult. Gas profile results below suggest that the model did not grossly over-exaggerate gas diffusion rates.

The fact that nitrogen addition enhanced field fluxes by only about 0 - 50%, while nitrogen and glucose addition enhanced fluxes by about a factor of 100, implies that soluble C was probably the most limiting factor for denitrifiers; this could be expected under dry conditions when both decomposition and nitrate leaching are reduced. However, both models fail to predict any increase in N2O flux with nitrate additions (DNDC flux drops dramatically). Both models tends to emphasize the reduction of nitrate to nitrite when nitrate concentration is high, limiting N2O and N2 production. This may be less common in the field if a single denitrifier is capable of causing the entire denitrification sequence (Firestone and Davidson 1989). In that case, denitrifier activity will tend to concentrate nitrite (and then nitrous oxide) in the vicinity of the denitrifiers, perhaps making them more preferred substrates.

Given that nitrate is not particularly limiting, and that, at least for the first irrigation, the model must calculate a reasonable anaerobic fractional volume, the very high fluxes for the first and third irrigations in the model are likely to be due to a misrepresentation of the soluble C pool available to the denitrifiers. Either the pool is too large or many constituents of the pool are not readily utilizable by denitrifiers.

There is large discrepancy between DX and DNDC as to the N2 flux for each of the treatments. There were no field measurements to resolve this, but it points to a
fundamental difference in the models. It is probably related to how the models use the various N-oxides as denitrifier substrate, DNDC by relative abundance and DX in fixed proportions. More testing of this is needed.

2.7.3. N2O Gas Profiles

**Control** - Model N2O gas concentration profiles increase with depth more rapidly than field observations (Fig. 2.29). Since fluxes are similar, this indicates that model gas diffusivity may be a bit low. The initial rise in the model results is due to initializing the entire profile to atmospheric concentration. The slow decline in profiles probably reflects the slow decline in nitrification as the soil dries.

**Nitrogen Treatment** - N2O gas profiles are much higher in the model than in the field for the first and third irrigations, especially in the deeper soil (Fig. 2.30). This corresponds to the models much higher surface fluxes. Results for the water treatment (and the third irrigation of the nitrogen + carbon treatment) are very similar.

**Nitrogen + Carbon Treatment (First Irrigation)** - Field gas concentrations rise much higher in the surface soil than model results, while fluxes were similar (Fig. 2.31.a). At depth (> 20cm) model gas concentrations are higher (Fig. 2.31.b).

**Discussion** - Although the control case has relatively good agreement between field and model, the irrigation flux peaks do not agree well so gas profiles should not either. The first irrigation peak for the nitrogen + carbon treatment suggests that model gas concentrations are not unreasonably high, given the flux predicted. As a test of this, Fig. 2.32 compares model profiles for the nitrogen treatment first irrigation (peak flux about 6 mg N/m²/d) against field profiles for the nitrogen + carbon treatment second irrigation (peak flux at least 4 mg N/m²/d). Model gas concentrations rise much higher than field values, again suggesting that model soil gas diffusivity is lower than in the field.
Figure 2.29 - Field and model N2O gas-phase concentration profiles for control plot at the Vegas site (also called Finca Jack site).
Figure 2.30 - (a) Field and model N2O gas-phase concentrations at 2 and 5 cm for nitrogen treatment plot at Vegas site (also called Finca Jack site). Results are very similar for water treatment. (b). Same as (a), but for 10, 20 and 40 cm.
Figure 2.31 - (a) Field and model N2O gas-phase concentrations at 2 and 5 cm for nitrogen + carbon treatment plot at the Vegas site (also called Finca Jack site). (b). Same as (a), but for 10, 20 and 40 cm.

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Figure 2.32 - Comparison of gas-phase N2O concentration profiles at the Vegas site (also called Finca Jack site). Field results are for nitrogen + carbon treatment irrigation #2; model results are for nitrogen treatment irrigation #1. These two cases had similar N2O flux peaks (see Figs 2.27.b and 2.28.b).

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2.8. Model Sensitivities and Shortcomings

The results for the Vegas site simulations (for both DX and DNDC) suggest that there are problems in the model treatments of both water/oxygen controls on denitrification and carbon substrate availability. These problems arise from the high sensitivity of model flux results to soil moisture, the critical WFPS value to initiate AFV (in the DX model), and the size of the soluble carbon pool. This section will discuss these sensitivities and shortcomings, both for DNDC and DX, and also for the other classes of models reviewed in Chapter 1.

2.8.1. Oxygen/WFPS Controls

Unless a soil is at or very near saturation it is unlikely to be completely anaerobic, yet significant denitrification is observed in soils that are not saturated, so there must be anaerobic zones within a partially aerobic soil that are the sites of denitrification. To date there have been three approaches to modeling this partial anaerobiosis—a rain event initiation model, general WFPS models, and microsite models. None is completely satisfactory.

Rain event initiation - DNDC initiates denitrification any time rain/irrigation exceeds 0.5 cm. It determines an active denitrifying zone (assumed fully anaerobic) based on rainfall amount (actually rainfall duration—all storms are assumed to have a rainfall intensity of 0.5 cm h⁻¹), soil saturated hydraulic conductivity, and soil porosity. DNDC assumes that all anaerobic zones are, in effect, compressed to the soil surface where soil carbon and nitrogen are generally highest. The model ignores antecedent soil water status, so a given rainstorm will activate the same soil volume no matter how wet or dry the soil was before the rain began. Also, in each model layer denitrification stops only when WFPS drops below 40%. Therefore, denitrification is generally limited by carbon or nitrogen, not by re-oxygenation. While this approach has the advantage of simplicity and the assurance of capturing every rain event, it
could improve its estimate of active denitrifying volume, in duration and perhaps also in depth. With a different approach, the sensitivity to rain intensity, which should affect WFPS behavior, needs to be investigated.

**WFPS controls.** A number of studies (generally lab incubations of soil cores) have concluded that little or no denitrification occurs if WFPS <60% (Klemmedtsson et al 1988; Linn and Doran 1984; Grundmann and Rolston 1987; Aulakh et al 1991; Doran et al 1990), or if WFPS is less than field capacity (Christensen et al 1990). Groffman and Tiedje (1991) found a correlation between WFPS and denitrification that was a function of soil texture. Since water itself is not the immediate factor controlling denitrification, it is considered to be a proxy for soil oxygen status. This presents a relatively straightforward modeling approach to oxygen controls on denitrification, adopted by a number of models (see Table 1.3 in Chapter 1). Since the models generally incorporate a soil water dynamics submodel, calculation of WFPS is already being done.

Modeling soil water dynamics, however, presents its own set of challenges, and several phenomena that can be of considerable importance are routinely ignored by standard soil water models (Feddes et al 1988). Most models operate by determining soil water potential profiles and then converting these to soil water contents, but hysteresis in soil water flow (generally ignored) makes WFPS a double-valued function of water potential—a soil losing water at a given potential will be wetter than a soil gaining water that is at the same potential (Hillel 1980). Recently much attention has been given to preferential flow paths for soil water (including macropore flow). Spatial variability in soil moisture due to preferential flow paths could play a strong role in creating anaerobic microsites for denitrification. Preferential flow is potentially a widespread phenomenon in uncultivated soils, but its importance is just beginning to be understood and it is rarely incorporated into soil moisture models (Feddes et al 1988). Parameterization of soil physical properties for a soil water
dynamics model can be done by using generalized formulas for various soil textures, but it must be recognized that an enormous amount of variability exists in the field (e.g., Clapp and Hornberger, 1978). Results using these parameters will generally follow patterns in actual soils but cannot be expected to accurately capture the situation at any particular site.

None of the models using a WFPS control of denitrification mention the sensitivity of their model to their parameterization. The DX model of Ch. 1 has a WFPS control of anaerobic fractional volume (AFV) or the size of the active denitrifying zone, with AFV increasing as WFPS increases above a critical value \(W_c\). The gas flux results are extremely sensitive to the parameterization of WFPS controls on AFV (see Section 2.5.2). Taking the water treatment case at Vegas as a test (see Section 2.7.2), the total predicted N2O flux for the three irrigations increases from 0.11 to 0.24 g N2O-N/ha (an increase of about 120%) as the parameter \(W_c\) drops from 0.41 to 0.38 (Fig. 2.33). For a fixed value of \(W_c\) changing the initial soil water content from 0.34 to 0.40 caused the total N2O flux to increase by about 50% (Fig. 2.34.b); in this case the difference occurs in the first irrigation and by the third irrigation the WFPS differences are negligible. An identical model simulation (except grass cover instead of bare soil) showed that the effect of the initial WFPS was still present, though diminished, 20 days later (Fig. 2.34.a).

It is very difficult to accurately model soil water content—as an example, in the simulations of Johnsson et al (1991), model soil water content differs from field values often by more than 10% and sometimes by more than 50% (their results are selected not because the results are particularly good or bad, but because theirs is the only paper to present field and model soil water results). Given this difficulty, a model of denitrification that has a fixed parameter value for initiating denitrification is not likely to produce good results at a variety of sites.

Another problem with using a fixed critical WFPS value, which arose in the
Figure 2.33 - N2O flux simulations for the water treatment plot at the Vegas site (also called Finca Jack site), as a function of model parameter $dnhwpf's$. The critical WFPS value at which anaerobic fractional volume is initiated, $W_C$, is given by $W_C = W_X + dnhwpf's$, where $W_X$ is the water content at field capacity (0.37 for the surface soil layer).
Figure 2.34 - (a) WFPS of second model layer (3.3 - 6.7 cm) as a function of initial WFPS at the Vegas site (also called Finca Jack site). (b) N2O flux simulations for the water treatment plot at the Vegas site (also called Finca Jack site), as a function of initial WFPS.
Vegas simulations of Section 2.7, is that a moderate rain on very dry soil may not wet the soil sufficiently to cause any denitrification, while it may cause a measurable response in the field. Conversely, a continuously wet, but not saturated, soil (either because of high clay content or limited water loss in the early spring or late fall) will be continuously denitrifying, at least until its substrates are depleted. This may or may not be the actual case in the field.

By using a fixed WFPS value of 60% for peak decomposition, the “dry” (low WFPS) soils of the Vegas site had very low decomposition rates in DNDC. The soluble C pool then becomes very small and N2O flux results are very sensitive to this. In a series of runs with the initial WFPS at 30%, 40%, and 50%, the N2O flux for the first irrigation at Vegas (water treatment) went from 0.0 to about 5 mg N m⁻² d⁻¹ to about 20 mg N m⁻² d⁻¹ (results not shown). The second irrigation produced no flux in all three cases, and the third irrigation was about the same for all three cases. The large differences in the first N2O peak are due not to enhanced duration or depth of the denitrification zone, but rather to an enhanced soluble C pool due to higher water contents and more rapid decomposition. So WFPS has both direct and indirect effects on denitrification.

Microsite models- The models of O₂ diffusion into soil aggregates or crumbs (e.g. Smith 1980; Refsgaard et al 1991; see Table 1.3 in Chapter 1) attempt to get at the fundamental process controlling partial anaerobiosis or anaerobic fractional volume (AFV). By numerically solving the diffusion equation for dissolved oxygen in saturated microsites, the method has a “first principles” appeal, but it relies on several assumptions. Soil heterogeneity is represented only by a log-normal distribution of aggregate radii. All aggregates are assumed to have uniform and equal diffusion coefficients for dissolved oxygen and potential microbial metabolic rates. Also, the model results will depend on the soil air-filled pore space oxygen concentration, which is rarely measured and must be calculated with a soil gas
diffusion model, itself a source of uncertainty since gas diffusivity is a function of WFPS. Perhaps most important, the model will also need a mechanism for delivering nitrate and soluble C to the anaerobic cores of the aggregates, and a method for determining their concentrations at the aggregate surface or within the aggregates.

Sexstone et al (1985), using a high resolution oxygen microelectrode, measured anaerobic cores in soil aggregates in rough agreement with predictions of the equations used by Smith (1980), but not all of these anaerobic cores actively denitrified, suggesting carbon or nitrogen limitations. Using a model for nitrate diffusion into aggregates Myrold and Tiedje (1985) suggested that nitrate diffusion could be limiting under "aerobic conditions" (i.e., not fully anaerobic) in unfertilized ecosystems, although carbon limitation, which they didn't model explicitly, appeared to limit denitrification in their incubation of a clay loam soil. Carbon substrate diffusion limitations are complicated by the wide array of potential C molecules (Beauchamp et al 1989), which could be expected to have a range of diffusion coefficients. Until microsite models develop a method for delivering substrates to the microsite— one is suggested by Myrold and Tiedje (1985)— and a method for assessing spatial variability of substrate and oxygen conditions, they will not be practical for field scale assessments.

2.8.2. Carbon Substrate Controls

Denitrifying bacteria require organic carbon compounds to supply energy and material for their growth and maintenance (e.g., Firestone 1982). Although C substrate limitations may be important in some circumstances (e.g., Myrold and Tiedje 1985; Jacobson and Alexander 1980; Stanford et al 1975; Burford and Bremner 1975), very little is known about the dynamics and even the nature of this substrate in the field (Beauchamp et al 1989), most field studies of denitrification do
not mention soil carbon or report only total soil organic C, and models to date have hardly tackled the issue (Table 1.2 in Chapter 1).

Results from the Vegas site suggest that the role of C substrates needs more attention. Both models, DX and DNDC, seriously overestimate N2O fluxes. The success of the first irrigation in the nitrogen + carbon treatment, a case where neither C nor N can be limiting, at least on the macroscale, suggests that the DX model has a reasonable portrayal of soil water controls on denitrification for that first irrigation; DNDC also matches field flux for this irrigation event. (The model clearly underestimates the degree of anaerobiosis for the second irrigation). As a test of model sensitivity, simulations of the water treatment (same WFPS and AFV dynamics) were done with the initial SOC at 1/2 and 1/5 of the field values of Mata (see Table 2.10 above), and also with the initial nitrate and ammonium concentrations at 1/2 and 1/5 of the values measured by Nobre. As soil carbon was reduced, N2O flux also dropped by about the same factor, while reducing soil inorganic nitrogen had little effect on N2O fluxes (Fig.2.35). Reducing SOC by 80% improved N2O fluxes estimates for both the water and nitrogen treatments (Figs. 2.36 and 2.37), but the simulated flux for the first irrigation of the N+C treatment dropped well below field values (Fig. 2.38). This drop occurred despite the abundance of C and N substrate and identical moisture controls on AFV, because microbial biomass, and hence denitrifier biomass, also decreased by 80%.

In addition, daily CO2 flux for the standard run is about 1 g CO2-C m⁻² d⁻¹, while for the reduced SOC run it is about 0.2 g CO2-C m⁻² d⁻¹. Measurements of CO2 flux were not made at this site, but Raich (1980) reports fluxes of about 5 g CO2-C m⁻² d⁻¹ for a forested site about 4 km away. Raich's site can be expected to have higher fluxes because (1) it was vegetated and thus measurements included root respiration (which increases the flux by perhaps 30% to 100%)—Raich and
Schlesinger 1992); (2) SOC content at Raich's site (≈8% for 0-5 cm; ≈5% for 5-10 cm; and ≈3% for 10-20 cm) was nearly three times as high as at the Vegas site (≈2.5% for 0-10 cm; ≈1.2% for 10-20 cm)—this should nearly triple CO2 flux; and (3) the Vegas site soils were rather dry during the field study, while Raich sampled under varied soil moisture conditions. However, the low SOC flux of 0.2 g CO2-C m⁻² d⁻¹ (only 2.5% of Raich's measured value) is probably too low, while the standard result of 20% of Raich's value (1 g CO2-C m⁻² d⁻¹) is reasonable.

Given reasonable CO2 fluxes, reasonable SOC values, and N2O fluxes that suggest there is less soluble C available to denitrifiers than the model estimates, several model changes are possible. The microbial efficiency (defined here as carbon assimilated/carbon respired) controls the ratio of CO2 production to soluble C availability; in DNDC and DX these values are 1/3 for microbial biomass decomposition, 1/2 for humads decomposition; and 2/3 for plant residue decomposition. (Note that for plant residue decomposition, the assimilated C is not considered soluble C available to denitrifiers; and also that for microbial biomass and humads decomposition a fraction of the carbon is neither assimilated nor respired, but is transferred to the next carbon pool.) If more CO2 were lost per unit C assimilated (lower efficiency), reduced decomposition rates or lower SOC would produce equal CO2 flux but less soluble C. The values for DNDC and DX are derived from laboratory studies, and may not be appropriate for La Selva soils (or the tropics in general). Differences could arise from differences in the nature of SOC compounds or soil microbial fauna or both. However there are some indications that these differences, if any, may not be that significant. SOC decomposition model results of Jenkinson (1991) and Li et al (in prep.) show good agreement for decomposition of rye grass and wheat straw in both tropical and temperate soils (with identical parameterizations), suggesting that soil microbial activity in both tropical and temperate soils is reasonably represented by a single model parameterization. The nature of SOC
compounds may also not be that different, though this is difficult to quantify. However, mean soil organic carbon contents and mean soil organic matter C:N ratios were not significantly different for a random selection of 61 tropical and 45 temperate soils, though tropical soils show higher variability in C:N ratios (Sanchez and Logan 1992). For the specific soils of the Vegas site, or any specific temperate or tropical site, detailed soil analysis would be required.

A major difference between tropical and temperate is soils the annual rate of plant litter input and SOC decomposition—both averaging about five times higher in the tropics (Sanchez and Logan 1992). This difference in rate of carbon cycling in soils, with roughly equivalent pool sizes, could be manifest in another model modification—reducing the residence time of soluble C in the soil solution. If this residence time is reduced, the same SOC pools, decomposition rates, and microbial efficiencies will result in a smaller soluble C pool. DNDC uses a residence time of about 1 day (bare soil) or 2 days (vegetation); DX has slightly longer residence times, with a loss rate of 1/36 h⁻¹ (bare soil) or 1/72 h⁻¹ (vegetation). If the soluble C loss rate (or assimilation rate) in DX is increased to 1/7 h⁻¹ (average residence time of about 1/3 day—thus more rapid turnover and a smaller soluble C pool), N₂O flux estimates for all treatments at Vegas improve (Figs. 2.39 - 2.41). The control treatment N₂O fluxes are from nitrification and do not change with this modification (not shown); also, CO₂ fluxes remain at about 1 g CO₂-C m⁻² d⁻¹. The soluble C pool residence times in both models are, at present purely internal model parameters.
Finca Jack Water Treatment

N2O flux sensitivity to initial soil carbon

(a)

N2O flux sensitivity to initial soil nitrogen

(b)

Figure 2.35 - (a) N2O flux simulations for the water treatment plot at the Vegas site (also called Finca Jack site), as a function of initial soil organic carbon. (b) N2O flux simulations for the water treatment plot at the Vegas site (also called Finca Jack site), as a function of initial soil inorganic nitrogen.
Figure 2.36- (a) Comparison of simulated and measured N2O gas flux for water treatment plot at the Vegas site (also called Finca Jack site). Simulations are for "standard" run, and for "low carbon" run, where initial SOC is set to 20% of standard (field) value. (b) Same as (a), but rescaled.
Figure 2.37- (a) Comparison of simulated and measured N2O gas flux for nitrogen treatment plot at the Vegas site (also called Finca Jack site). Simulations are for "standard" run, and for "low carbon" run, where initial SOC is set to 20% of standard (field) value. (b) Same as (a), but rescaled.
Figure 2.38- (a) Comparison of simulated and measured N2O gas flux for nitrogen + carbon treatment plot at the Vegas site (also called Finca Jack site). Simulations are for "standard" run, and for "low carbon" run, where initial SOC is set to 20% of standard (field) value. (b) Same as (a), but rescaled.
Figure 2.39 - Comparison of simulated and measured N2O gas flux for water treatment plot at the Vegas site (also called Finca Jack site). Simulations are for "standard" run, and for "low soluble carbon" run, where residence time (and hence size) of SOC pool is set to 20% of standard value. (b) Same as (a), but rescaled.
Figure 2.40 - Comparison of simulated and measured N2O gas flux for nitrogen treatment plot at the Vegas site (also called Finca Jack site). Simulations are for "standard" run, and for "low soluble carbon" run, where residence time (and hence size) of SOC pool is set to 20% of standard value. (b) Same as (a), but rescaled.
Figure 2.41 - Comparison of simulated and measured N2O gas flux for nitrogen +
carbon treatment plot at the Vegas site (also called Finca Jack site). Simulations
are for "standard" run, and for "low soluble carbon" run, where residence time
(and hence size) of SOC pool is set to 20% of standard value. (b) Same as (a), but
rescaled.
CHAPTER 3

SUMMARY AND CONCLUSIONS

3.1. Summary of Model Revisions and the Vegas Site Study

Several modifications have been made to the soil climate submodel presented in Li et al (1992a). Most relevant to the Vegas study site, a routine to calculate bare soil evaporation has been added, and also a new parameterization relating soil water content, soil water tension, and hydraulic conductivity for low bulk density soils, both following Federer's BROOK90 (Federer 1993). Parameter determination for the Vegas site was difficult due to a high degree of scatter in the preliminary data, but model soil water tension results follow the pattern of the field data at all depths except 40 cm. The major discrepancy between field and model is that the model cannot simulate the very low observed tensions immediately following an irrigation.

Two major revisions to the soil biogeochemistry components of DNDC were made. First, a gas phase was added, and gas phase diffusion of N2O, N2, CO2, O2, and NH3 was added as a control on their surface fluxes. Second, a new model of anaerobic fractional volume (AFV) was developed to simulate oxygen control of denitrification activity and to allow for simultaneous decomposition and denitrification. AFV is a function of WFPS (water-filled pore space) and gas-phase oxygen concentration. As AFV increases or decreases denitrifier substrate and biomass is transferred between anaerobic (i.e., actively denitrifying) and aerobic (inactive) zones. In addition, there is a solution phase diffusional transfer between the two zones. Model results were very sensitive to the “effective diffusion path length” of this diffusional transfer. This is problematic because there are no good field data to parameterize this “length”, which is really a combination of anaerobic and aerobic zone separation and contact.
area. The model results were also very sensitive to the critical WFPS at which AFV is initiated—this is also problematic because of the difficulty of reliably modeling WFPS.

The model responded to changes in external parameters (soil physical and chemical status and weather) in agreement with general results of field and lab studies, except that, for bare soil, increased nitrate concentrations led to decreased N2O and N2 fluxes (DNDC also behaves this way under certain circumstances). This is a result (for both DX and DNDC) of the N-oxide reduction sequence (nitrate -> nitrite -> nitrous oxide -> dinitrogen) and their preferential reduction of nitrate to nitrite. Increasing the soluble C availability ten-fold in DX caused this behavior to change, so that enhanced nitrate led to enhanced N2O and N2 production. However, I think it is misleading to consider the problem (if it is one) to be a result of carbon limitation. Instead, it may be a problem of using bulk soil solution concentrations to determine the rate of reactions. Bulk soil solution nitrate concentration (the state variable of both models) may be an indication of potential denitrification, but if denitrification occurs at microsites (and it must because each denitrifier is a microsite) then very local concentrations will become the controlling factor once denitrification is initiated.

The revised model (DX) was calibrated (internal parameters fixed) against four field studies with good results, and compared with DNDC in a separate simulation. DX gas flux peaks are much sharper than those of DNDC because the gas phase diffusion in DX is more rapid than the empirical gas release formulation of DNDC.

A field study in Costa Rica provided detailed N2O flux and ancillary data to test the model. DX model results, in general, overestimate fluxes by a factor of five to ten. However, peak dynamics (rise time and duration) are well captured by the model, and the nitrogen + carbon fertilization simulation is in good agreement with the field results for the first irrigation, while the glucose was present in the soil. These results suggest problems in the model treatment of both WFPS controls and carbon
substrate (see next section). Comparing DX to DNDC, DX has improved peak shape dynamics and an improved treatment of soil water (which DNDC will soon adopt). It also has a smaller response to nitrate fertilization, though both models respond in the wrong way. One drawback to DX is the fixed WFPS value to initiate AFV. For dry soils a rain event that causes denitrification may not wet the soil to this level (e.g., DX model N2O flux for all treatments for irrigation #2), while DNDC will respond to every rain event. DNDC produces no flux for the second irrigation because its soil moisture is very low, decomposition has nearly ceased, and the soluble carbon pool is near zero.

A final question is whether low soil oxygen partial pressure caused or enhanced denitrification, either in the glucose fertilization case or below an irrigation “wetting front”. This never occurred in the model, although there was a clear reduction in oxygen when glucose was added. This may be a realistic model result or a result of faulty parameterization. Nonetheless, the model produced the effects observed at Vegas without activating its low-oxygen routine. Further studies are needed.

3.2. Conclusions and Suggestions for Further Work

The suggestions for field studies below are made by a modeler. Ideally, of course, everything of importance would be measured. But quantity of data can compromise quality of data. And, what is important? My suggestions are based on data I would like to have available, not on the practicality of measuring it.

3.2.1. Oxygen/WFPS Controls

Models in General - The models that use a WFPS control on denitrifier activity need to know, and should report, how sensitive their parameterization is to WFPS, and the reliability of the WFPS values they use. Although a variety of studies report little or no denitrification below 60% WFPS, I think that a fixed functional representation
cannot work in a wide variety of ecosystems, and needs to be tuned to the WFPS behavior and predictions of a particular site. Although the concept of “field capacity” troubles soil physicists with its imprecision (e.g., Hillel 1980b), I suspect that it is actually very important to the ecology of soils, particularly in humid ecosystems. It is, in some sense, the most probable state of soil moisture, and it is likely that soil fauna find conditions in the vicinity of field capacity to be optimal. If so, conditions wetter than this would begin to generate denitrification. It also seems that field capacity should be a more widely applicable parameter than a fixed value of WFPS = 60%.

**DNDC/DX** - The different approaches of DNDC and DX each have their advantages, and some intermediate approach would probably improve both. DNDC’s rain event initiation ensures that every significant rain event will generate denitrification if substrate is present, which seems to be corroborated in the field. DX’s WFPS control of AFV ensures that soil texture and antecedent moisture conditions play a stronger role in controlling denitrification, which also seems appropriate.

The idea of AFV as a function of WFPS is a middle ground between the detailed soil crumb/anaerobic core models and the simple WFPS reduction factor models. It provides a simple mechanism for separating regions of decomposition and denitrification, while allowing them to interact via expansion/contraction and diffusional transfer. However, model results are very sensitive this diffusional transfer and there is no field data to quantify it. At present it probably raises more questions than it answers, and a more direct WFPS control may be sufficient. Inclusion of oxygen in DX has had no effect on results so far.

**Field Studies** - If the modeling goal is event scale simulations, precipitation data is essential, especially if it happens to be anomalous for the site. For annual flux estimates DNDC is successful using mean climatic data. Basic soil texture data is also essential. Since most denitrification models are driven by soil moisture, some
measure of soil moisture would be useful. Ideally, this would be a series of moisture measurements capturing the soil moisture dynamics, but at a minimum it should include a representative value of soil water content at “field capacity”, when the soil is “wet”, and when the soil is “field dry”.

3.2.2. Carbon Substrate

Models in General and DNDC/DX - Of the field-scale models that predict N2O flux, DNDC/DX is the only model to include a treatment of carbon substrates. The treatment is rudimentary, with a quasi-pool of “soluble, available, and utilizable organic carbon”, and N2O production in both models is very sensitive to the size of this pool. Refinements of this part of the model will depend on field studies to answer some very fundamental questions. Are there differences in the nature or behavior of carbon substrates that are a function of ecosystem (e.g., forest vs. grassland) or climatic region (e.g., temperate vs. tropical)? Are some soluble C compounds preferred over others by denitrifiers? How does microsite availability vary among carbon compounds? Are there physical or chemical controls on this? Can the value to denitrifiers of the various soluble C compounds be quantified on a single scale—a sort of “glucose-equivalent” value?

Field Studies - Some sense of the size and turnover rate of the soluble C pool is essential to assess its importance in controlling denitrification at a particular site. At a bare minimum, total SOC should be measured. CO2 flux (soil respiration) measurements will give an estimate of the decomposition rates in the soil, and may correlate with potential denitrification at a site. Measurements of soil solution dissolved organic carbon (total DOC) will quantify the size of the soluble C pool. All three measurements could help to untangle the role of carbon in denitrification at a site.
3.2.3. Additional Suggestions

**Gas Diffusion** - Inclusion of gas phase diffusion had a significant effect on the timing of the release of N2O produced by denitrification. Gas diffusion calculations are very time-consuming computationally (requiring a timestep of 0.1 hours as opposed to 1 hour for the rest of the model), and perhaps are impractical for large scale applications. The results suggest, though, that DNDC's empirical formulation may underestimate release rates, at least for sandy soils. It would be possible to replace the diffusion routine by an improved empirical formula.

Gas phase diffusion may be more important for studying methane consumption by soils, where the general consensus is that uptake is diffusion (or at least substrate delivery) limited most of the time (e.g., Crill 1991). This limitation may be due to gas phase diffusion, or, more likely I believe, to the solubility of methane and its solution phase diffusion to the methanotrophs.

**Nitrogen** - The most apparent problem DNDC and DX have with nitrogen is that they predict reduced denitrification as nitrate concentrations increase when there is no vegetation competing for the substrate. While perhaps not important on the global scale, it suggests that certain dynamics of the nitrogen reduction sequence are missing from the models. I think it is due to using soil solution average concentrations to calculate reduction rates, which is not what the denitrifiers experience in their very local environment. This returns us once again to the challenge of representing the average macroscopic behavior of a highly variable, microscopic system.

Both DNDC and DX predict that most denitrifier activity results in the production of nitrite (rather than nitrous oxide or dinitrogen), and both models assume that this nitrite is immediately oxidized to nitrate when aerobic conditions return. As a result, the models suggest that the majority of the denitrifier activity has little impact on the soil N cycle. Most field studies of denitrification do not measure soil nitrite concentrations, as nitrite is a very dynamic and reactive species.
(Stevenson, 1986), so there is very limited data to test this model result against. However, if soluble C dynamics is crucial to model success, and the reduction of nitrate to nitrite consumes most of the soluble C in the models, testing the nitrite dynamics of the model will be very important.
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CHAPTER 4

A MODEL OF NORTHERN PEATLAND SOIL CLIMATE AND METHANE FLUX

4.1. Methane from Northern Peatlands and the Role of Climate.

Methane is an important constituent in the global atmosphere, even though it is only present in trace amounts (1.75 ppmv—parts per million by volume; Watson et al, 1990). Rodhe (1990) estimates the greenhouse effect of methane to be 15% of the total effect, second in strength only to carbon dioxide. In addition, methane plays important roles in both tropospheric and stratospheric chemistry (e.g., Warneck, 1988). Methane emissions to the atmosphere from natural sources are the net result of anaerobic microbial methane production and potential subsequent oxidation by microbes which use methane as an energy source. For example, in a wetland environment production of methane will take place in water-saturated, anaerobic zones of the soil. As the methane diffuses to the atmosphere through aerobic zones in the soil, or by transport via plants (Dacy and Klug, 1979; Sebacher et al, 1985; Chanton et al, 1992), microbial oxidation can occur, reducing the net flux to the atmosphere (Fechner and Hemond, 1992).

Total methane flux to the atmosphere from natural and anthropogenic sources is estimated to be about 550 Tg/y (teragram (Tg) = 10^{12} g), and the annual increase in the atmospheric burden is about 0.5 - 1.0% per year (Cicerone and Oremland, 1988; Watson et al, 1990, Khalil et al, 1993). Assessments of global area of natural wetlands by Matthews and Fung (1987) and Aselmann and Crutzen (1989) show large wetland areas to be concentrated in the boreal/subarctic zone (45°-73°N; about 3 million km²) and the tropics (20°N-20°S; about 1.5-2 million km²), while temperate wetlands occupy only about 0.8 million km². Bartlett and Harriss (1993)
use these area estimates and field flux measurements reported to date to estimate the
global flux of methane from natural wetlands at 105 Tg/y, and the boreal/subarctic
contribution to be about 35 Tg/y. Fung et al (1991), using atmospheric transport
models and spatial and temporal patterns in atmospheric methane concentrations,
arrive at similar numbers.

Boreal and sub-arctic peatlands have a soil carbon pool of about 450,000 Tg C
and the estimated accumulation rate is about 75 Tg C/y (Gorham, 1991). In these
units the methane carbon flux out of these peatlands is estimated at 26 Tg C/y, and is
thus a major component in their carbon balance. A significant change in the methane
flux from northern peatlands would play an important role in the carbon balance of
these ecosystems as well as in the atmospheric methane budget.

There is intriguing evidence from deep ice cores that atmospheric methane
concentration is positively correlated with climate variations, or at least surface
temperature variations (Chappellaz et al, 1990). The ice core record from Vostok,
East Antarctica, extending back about 160,000 years, shows six distinct peaks in
atmospheric methane concentration (at levels of 0.6 - 0.7 ppmv), separated by
periods of lower concentration (about 0.4 - 0.5 ppmv). The surface temperature
record contained in the ice core, determined by the deuterium ($^{2}$H) to hydrogen ($^{1}$H)
isotopic ratio, is noisier, but contains four clear peaks at the same times as four of the
methane peaks, and oscillations at the other two methane peaks. Atmospheric methane
concentrations are highest during interglacial (warm) periods and lowest during
glacial advance (cold) periods. It is interesting to note that the ice core data indicate
that atmospheric methane concentrations during past geologic warm periods (and even
as recently as the 1600s) was approximately 0.7 ppmv, compared to the current
concentration of 1.75 ppmv (Khalil and Rasmussen, 1987).

The existing ice core record is not of sufficient resolution to be able to imply a
cause and effect relationship between methane concentration and mean surface
temperature. However, a spectral analysis of the methane concentration time series yielded four significant peaks with periods of 122.0, 41.7, 24.8, and 19.0 thousand years (Chappellaz et al, 1990). These are similar to the periods of the major astronomical climate forcings or Milankovitch cycles (Henderson-Sellers and McGuffie, 1987). These astronomical climate forcings are clearly external to the climate system, and cannot be a feedback response to another climate forcing.

On the other hand, the atmospheric methane concentration could change in response to climate change. A changing climate will have both an immediate and a delayed impact on a wetland ecosystem. The immediate response will be a change in the wetland soil thermal and hydrological regimes—the soil climate. Over longer time periods, the wetland response to climate change could be a change in areal extent, as well as plant growth rates and species composition. This study will focus on the immediate response of soil climate to surface climate, and the resulting impact on methane emissions from peatlands, addressing the question (see Figure 3.2), What role may northern peatland methane flux play in near-term climate change?

4.2. The Role of Soil Climate in Modulating Methane Fluxes

Soil climate (soil temperature and soil moisture status), which is driven by the surface climate, plays a strong role in the flux of methane from northern peatlands (Figure 4.1). Metabolic activity of soil microbes in peat is strongly temperature dependent. This holds for methane producing bacteria (methanogens) as well as for methane consuming bacteria (methanotrophs) and the microbes in the decomposition chain that produce substrates for the methanogens from soil organic matter. This has been demonstrated in laboratory incubations. Kelly and Chynoweth (1981) incubated sediments from small lakes in Michigan at 4.5, 9, 19, and 29°C. They observed methane production Q_{10} factors ranging from 1.9 to 3.1, with an average of 2.4. Svensson (1984) incubated peat cores from an acid subarctic mire at Stordalen,
Figure 4.1 - Climate controls on methane flux from terrestrial ecosystems and the potential for a feedback. The surface climate (or weather) determines the soil climate, which strongly influences methane fluxes, which can affect atmospheric radiative properties (the greenhouse effect), which can affect weather.

**Terrestrial Methane Flux and Climate**

**Surface Climate**
- radiation
- wind speed
- precipitation
- season length
- air temperature

**Soil Climate**
- soil moisture
- soil temperature
- depth to water table
- depth to permafrost

**Methane Flux to the Atmosphere**
- change in greenhouse radiative forcing

**IS THE FEEDBACK POSITIVE or NEGATIVE?**
- STRONG or WEAK?

**Methane Production and Oxidation**
- nutrient availability
- soil temperature controls
- aerobic/anaerobic controls
- methane diffusion pathways

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Sweden. The cores (peat derived from *Sphagnum* spp. and *Eriophorum* spp.) were incubated anaerobically at 2, 5, 10, 15, 20, 24, 28, and 37°C for one to several months, and methane production was measured. He observed low production rates at low temperatures, highest production at 20° and 28°C, and much lower production at 37°C. Westerman and Ahring (1987) incubated cores from a Danish alder swamp at a range of temperatures from 0° to 25°C, and observed methane production Q_{10} values of 3.5 to 5.5 for the temperature range of 5 to 15°C. Williams and Crawford (1984) collected peat cores from a forested sphagnum peatland in Minnesota. Laboratory incubations showed that cores from 10-90 cm depth showed increasing methane production (190% to 450%) for temperature increase from 4° to 30°C. Cores from 120 cm and 210 cm had peak methane production at 12°C.

The other microbial process that will have a significant impact on methane flux is methane oxidation by methanotrophic bacteria (e.g. Cicerone and Oremland, 1988; Oremland and Culbertson, 1992). In terrestrial ecosystems methanotrophs generally require oxygen to consume methane and thus reside in the aerobic portion of soil profiles. In wetlands this is generally restricted to the near surface (at depths that are frequently above the water table), or in the vicinity of the roots of plants that pump oxygen below the water table (e.g., rice). Yavitt et al (1988) studied potential methane production and oxidation in peat cores from moss-dominated temperate wetlands (West Virginia). They found that potential oxidation rates were 11% - 100% of potential production rates, and that oxidation was by aerobic methanotrophs. At a temperate sphagnum bog (Massachusetts), Fechner and Hemond (1992) estimate methane flux and oxidation rates from methane concentration profile data and estimates of molecular diffusion rates. They conclude that oxidation in the aerobic peat above the water table consumes nearly 90% of the methane that diffuses up from the saturated zone.
The role of soil water in peatland methane flux is somewhat different than the role of soil water in upland soil trace gas fluxes. Methanogenesis is a strictly anaerobic process (Cicerone and Oremland, 1988) and occurs in saturated soils (i.e., below the water table). There are no reports in the literature that anaerobic "microsites" exist above the water table to any significant extent in sphagnum peats, and, based on peat hydraulic properties (see Section 4.3.4) they should not play a significant role in peatland trace gas production, as they may in upland soils (see Chapters 1-3). Therefore, a common soil climate index for water effects is depth to water table.

In general, depth to water table probably influences methane flux to the atmosphere in several ways:

- Depth to the water table controls the length of the diffusive pathway from the zone of methane production to the atmosphere (also expressed as the residence time of the methane in the soil). As this path length increases, the opportunity for methane oxidation may increase.

- In general in the summer months (the period of high fluxes) the peat is warmest at the surface and cools rapidly with depth (this will be especially true for regions underlain by shallow permafrost). Hence a higher water table will allow methane production to occur in the warmer peat, which should enhance production rates.

- Most sphagnum bogs receive their primary nutrient inputs only from the atmosphere. Root exudates and aerobic decomposition in the surface layer will generate the organic substrates required by the methanogens. Thus the richest substrate pool may be near the surface and may favor high rates of production when the water table is near the surface. Fens, which receive some lateral groundwater or surface water flow, are typically more nutrient rich systems and may also have a nutrient gradient with depth. This has been little studied in northern wetlands.

- The microbial ecology of methanotrophs is, as of yet, poorly understood. They seem to exist predominantly in a narrow band of peat just above the water, at the interface
of the zone of production and the zone of potential oxidation (Fechner and Hemond, 1992). There may be ecological factors (e.g., availability of other nutrients) that cause them to prefer shallower or deeper water tables.

Laboratory incubation of peats to study the effect of water content on methane production by Svensson (1976) showed little flux until the water content exceeded 2000% of the core dry weight. Moore and Knowles (1989), studying cores from three peatlands in Quebec, showed that methane fluxes fell dramatically (and CO₂ fluxes increased) as the water table was lowered. Since methanogens require highly anaerobic conditions, other incubations reported in the literature have been done under anoxic conditions (e.g., Svensson, 1984; Williams and Crawford, 1984; Westerman and Ahring, 1987).

The effects of soil climate on methane flux from wetlands is more difficult to interpret than highly controlled laboratory incubations. Generally, several controlling variables are changing at the same time (e.g., rising temperature and falling water table as summer progresses). Some clear signals can be observed, though. The strongest, for northern peatlands, is the annual signal in methane flux. In central Alaska, a four year study by Whalen and Reeburgh (1988, 1992) measured high fluxes in June, July, and August, and little or no flux in the winter months. In northern Minnesota, a two year study by Dise (1992, 1993) also measured highest fluxes in the summer months, with smaller, but not negligible, winter fluxes (Nov. - March) of 5-20% of the estimated annual emission. In each case the high fluxes of summer correspond with the period of warmest peat temperatures, significant thaw layer thickness (in Alaska), and also with the period of most rapid plant growth.

Numerous seasonal studies of methane flux in northern wetlands have found correlations between emissions and peat temperature (e.g. Crill et al (1988) and Dise et al (1993) in Minnesota; Bartlett et al (1992) and Morrissey and Livingston (1992) in Alaska; and Moore et al (1990) in eastern Canada). However, Roulet et al
(1992a) found a correlation between methane flux and temperature only for three of twenty-four sites across low boreal Canada. Svensson and Rosswall (1984) found a correlation between flux and temperature only for the wetter sites they studied; drier zones showed no correlation.

The correlation between methane flux and depth to water table is often less direct. Roulet et al (1992a) found no significant correlation between instantaneous flux rate and depth to water table for any of their 24 sites in low boreal Canada. However, the highest fluxes were observed at those sites that remained saturated to the surface throughout the summer. In addition, they found a correlation between mean seasonal methane flux and mean summer water table location for the aggregated data of the 24 sites. Two transect surveys in Alaska (Sebacher et al 1986; Whalen and Reeburgh 1990) showed a correlation between depth to water table and methane flux that explained some of the variation they observed between sites. These were not, however, correlations between depth to water table and flux at single sites. Moore et al (1990), Dise et al (1993) and Tom and Chapin (1992) all also reported that depth to water table explained some of the variation in methane fluxes between sites. Eddy correlation measurements, which integrate over a larger scale than the chamber method results discussed above, detected higher methane fluxes from wetter regions than drier regions (e.g., Fan et al 1992).

In northern Minnesota, Dise et al (1993) studied the direct effect of depth to water table on methane fluxes by constructing two bog "corrals", 1.2 meter square, that allowed them to maintain artificially high water tables without serious disturbance to the bog ecology. They found that higher water tables enhanced fluxes. Raising the water table to the surface from its natural level of 6 to 10 cm deep throughout one summer approximately doubled the methane fluxes.

It is clear from these field studies that peat climate has an impact on methane flux from northern wetlands, and that both temperature and moisture are likely to
play a role, though with different impacts at different sites. A model of methane flux from northern peatlands should therefore model the peat climate as a basis for predicting flux.

4.3. The Peat Soil Climate Model

4.3.1. General Structure

In a model of sphagnum peat development, Clymo (1984) characterizes a sphagnum peat as a two-layered entity—a surface layer (the acrotelm), consisting of live and dead but uncollapsed and relatively undecomposed sphagnum, and characterized by very high porosity and hydraulic conductivity and periodic aerobic conditions; and a submerged layer below (the catotelm), consisting of collapsed and partially to significantly decomposed underlying peat that is usually water saturated. The deeper layer has lower porosity and much lower hydraulic conductivity than the surface layer. As the peat accumulates at the surface where sphagnum growth occurs, underlying peat is slowly crushed. As the surface layer peat moves deeper and loses some of its structural integrity through decomposition, it collapses into the denser submerged layer. The deeper layer is generally saturated and therefore decomposes slowly—more slowly than it receives additions from the surface layer above, which is why the peats accumulate, often to many meters depth. This paradigm is adopted for the peat soil climate model. The model profile consists of two distinct layers, each uniform over its depth (Figure 4.2). The core of the model is one-dimensional (vertical), with no horizontal transport phenomena within the peat.

4.3.2. Modeling Soil Temperature

Heat transfer in peats, like heat transfer in upland soils, is dominated by diffusion (Farouki, 1981; Hillel, 1980) and can be modeled by standard methods.
Figure 4.2 - A two-layer peat model. The surface layer (acrotelm) consists of live, fresh and slightly decomposed plant material, has a very high porosity, conducts water very rapidly, and has low water retention ability. The deep layer (catotelm) consists of decomposed peat, has a high porosity, does not conduct water very rapidly, and has a moderate water retention ability.
This process is modeled mathematically as

\[ c \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z}\right) \]  

(4.1)

where \( T \) is the soil temperature (°C), \( z \) is the depth (positive down from the surface in cm), \( c \) is the soil volumetric heat capacity (J cm\(^{-3}\) °C\(^{-1}\)), \( k \) is the soil thermal conductivity (W m\(^{-1}\) °C\(^{-1}\)), and \( t \) is time (s). A one-dimensional (vertical) model requires (1) a numerical technique for integrating the diffusion equation (Eq. 4.1), (2) peat thermal properties, (3) boundary conditions, and (4) initial conditions. In addition the model presented here has a freeze/thaw component to track frost penetration in the winter months.

**Numerical Technique:** A standard numerical approach for modeling diffusion in porous media (e.g. heat or moisture in soils) is the finite element method, or FEM (e.g. Huyakorn and Pinder, 1983). Basically, the profile is discretized into a series of elements with uniform properties, and the model uses a Crank-Nicolson numerical integration technique (Press et al. 1986). A FORTRAN77 code was written for one-dimensional heat diffusion, and tested it against several analytical solutions (uniform semi-infinite soil slab with sinusoidal and pulse function surface conditions; a two-layer soil with sinusoidal surface conditions).Element thickness is small near the surface for higher resolution, and larger at depth where change is more gradual. A typical profile of element thicknesses is (from the surface down) 1.5, 2.5, 4, 4, 6, 6, 6, 15, 15, and 20 cm, for a total profile depth of 80 cm. The model time step is typically about 20 minutes.

**Peat Thermal Properties:** A straight-forward method is to consider both the soil heat capacity and thermal conductivity to be the volume-weighted, arithmetic mean of the solid and liquid phases (Farouki, 1981). The gas phase is ignored because its thermal conductivity and heat capacity are both so much smaller than the corresponding solid or liquid values that it makes a minor contribution to the heat transfer process under normal field conditions. Thus,
\[ c = (1-n)c_{\text{sol}} + n c_{\text{liq}}W \]  
\[ k = (1-n)k_{\text{sol}} + n k_{\text{liq}}W \]

where \( c \) is the volume heat capacity (J cm\(^{-3}\) °C\(^{-1}\)), \( k \) is the thermal conductivity (W m\(^{-1}\) °C\(^{-1}\)), \( n \) is the soil porosity, \( W \) is the fractional water-filled-pore-space, or WFPS (1 ≥ \( W \) ≥ 0), and the subscripts refer to the solid and liquid soil components.

In a model of sphagnum peat, the "soil" is living sphagnum and sphagnum peat. It has no mineral component. Therefore,
\[ c = (1-n)c_{\text{org}} + n c_{\text{liq}}W \]  
\[ k = (1-n)k_{\text{org}} + n k_{\text{liq}}W \]

where the subscript 'org' refers to organic matter, as opposed to mineral soil, and \( n \) is the porosity of either the surface layer or the deeper layer.

**Boundary Conditions:** The simplest surface boundary condition, and the one adopted here, is to assume that the soil surface temperature (skin temperature) is equal to the local air temperature. This temperature is applied to the first model node (\( z = 0 \) cm). A more detailed approach is to perform a surface energy balance—balancing radiation, sensible and latent heat exchange with the atmosphere, and heat flux into the soil. This generally requires an iterative solution, and is significantly more computer intensive. It also requires climate data that is not readily available for all sites (radiation, wind speed, relative humidity). Input weather data for the peat temperature model are daily air temperatures.

The boundary condition at the bottom of the modeled soil profile is given by the heat flux resulting from the temperature gradient between the bottom node and the mean annual air temperature at a depth where oscillations are negligible. This is discussed in more detail in Section 4.4.5.
4.3.3. Modeling Freeze/Thaw

Modeling the freezing and thawing of soil water is a very tricky numerical problem. There is a moving phase boundary, whose motion depends on the solution to the heat transfer problem. The latent heat of fusion for water ($L_f \approx 80 \text{ cal g}^{-1}$) is much larger than the heat capacity of either phase (water $\approx 1 \text{ cal g}^{-1} \cdot \text{C}^{-1}$; ice $\approx 0.45 \text{ cal g}^{-1} \cdot \text{C}^{-1}$) so there is an abrupt discontinuity in the thermal properties. For pure water, the heat capacity appears to be infinite at 0°C because heat is added or removed with no change in temperature as the water freezes or the ice melts. In soils however, the soil water freezes over a finite temperature range (Williams and Smith, 1990). Lunardini (1988, 1981) reviews a variety of methods for modeling phase change in soils. I have adopted the apparent heat capacity approach. The soil water is assumed to freeze continuously and uniformly over a finite temperature range (say 0°C to -1°C). The fraction of the water that is frozen in a model element at some temperature, $T$, is given by

$$ F_{\text{ice}} = \frac{T - T_{\text{sol}}}{T_{\text{liq}} - T_{\text{sol}}} $$

where $F_{\text{ice}}$ is the fraction of the soil water that is frozen, $T_{\text{sol}}$ is the temperature at which all soil water is frozen, and $T_{\text{liq}}$ is the temperature at which all soil water is liquid. While the soil temperature is in this freeze/thaw range the soil contains a mixture of ice and water, so the soil thermal properties are given by

$$ c = (1-n)c_{\text{org}} + n W [(1-F_{\text{ice}})c_{\text{wat}} + F_{\text{ice}} c_{\text{ice}}] + L_f/(T_{\text{liq}}-T_{\text{sol}}) $$

$$ k = (1-n)k_{\text{org}} + n W [(1-F_{\text{ice}})k_{\text{wat}} + F_{\text{ice}} k_{\text{ice}}] $$

where $L_f$ is the latent heat of fusion for water. Adding the latent heat term in Eq. 4.7, and thus making it the apparent heat capacity, gives the soil/water an enormous heat capacity over the freeze/thaw range, and hence slows the temperature transition across that range.

The model considers the upper ice/water boundary to be at the depth where the temperature is equal to $T_{\text{freeze}}$, where
\[ T_{\text{freeze}} = 0.5(T_{\text{sol}} + T_{\text{liq}}). \] (4.9)

The phase change boundary location in each element is determined by interpolation of the nodal temperatures. Ice thickness is calculated as the sum of each layers ice content, if the content is greater than 20%. The model can only keep track of a single ice layer, but in non-permafrost regions this should be sufficient.

4.3.4. Modeling the Bog Water Table and 1-D Soil Moisture

At our current level of data and understanding of peat hydraulic properties, a model of sphagnum peat hydrology must be different than traditional soil hydrology models (e.g. Richard's Equation for unsaturated soils, see Bras, 1990). Sphagnum peat is not a traditional soil and parameters relating peat water content, water tension, and peat hydraulic conductivity are not available. The limited data set of Boelter (1964, 1969) and Boelter and Blake (1964) demonstrate the difference between peat and mineral soil (Figure 4.3). Peats have a very high water content at saturation, and lose water rapidly at low tensions. This process is very difficult to measure, and collecting undisturbed peat cores, especially the surface layer, is very difficult.

The submerged layer (deep, partially decomposed peat) has fairly low hydraulic conductivity (similar to mineral soils) and would probably be amenable to such a traditional model structure. However, deep peats are generally constantly saturated; water movement there, if any movement occurs, is extremely slow (Romanov, 1968). Most of the water table fluctuations and vertical infiltration of water occurs in the surface layer (living and slightly decomposed, uncompressed, dead sphagnum). The surface layer, however is on the order of 90-95% pore space, has enormous hydraulic conductivities, and loses much of its water at the least bit of suction (Boelter, 1964, 1969). It behaves more like a sponge than a soil.

Because traditional soil hydrology models do not work well for peats, I have developed a sphagnum bucket/sponge model. The model is basically a water balance
model for a two-layer bog (Figure 4.4), with an algorithm for distributing the water in the profile (inputs: rainfall, snowmelt, run-on; outputs: evaporation and drainage; run-on and drainage, not integral to the 1-D model, are discussed in Sections 4.3.5 and 4.4.6). Water movement in the peat is not calculated.

The 1-D model assumes two things: (1) the water content drops from 100% WFPS (saturation) to some lower value immediately at the water table, and (2) above that, in both the surface layer and the deeper layer, the water content falls off linearly with height above the water table (Figure 3.5). The first assumption reflects the rapid dewatering of peat under a weak suction; the second assumption allows for a weak capillary effect in the peat (Boelter 1964, 1969). The second assumption (linearity) also allows for a simple analytic inversion to derive depth to water table from peat water content. The required parameters are thus: surface layer depth, surface layer and submerged layer porosities, surface layer and submerged layer WFPS just above the water table, gradient of capillary water content above the water table \( (dW/dz) \) for each layer, and maximum water table depth (the depth to which evaporation can lower the water table). Given these, the total water content in the profile, \( W_t \) for a given water table depth, \( z_w \) is

\[
W_t = \int_{z_b}^{z_w} n(z) \, dz + \int_{z_b}^{z_w} n(z) \, W(z) \, dz
\]

\[ (4.10) \]

where \( z_b \) is the maximum possible water table depth, and the porosity, \( n \), is a function of \( z \) in that it can have different values in the surface layer and the deeper layer. Since \( W(z) \) is a simple polynomial, Eq. 4.10 can be integrated and inverted to give the functional relationship for the water table depth for any profile water content, as well as peat WFPS above the water table. The model works with this inverse function. First it solves the water balance for each time step, and then it determines the water table depth and profile distribution from the profile water content.
Soil water content (volume basis) vs. soil water tension for sphagnum peat and loam soils.

Sphagnum data from Boelter & Blake (1964).
Loam values from Clapp & Hornberger parameters (1978).

Figure 4.3 - Peat soil and mineral soil (loam) water contents as a function of soil water tension. For peats, a rapid de-watering at low tension occurs, the details of which are not clear from the limited data set. This property makes traditional unsaturated zone hydrological models difficult to parameterize for peat soils.

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Figure 4.4 - A model for unsaturated water content for the two-layer peat of Figure 4.2. $W_1$ and $W_2$ are parameters for determining the unsaturated water content of the surface layer; $W_3$ and $W_4$ for the deep layer. Heavy lines I, II, and III represent three possible water content profiles. Line I represents the peat at its driest, when the depth to water table ($Z_w$) is maximum. Line II represents the water profile when the water table is in the deep layer. Line III represents the water profile when the water table is in the surface layer.

I - water table at maximum depth
II - water table in catotelm
III - water table in acrotelm
4.3.5. Water Inputs and Outputs

For a true ombrotrophic, domed bog all water movement is vertical, so water inputs will be precipitation and snowmelt, and water loss will be through evaporation. For a peatland with a connection to a regional watershed (e.g., a fen) there are also potential water inputs due to stream flow, groundwater inflow and surface water flow or seepage. There can also be water loss due to stream outflow and/or groundwater outflow.

Precipitation and Snowmelt: Daily precipitation is part of the input data set (along with air temperature and net radiation); snowmelt is calculated as a function of air temperature and time of year (Section 4.3.6).

Evaporation Water Loss: Since sphagnum vegetation is short and a sphagnum terrain is relatively smooth (compared to a forest), it will have a relatively high resistance to turbulent exchange with the atmosphere. Thus it is likely that available energy will dominate evaporative losses, rather than vapor pressure deficit and turbulent mixing due to wind (Romanov, 1968). Also, sphagnum is a non-vascular plant and does not transpire water. Evaporation losses are calculated in the model using the Priestley-Taylor equation (Rouse et al, 1977)

\[ PE = a \left( \frac{\Delta}{\Delta + g} \right) (R_{net} - Q_{soil}) \]  (4.11)

where \( PE \) is the potential (maximum evaporation, mm d\(^{-1}\)), \( a \) is a parameter, \( \Delta \) is the slope of the saturation water vapor pressure curve at the local air temperature, \( g \) is the psychrometric constant (66 Pa °C\(^{-1}\)), \( R_{net} \) is the net radiation, and \( Q_{soil} \) is the heat flux into the soil (assumed to be zero for this calculation), which is generally a small fraction of the net radiation (Rouse, 1984). If the air temperature or the net radiation are less than zero, then evaporative losses are set to zero. The coefficient \( a \) is taken as 1.26, based on the work of Rouse, et al. (1977). Since peat can only wick water up to a certain height and only with increasing difficulty as the water table...
drops (Boelter and Verry, 1977), evaporative loss is reduced from the Priestley-Taylor demand as the water table drops. This is modeled as

\[ E = PE \quad \text{if} \quad z_w < z_{ET} \]  
\[ E = PE \left( \frac{(z_w - z_b)}{(z_{ET} - z_b)} \right)^m \quad \text{if} \quad z_w \geq z_{ET} \]  

where \( E \) is the actual evaporative water loss, \( z_{ET} \) is the water table depth at which evaporation begins to fall from its maximum value, and \( m \) is a parameter.

If net radiation data is unavailable, evaporative demand is calculated with Thornthwaite's Equation (Dunne and Leopold, 1978)

\[ PE = 1.6 * DL * \left[ 10.0 * T / I \right]^a \]  

where \( DL \) is daylength (as a fraction of 12 hours), \( T \) is daily air temperature (°C), \( I \) is an annual heat sum \( I = S \left[ T_m / 5 \right]^{1.5} \), \( T_m \) is the monthly mean temperature (°C), and the sum is over the year), and

\[ a = 0.49 + 0.0179 * l - 0.00000771 * l^2 + 0.000000675 * l^3 \]  

_Run-on_: Run-on was modeled as a function of precipitation and regional waterbalance. For several days following a rain event (the number of days is a model parameter), run-on is given by

\[ R = (ppt - 2.5) * \left( \frac{\text{totwat}}{\text{watcap}} \right) \]  

where \( R \) is the run-on (mm/d), \( ppt \) is the rain event precipitation (mm/d, note that \( R = 0 \) if \( ppt < 2.5 \) mm/d), \( \text{totwat} \) is the current bucket water content (mm), \( \text{watcap} \) is the bucket water capacity excluding pooled water (mm). The last term, \( \left( \frac{\text{totwat}}{\text{watcap}} \right) \), simulates the effect of the regional water balance—if the water table is low, presumably the region is dry and more of the water in a storm would be held by the soil and used by the vegetation, and less would flow into the fen. There is no field data (except the depth to water table data) from the fen to calibrate these factors.

*Runoff Water Loss*: The profile loses water by runoff and evaporation. Runoff is modeled as a drainage that depends on the depth to the water table. Water is allowed to pool over the sphagnum to a certain height (\( z_{pool,\text{max}} \), an input parameter). Water
will drain from the profile at a maximum rate when the water table is at this maximum pool height (any water inputs above this maximum are assumed to be immediately lost). As the water table drops from this maximum value, the drainage, $Q_{dn}$, falls to zero as the water table reaches some depth, $z_{crit}$. The drainage rate is given by

$$Q_{dr} = Q_{dr,max} \left(\frac{z_w - z_{crit}}{(z_{pool,max} - z_{crit})^2}\right)$$

where $Q_{dr,max}$ is the maximum drainage rate and $z_{crit}$ is the depth at which drainage stops (model parameters). As with run-on, the only field data for calibration is the depth to water table. For run-off two storms in Nov. 1991 provided much of the basis for parameterization (see Fig 4.17,a below).

Role of Ice in Bog Model Hydrology: The minimum ice thickness to have a hydrological impact ($z_{ice}$) is set at 1 cm. At that point the ice layer becomes impervious to water and any liquid water inputs will pool on top of the ice. The water table is then considered to be either the top of the ice layer or the surface of the pooled water, if any exists.

4.3.6. Modeling the Snowpack and Snowmelt

The snowpack's role in soil climate is two-fold. First, it affects the ground thermal regime by providing an insulating layer between the soil and the atmosphere, and by its high albedo it modifies the radiation balance at the surface. Second, it affects the soil moisture regime by storing precipitation water as snow and releasing it later as snowmelt.

There are two reasons why a snowpack/snowmelt model component is of secondary importance for this model: (1) its influence on the thermal regime occurs during the winter when methane fluxes are minimal (Whalen and Reeburgh, 1988; Dise, 1992), and (2) for wetlands, snowmelt serves only to recharge the "bucket" to capacity, with additional meltwater leaving as runoff. Some northern wetland
modelers avoid the issue by initializing their model in spring with a saturated, isothermal (0°C) profile (N. Roulet, pers. comm.). It may be of importance, however, when considering climate change scenarios near the southern edge of permanent winter snow.

Precipitation is considered to be all snow if $T_{air} < 0^\circ C$ and all rain if $T_{air} > 0^\circ C$. Snowfall density is calculated as

$$\rho = \min(\max(\rho_{\text{min}}\rho_{\text{max}} + (\partial\rho/\partial T)T_{air}),\rho_{\text{max}})$$  \hspace{1cm} (4.17)

where $\rho$ is the snow density (g cm$^{-3}$), $\rho_{\text{min}}$ and $\rho_{\text{max}}$ are maximum and minimum allowable densities, and $\partial\rho/\partial T$ is a rate of change of density with air temperature (g cm$^{-3}$ °C$^{-1}$), and $\max$ and $\min$ are functions which choose the maximum or minimum of values within their brackets. Snow accumulates into a snowpack whose density, $\rho$, is determined by

$$\rho_{\text{new}} = \min(\max(\rho_{\text{old}}\rho_{\text{min}}\rho_{\text{max}} + (\partial\rho/\partial T)T_{air}),\rho_{\text{max}})$$  \hspace{1cm} (4.18)

and

$$\rho_{\text{new}} = \begin{cases} 
\rho_{\text{new}} & \text{if snowdepth} < 5 \text{ cm} \\
(\rho_{\text{new}} + \rho_{\text{old}})/2 & \text{if} 5 \text{ cm} < \text{snowdepth} < 10 \text{ cm} \\
(\rho_{\text{new}} + 2\rho_{\text{old}})/3 & \text{if} 10 \text{ cm} < \text{snowdepth} < 20 \text{ cm} \\
(\rho_{\text{new}} + 3\rho_{\text{old}})/4 & \text{if} \text{snowdepth} > 20 \text{ cm} 
\end{cases}$$ \hspace{1cm} (4.19a-d)

where $\rho_{\text{old}}$ is the snow density of the previous day. A deeper snowpack thus increases its density more slowly. Snowmelt is determined by air temperature and day of year only, following the work of Anderson, as discussed in Bras (1990).

$$Q_{\text{melt}} = 0.5 T_{air} [(M_{\text{max}} + M_{\text{min}})(1+ \sin(2\pi(\text{doy}+81)/365))]$$ \hspace{1cm} (4.20)

where $Q_{\text{melt}}$ is the snowmelt per hour, $M_{\text{max}}$ and $M_{\text{min}}$ are snowmelt parameters, and doy is the day of the year (Jan. 1 = 1). If $T_{air}$ is less than 0°C then no snowmelt occurs. When a snowpack "exists" for the model (depth ≥ 1 cm) the thermal model adds one snow element, and assigns the air temperature to the snow surface rather than the peat surface. Snowpack effect on the albedo is not modeled, but is assumed to be
reflected in the local air temperature. Snowmelt water is a direct input into the bucket water balance. Snow thermal properties (heat capacity and thermal conductivity) are assumed constant.

4.4. Model Results

The peat soil climate model results will be compared to field measurements made at Sallie's Fen in Barrington, NH. All field measurements reported in this and the next section were made by Patrick Crill and colleagues, and are as yet unpublished. I will not describe the methodology and instrumentation of these measurements in detail because I did not participate in the data collection. Discussion of model sensitivity is incorporated into the discussion of model results.

4.4.1 Sallie's Fen, NH

Sallie's Fen is a 1.7 hectare poor fen (i.e., it receives some water and nutrient inputs from the surrounding watershed) perched on glacial till in Barrington NH. Peat depths range from one to more than four meters; fen water pH ranges from about 4.5 to 6.5, the higher values occurring where a small stream enters the fen (Figure 4.5). At the low pH end, the fen is dominated by *Sphagnum* spp. and *Carex* spp. Methane flux measurements have been made at several sites in this part of the fen since mid-1990. Since September 1991 a meteorological tower and data logger have collected hourly average air (25 and 50 cm) and peat (various depths) temperatures, averaging measurements taken each minute. In addition, net radiation, liquid precipitation (tipping bucket), wind speed, depth to water table and bog surface height (floats and potentiometers), and heat flux at 5 cm are recorded hourly. At four additional wells installed along the boardwalk, depth to water table is read each time methane fluxes are measured (about once a week). All field instruments were installed and are operated by Patrick Crill and colleagues.
Figure 4.5 - Sallie's Fen, Barrington NH. Total area about 1.7 ha.
4.4.2. Model Input Data

The peatland soil climate model requires daily average air temperature, daily liquid precipitation, and, if available, hourly net radiation data. Hourly net radiation data is transformed into a daily value by integrating the positive hourly values through the day and averaging them over the number of hours of positive net radiation. The model input is then the hourly average positive net radiation and the number of hours of positive net radiation.

Due to instrument problems there are several large gaps in the temperature data, and two small gaps (one to a few days) in the other data. Data necessary for driving the model (daily air temperature, daily precipitation, and hourly net radiation) were obtained at the fen, and if unavailable there, from the Durham NH weather station, about 10 km from Sallie's Fen, operated by the National Weather Service (no net radiation data is collected there). Fen daily air temperature (5 pm to 5 pm, to match the NWS data) was calculated as either the average of the warmest and coldest hourly temperatures recorded at the fen, or as the daily average air temperature in Durham minus 0.56°C. This correction is the average deviation between Durham and Sallie's Fen daily air temperatures for the periods 2 Sep through 29 Dec 1991 and 4 Jan through 26 May 1992 and 8 Aug through 30 Sep 1992. Durham air temperatures were used in the model input file for 1 Apr through 1 Sep 1991; 30 Dec 1991 through 3 Jan 1992; and 27 May through 7 Aug 1992.

Precipitation data was collected at Sallie's Fen for most of the study period and used as the input for the model. For those days with missing precipitation data (30 Dec 1991 - 3 Jan 1992 and 3 - 7 Aug 1992) Durham precipitation was used. The tipping bucket gage installed at Sallie's Fen records only liquid precipitation or snowmelt from snow collected in the funnel. Therefore snowfall precipitation was taken from the Durham record (as snowfall water content) and obvious snowmelt readings in the
Sallie's Fen record were set to zero. If the Durham precipitation value was "trace" it was set to 0.254 mm water.

4.4.3. Model Parameters

The model simulation period is 1 Apr 1991 through 30 Sep 1992. The model was initialized with a uniform peat temperature of 1°C, and an initial bucket water content of 22.7 cm of water, to nearly match the 2 Apr 1991 field water table depth of 42 mm. Model parameter values for the results in Sections 3.4.4 - 3.4.6. are listed in Tables 4.1.a, 4.1.b, and 4.1.c. Sensitivity of the model results to those parameters is discussed in Sections 4.4.4 - 4.4.6.

The monthly average air temperature, as recorded at Durham, was warmer than the 1951-1980 normals for April 1991 through February 1992 (and particularly so in April and May 1991) and cooler than normal for March through August 1992 (particularly July) (see Figure 4.6.a). Monthly precipitation was slightly below normal in 1991 until August, when Hurricane Bob delivered over 180 mm in one day (the monthly average for August is 84 mm). September 1991 was also a wet month. Precipitation was below normal from October 1991 through May 1992 then above normal for June, July and August 1992 (see Figure 4.6.b).

4.4.4. Temperature Results

Simulated peat temperatures are compared with field values for 4 cm, 8 cm, 12 cm, 18 cm, and 45 cm in Figures 4.7.a&b - 4.11.a&b. Overall, the model captures the seasonal signal quite well at all depths. It also captures the patterns of oscillations superimposed on the annual signal by passing cold and warm fronts. However, at shallower depths (4 cm, 8 cm, and 12 cm) the model oscillations are often of a smaller magnitude than the field. At 18 cm and 45 cm the oscillations are more equal.
Table 4.1.a - Bog Model Parameters - Thermal

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_{dp}$</td>
<td>135 cm</td>
<td></td>
<td>depth of constant temp.</td>
<td>none†</td>
</tr>
<tr>
<td>$T_{liq}$</td>
<td>0.0 °C</td>
<td></td>
<td>water begins to freeze</td>
<td>Williams &amp; Smith</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1990</td>
</tr>
<tr>
<td>$T_{sol}$</td>
<td>-1.0 °C</td>
<td></td>
<td>ice begins to melt</td>
<td>Williams &amp; Smith</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1990</td>
</tr>
<tr>
<td>$z_{ice}$</td>
<td>1.0 cm</td>
<td></td>
<td>ice is impermeable</td>
<td>none†</td>
</tr>
<tr>
<td>$k_{org}$</td>
<td>$2.5 \times 10^4$ erg s$^{-1}$ cm$^{-1}$ K$^{-1}$</td>
<td>thermal cond. - organic</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$k_{wat}$</td>
<td>$5.7 \times 10^4$ erg s$^{-1}$ cm$^{-1}$ K$^{-1}$</td>
<td>thermal cond. - water</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$k_{ice}$</td>
<td>$2.2 \times 10^5$ erg s$^{-1}$ cm$^{-1}$ K$^{-1}$</td>
<td>thermal cond. - ice</td>
<td>Williams &amp; Smith</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1990</td>
</tr>
<tr>
<td>$k_{snow}$</td>
<td>$1.2 \times 10^4$ erg s$^{-1}$ cm$^{-1}$ K$^{-1}$</td>
<td>thermal cond. - snow</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$c_{org}$</td>
<td>$2.5 \times 10^7$ erg cm$^{-3}$ K$^{-1}$</td>
<td>heat capacity - organic</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$c_{wat}$</td>
<td>$4.2 \times 10^7$ erg cm$^{-3}$ K$^{-1}$</td>
<td>heat capacity - water</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$c_{ice}$</td>
<td>$1.9 \times 10^7$ erg cm$^{-3}$ K$^{-1}$</td>
<td>heat capacity - ice</td>
<td>Williams &amp; Smith</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1990</td>
</tr>
<tr>
<td>$c_{snow}$</td>
<td>$2.5 \times 10^6$ erg cm$^{-3}$ K$^{-1}$</td>
<td>heat capacity - snow</td>
<td>Hillel 1980</td>
<td></td>
</tr>
<tr>
<td>$L_f$</td>
<td>$3.3 \times 10^9$ erg cm$^{-3}$</td>
<td>latent heat of fusion</td>
<td>Hillel 1980</td>
<td></td>
</tr>
</tbody>
</table>

† Based on field data from Sallie’s Fen, NH (P. Crill, pers. comm.)
Table 4.1.b - Bog Model Parameters - Hydraulic

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_a$</td>
<td>0.90</td>
<td>cm$^3$ cm$^{-3}$</td>
<td>surface layer porosity</td>
<td>Boelter &amp; Verry 1977</td>
</tr>
<tr>
<td>$n_c$</td>
<td>0.80</td>
<td>cm$^3$ cm$^{-3}$</td>
<td>submerged layer poros.</td>
<td>Boelter &amp; Verry 1977</td>
</tr>
<tr>
<td>$z_{acr}$</td>
<td>12</td>
<td>cm</td>
<td>surface layer depth</td>
<td>none(1)</td>
</tr>
<tr>
<td>$z_b$</td>
<td>30.0</td>
<td>cm</td>
<td>maximum evap. depth</td>
<td>Boelter &amp; Verry 1977</td>
</tr>
<tr>
<td>$z_{pool,max}$</td>
<td>5.0</td>
<td>cm</td>
<td>maximum pool height</td>
<td>none†</td>
</tr>
<tr>
<td>$z_{crit}$</td>
<td>8.0</td>
<td>cm</td>
<td>maximum draining depth</td>
<td>none†</td>
</tr>
<tr>
<td>$Q_{dr,max}$</td>
<td>2.0</td>
<td>cm water d$^{-1}$</td>
<td>maximum draining rate</td>
<td>none†</td>
</tr>
<tr>
<td>expon,$dr$</td>
<td>2.0</td>
<td>----</td>
<td>drainage expon. param.</td>
<td>none†</td>
</tr>
<tr>
<td>run-on dur</td>
<td>4.0</td>
<td>days</td>
<td>run-on duration</td>
<td>none†</td>
</tr>
<tr>
<td>$a$</td>
<td>1.26</td>
<td>----</td>
<td>Priestley-Taylor param.</td>
<td>Rouse et al 1977</td>
</tr>
<tr>
<td>$m$</td>
<td>4.0</td>
<td>----</td>
<td>actual evap. param.</td>
<td>none†</td>
</tr>
<tr>
<td>$z_{ET}$</td>
<td>8.0</td>
<td>cm</td>
<td>critical evap. depth</td>
<td>Boelter &amp; Verry 1977</td>
</tr>
<tr>
<td>$W_1$</td>
<td>0.2</td>
<td>----</td>
<td>capillary water param.</td>
<td>Boelter 1964,1969*</td>
</tr>
<tr>
<td>$W_2$</td>
<td>0.35</td>
<td>----</td>
<td>capillary water param.</td>
<td>Boelter 1964,1969*</td>
</tr>
<tr>
<td>$W_3$</td>
<td>0.4</td>
<td>----</td>
<td>capillary water param.</td>
<td>Boelter 1964,1969*</td>
</tr>
<tr>
<td>$W_4$</td>
<td>0.7</td>
<td>----</td>
<td>capillary water param.</td>
<td>Boelter 1964,1969*</td>
</tr>
</tbody>
</table>

† Based on field data from Sallie's Fen, NH (P. Crill, pers. comm.)
* These parameter values are inferred from limited data presented in the reference cited.
Table 4.1.c - Bog Model Parameters - Snow

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{max}}$</td>
<td>0.30</td>
<td>g cm$^{-3}$</td>
<td>max. snow density</td>
<td>Bras, 1990</td>
</tr>
<tr>
<td>$\rho_{\text{min}}$</td>
<td>0.05</td>
<td>g cm$^{-3}$</td>
<td>min. snow density</td>
<td>Bras, 1990</td>
</tr>
<tr>
<td>$\partial \rho / \partial T$</td>
<td>0.025</td>
<td>g cm$^{-3}$ °C$^{-1}$</td>
<td>snow density param.</td>
<td>none†</td>
</tr>
<tr>
<td>$M_{F_{\text{max}}}$</td>
<td>0.025</td>
<td>cm water h$^{-1}$ °C$^{-1}$</td>
<td>snowmelt factor</td>
<td>Bras, 1990</td>
</tr>
<tr>
<td>$M_{F_{\text{min}}}$</td>
<td>0.0125</td>
<td>cm water h$^{-1}$ °C$^{-1}$</td>
<td>snowmelt factor</td>
<td>Bras, 1990</td>
</tr>
</tbody>
</table>

† Based on field data from Sallie's Fen, NH (P. Crill, pers. comm.)
Figure 4.7 - (a) Model (heavy line) and field 4 cm peat temperatures for 1991. (b) Same as (a) but for 1992.
Figure 4.8 - (a) Model (heavy line) and field 8 cm peat temperatures for 1991. (b) Same as (a) but for 1992.
Figure 4.9 - (a) Model (heavy line) and field 12 cm peat temperatures for 1991.  
(b) Same as (a) but for 1992.
Figure 4.10 - (a) Model (heavy line) and field 18 cm peat temperatures for 1991. (b) Same as (a) but for 1992.
Figure 4.11 - (a) Model (heavy line) and field 45 cm peat temperatures for 1991.
(b) Same as (a) but for 1992.
The model tends to be one to three degrees warmer than the field data during all but the winter months, when it is instead a degree or two cooler. The other notable differences are that at 18 cm the model freezes and thaws about one month before the field data, and the model drops below 0°C at 45 cm (but not below -1°C, and thus is only partly frozen) while the 45 cm field temperatures are always above 0°C. In addition, the field and model data at 45 cm are in strong disagreement for August and Sept. 1992; the model temperatures appear more reasonable there.

In a sensitivity study of peat temperatures, a sinusoidal air temperature signal with a period of 7 days, a mean of 15°C, and an amplitude of 8°C was applied, and comparisons were made of the 12 cm peat temperature for nine different parameter choices (Figure 4.12 and Table 4.2). The water table and unsaturated water content were held constant during each sensitivity run (no rain nor evaporation nor drainage). The largest amplitude oscillations occurred in Runs 2 and 4, when the water table was at the surface. Run 4 had lower porosity values than Run 2, and therefore more organic matter and less water, but the temperature behavior was identical. The next largest amplitude oscillation, Run 8, had a high water content in the unsaturated surface layer ($W_1 = 0.4$, $W_2 = 0.5$, average degree of saturation = 0.5). The lowest amplitude oscillation, Run 5, has a low water content in the unsaturated surface layer ($W_1 = 0.05$, $W_2 = 0.1$, average degree of saturation = 0.075). So, even though the heat capacity increases with increased water content, the thermal conductivity increases to a greater extent, and temperature signals propagate more readily in the model as water content increases.

Thus a possible explanation for the smaller temperature oscillations in the model may be that the $W_1$ and $W_2$ parameters are too low, and so the surface layer contains too much air and insulates the peat from oscillations in the air temperature. These parameters will also affect $tdepth$ to water table results (Section 4.4.6). As these values increase (decrease) the water table will raise and lower more slowly.
Air and 12 cm Peat Temperature
for sensitivity runs

Figure 4.12 - Sensitivity of 12 cm model peat temperatures to various parameter values. The surface temperature is sinusoidal (period = 7 days, amplitude = 8°C, mean = 15°C). Surface temperature signals propagate more readily as the peat gets wetter.
Table 4.2. Parameters for temperature sensitivity runs

<table>
<thead>
<tr>
<th>run</th>
<th>Zacr (cm)</th>
<th>aporos</th>
<th>cporos</th>
<th>W1</th>
<th>W2</th>
<th>W3</th>
<th>W4</th>
<th>inmois (cm)</th>
<th>dtwt (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.10</td>
<td>0.20</td>
<td>0.4</td>
<td>0.7</td>
<td>18.80</td>
<td>8.0</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.10</td>
<td>0.20</td>
<td>0.4</td>
<td>0.7</td>
<td>24.80</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>0.8</td>
<td>0.7</td>
<td>0.10</td>
<td>0.20</td>
<td>0.4</td>
<td>0.7</td>
<td>16.36</td>
<td>8.0</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.8</td>
<td>0.7</td>
<td>0.10</td>
<td>0.20</td>
<td>0.4</td>
<td>0.7</td>
<td>21.80</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>0.9</td>
<td>0.8</td>
<td>0.05</td>
<td>0.10</td>
<td>0.4</td>
<td>0.7</td>
<td>18.14</td>
<td>8.0</td>
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<td>0.4</td>
<td>0.7</td>
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<td>8.0</td>
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<td>0.10</td>
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<td>0.4</td>
<td>0.7</td>
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<td>4.0</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.20</td>
<td>0.4</td>
<td>0.7</td>
<td>19.20</td>
<td>8.0</td>
</tr>
</tbody>
</table>
(quickly). A second possible explanation is that the model uses the air temperature as the surface or skin temperature, although the two are likely to be different. Some surface (but not skin) peat temperature measurements were made, but not enough to characterize the relationship between surface and air temperature. De Vries (1958) states that, when considering annual oscillations, surface temperatures tend to have an amplitude of about 1.2 times the air temperature. What this factor would be for weekly (not annual) oscillations in a wetland peat (not mineral soil) is unknown, but if it were greater than 1.0, it could explain some of the difference between model and field behaviors.

A third possible explanation is that the field data are in error. Figure 4.13 shows air temperature and field and model 12 cm peat temperature for 1 Aug through 31 Oct 1991. The field temperature is consistently lower than the air temperature and has oscillations that are generally about half the magnitude of the air temperature oscillations. The model temperature generally oscillates within the extremes of the air temperature, and with about 1/4 the amplitude of the air temperature. The model, based on theory, behaves more as the theory would predict.

4.4.5. Ice Results

The model ice routine over freezes and has difficulty thawing the ice from below (Figure 4.14). Field ice data were collected five times during the winter by drilling a series of holes in the ice in various places in the fen, and measuring ice thickness; mean values and range are plotted. The model ice thickness is near the extreme field value for much of the winter, and in April the model has a reasonable surface thaw depth but too much ice below it. Ice thickness (depth of freeze) in the model was insensitive to most parameters tested (porosities, freeze/thaw temperature range) but was sensitive to the depth at which the constant mean annual air temperature was applied in the model. Heat diffusion theory predicts a damping depth
Figure 4.13 - Air temperature and field and model 12 cm peat temperature. The field temperature has higher amplitude oscillations than the model, and tends to remain below the air temperature, while the model oscillates within the range of the air temperature oscillations.
Figure 4.14 - Field and model ice and snow depths. The model tends to overestimate the ice and has difficulty melting it from below in the spring. The model tends to underestimate snow depth, probably because model snowfall densities are too high.

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of about 1 meter for a saturated peat (Hillel, 1980), so the temperature oscillations would be very small by about 5 meters. However, the model assumes a linear temperature gradient between its deepest node (80 cm) and the point of constant mean annual temperature, while the amplitude of temperature oscillations falls off exponentially with depth. Therefore, when the bog surface is cold, placing a constant temperature point at 5 meters will cause the peat at 80 cm to gain too little heat from below (small temperature gradient), and the ice will grow too thick. The opposite effect in the summer will cause the model peat at 45 cm to be too warm. With the constant temperature at 5 meters, ice depths were about 60 cm and summer peat temperatures at 45 cm were about 18°C. By setting the constant temperature depth at 1.35 meters (larger temperature gradient), ice depth and 45 cm summer peat temperatures are quite close to field values (Figures 4.14, 4.11.a, and 4.11.b). However, in the model the deeper peat (18 cm and 45 cm) appears to warm too quickly in the spring (while, in contrast, the ice does not melt away from below very fast). Perhaps a variable depth to constant temperature (or a variable bottom temperature gradient) would achieve better results.

4.4.6. Water Table Results

Matching Sallie's Fen depth to water table (DTWT) proved to be very difficult. For the period 1 Apr 91 through 30 Sep 91 field DTWT are the average of weekly measurements at four wells; From 1 Oct 1991 on there was continuous monitoring at a single well (hourly averages of once-a-minute measurements are recorded on a datalogger, and these are averaged into daily values). In mid-July 1991 the DTWT in the field was about 310 mm (Figure 4.15.a); 300 mm was chosen as the maximum DTWT in the model (Table 4.1.b). In mid-August 1991 Hurricane Bob's 181 mm of rain brought the water table back to the surface. In the summer of 1992 DTWT was generally about 30 to 80 mm, and only briefly dropped below 100 mm (Figure
Figure 4.15 - (a) Field and model depth to water table for April through September 1991. The heavy line down from the top is the daily precipitation (scale on right). Model depth to water table is the average of four well readings. (b). Same as (a) but for October 1991 through September 1992. Model depth to water table is measured continuously at a single well.
4.15.b). The weather for these two summers does not appear to be that different (except for the hurricane) and the model DTWT is not that different from one summer to the next. 1992 was drier in April and May and wetter in June and July than 1991; and 1992 was cooler from May through Aug than 1991. The model DTWT for 1992 is close to the field values except for late May and June when it drops too low and then has a much weaker response than the field to two moderate storms in early June (Figure 4.15.b).

Several model parameters will control model DTWT given an evaporative demand: depth of the surface layer \( z_{acr} \), porosities of the surface and deeper layer, the unsaturated water content parameters \( W_1, W_2, W_3, \) and \( W_4 \), and two parameters controlling how actual evaporation compares to evaporative demand as the water table falls (see Eqs. 4.12 and 4.13). This limits evaporation only when the water table is below a critical value \( z_{ET} \).

A series of sensitivity runs to study the behavior of the water table consisted of 60 days with \( PE = 2.6 \) mm/d, no rain, and beginning with a saturated profile. Figure 4.16 compares four runs with all parameters the same except the exponent in Eq. 4.13. Drainage occurs until the water table drops to 8 cm, which is also the depth of the surface layer \( z_{acr} \), and the critical evaporation depth \( z_{ET} \) for these runs. The exponent, \( m \) in Eq. 4.13 exerts strong control over how quickly the water table drops below this level. All of the other parameters (porosities, \( z_{acr} \), \( W_1 \) and \( W_2 \)) determine how much water is available for evaporation in saturated peat, and also how much precipitation is needed to raise the water table. Increasing the surface layer thickness, \( z_{acr} \), slows the drop of the water table because the surface layer's higher porosity and lower water retention parameters \( W_1 \) and \( W_2 \) vs. \( W_3 \) and \( W_4 \) allow it to lose much more water than the deeper layer. Conversely, it takes much more precipitation to raise the water table a given distance in the surface layer than in the deeper layer. Only the exponent parameter and the critical depth control evaporative
Figure 4.16 - Sensitivity of model depth to water table to exponent in actual evaporation equation (Eqs. 4.12 and 4.13).
loss without affecting the water table response to precipitation.

In several model runs with various parameter values, the DTWT always dropped lower in the summer of 1992 than in the summer of 1991, in sharp contrast to the field data. Therefore, the model could be parameterized to try to match either year, but not both. I have chosen to try to match 1992 water table values because the continuous field data gives a much clearer picture of the fen water table dynamics.

Water table values when the fen is frozen, roughly mid-December 1991 through March 1992, are not reliable; the instrument float was frozen in place and the model is trying to keep track of ice levels and melt water with unknown reliability.

Since Sallie's Fen is a fen, and thus is actively connected to the regional watershed by inflowing and outflowing streams, as well as, perhaps, ground water seeps in and/or out, the model must incorporate features beyond the one-dimensional bucket of Figure 4.4. Figures 4.17.a&b show clear motivation for both the drainage and run-on features discussed in Section 4.3.5. In November 1991, when evaporative demand is low, the DTWT drops quickly to about 6 to 8 cm (Figure 4.17.a). This could only be due to some sort of drainage loss, which appears to taper off as the water table lowers. In June 1992, following two moderate storms about 1 week apart (33.5 mm and 48.2 mm), the water table continues to rise for several days after the second storm before slowly dropping (Figure 4.17.b). Presumably, this is due to stream and/or subsurface inflow from the surrounding watershed. This run-on response in June 1992 seems to be much more dramatic than for any other rain events.

Sallie's Fen is part of a larger watershed (roughly 40 hectares) which its water table reflects. One possible explanation for the very different water table behaviors of 1991 and 1992 is that in 1991, with a very warm and slightly dry spring and early summer, the regional water balance was negative and the watershed water table was low. The model, which restricts water loss when the water table drops below 12 cm (both due to the physical nature of peat evaporation, Boelter and Verry
Figure 4.17 - (a) Model and field depth to water table for November 1991. Note how field water table drops off after each precipitation event. This is assumed to be due to fen drainage. (b) Model and field depth to water table for June 1992. Note how field water table continues to rise for several days after the second precipitation event. This is assumed to be due to run-on from the surrounding watershed.
1978, and in order to better fit 1992) would not be able to approximate this regional drying. In 1992, the spring and summer were relatively cool and, although precipitation in April and May was below normal, June and July were above normal, so the regional water balance would presumably be more neutral. The current model is unable to handle a sophisticated coupling to the local watershed, using only simple run-on and drainage models of Section 4.3.5.

Another possible cause of divergence between the model and the field is that model precipitation is based on a single point measurement, either at Sallie's Fen or in Durham, while the fen water balance is driven by the mean watershed precipitation which sometimes may be poorly represented by a single point measurement (e.g., Dunne and Leopold, 1978).

4.5. Methane Flux Correlation to Soil Climate at Sallie's Fen

4.5.1. Flux Measurements at Sallie's Fen

Methane flux measurements have been made at Sallie's Fen (roughly once a week) since June 1990 by Patrick Crill and colleagues. The techniques used are described in Crill et al (1988). Flux values used here (as yet unpublished) are the average of three chamber measurements spaced about 20 m apart (see Figure 4.5), measured sequentially (about 20 minutes apart), generally in the late morning. Figure 4.18 shows the fluxes over the measurement period (through August 1992).

4.5.2. Flux Correlations to Peat Temperature

Due to instrument problems peat temperature was not recorded every time a flux was measured. The 18 cm peat temperature record is the most complete, so I have chosen to correlate flux with it. Correlations with the less complete 12 cm temperature data give similar results. Due to the generally higher fluxes in the summer than the winter (Figure 4.18) we can expect, and find, a good correlation
Figure 4.18 - Measured methane fluxes at Sallie's Fen NH for 1990 - 1992.
between flux and 18 cm peat temperature (Regression #1a in Table 4.3 and Figure 4.19.a; all linear regression statistics are generated with StatView SE on the Macintosh, Abacus Concepts Inc., Berkeley, CA, 1988)

\[
\ln(CH_4 \text{ flux}) = 3.646 + 0.135 \times T_{18}
\] (4.21)

However, Figures 4.18 and 4.19.a show that there is a great deal of scatter in the summer months that this correlation cannot explain. The regression was improved by excluding fluxes measured soon after rain events (Regressions #1b &1c; see also Section 4.5.4 below).

4.5.3. Flux Correlation with Depth to Water Table

Flux correlation with DTWT is less strong than with 18 cm peat temperature, and also gives the unexpected result of higher fluxes as the water table drops (Regression #2a and Figure 4.19.b).

\[
\ln(CH_4 \text{ flux}) = 4.263 - 0.008 \times DTWT
\] (4.22)

This is partly due to the fact that winter fluxes are low and winter water tables are high. When only those data are used that have an 18 cm temperature greater than 10°C (Regression #2b), the relationship changes improves slightly and the dependence on DTWT decreases somewhat, but there is still a tendency of higher fluxes with lower water tables.

4.5.4. Flux Correlation with Recent Precipitation

It was observed that fluxes were often low soon after a rain event (P. Crill, pers. comm.), so methane flux was compared with a constructed variable to represent recent precipitation (Weighted Recent Precipitation or WRP)

\[
WRP = ppt_0 + 0.8 \times ppt_1 + 0.6 \times ppt_2 + 0.4 \times ppt_3 + 0.2 \times ppt_4
\] (4.23)

where \(ppt_i\) is the daily precipitation \(i\) days ago. This variable’s impact on fluxes depends on the rainstorm’s magnitude, and it will affect fluxes for 4 days after it
occurs, but the effect falls off linearly with time. This effect could be due to (1) the delivery of oxygenated rainwater, streamwater, and surface inflow water to the fen surface, and hence enhanced methane oxidation in the water column and lower flux; (2) a flushing of methanogen substrates due to horizontal water flow across the fen, and hence less methane production and lower flux; and/or (3) a flushing of dissolved methane out of the fen due to horizontal water flow across the fen, and hence lower flux from the fen.

When all data is included there is little correlation between flux and WRP (Regression #3a), but when cool weather fluxes are removed ($T_{18} < 10^\circ C$, open circles in Figure 4.20) there is a clear relationship of lower fluxes when WRP is large (solid circles in Figure 4.20, Regression #3b).

\[
\ln(CH_4 \text{ flux}) = 6.074 - 0.021 \times WRP \tag{4.24}
\]

This relationship is slightly stronger than that of flux with DTWT. This or a similar variable, may also help to explain some of the high variability observed in the summer fluxes.

Presently there is no data from Sallie's Fen on water inflow or outflow, little data on dissolved methane concentrations, none on dissolved oxygen concentrations, and no detailed, rain-event, flux time series, so this effect can only be noted but not explained. Although there is undoubtedly a better variable to represent the effect of rain events on fluxes (time rate of change of water table perhaps), there is little reason to try to determine it until there is a more complete data set collected, and a better understanding of the phenomenon.
Sallie's Fen NH 1990 - 1992
Methane flux vs. 18 cm peat temperature

(a)

\[
\ln(\text{CH}_4 \text{ flux}) = 3.65 + 0.135 (T_{18})
\]

\[r^2 = 0.54\]

Methane flux vs. water table location

(b)

\[
\ln(\text{CH}_4 \text{ flux}) = 4.263 - 0.008(Z_{w})
\]

\[r^2 = 0.199\]

Figure 4.19 - (a) Linear regression of log methane flux versus field measured 18 cm peat temperature using all available data (this and all other regressions are summarized in Table 4.3). There is a clear, positive correlation between peat temperature and methane flux. (b) Linear regression of log methane flux versus field measured depth to water table, using all available data.

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Figure 4.20 - Linear regression of log methane flux versus weighted recent precipitation (WRP). The open circles are for cool season data ($T_{18} < 10^\circ C$), while the solid circles are for warm season data ($T_{18} > 10^\circ C$). The regression is for only the warm season data (solid circles).
Table 4.3 - Linear Regressions of Log Methane Flux vs. Soil Climate Variables

\[ \ln[\text{CH}_4 \text{ flux}] = a + b \cdot T_{18} + c \cdot DTWT + d \cdot WRP \]

<table>
<thead>
<tr>
<th>#</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>n (1)</th>
<th>SEE (2)</th>
<th>(r^2)</th>
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<tr>
<td>1a</td>
<td>3.646 ± .029</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>74</td>
<td>0.905</td>
<td>.542</td>
</tr>
<tr>
<td>1b</td>
<td>3.569 ± .037</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>38</td>
<td>0.793</td>
<td>.719</td>
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<tr>
<td>1c</td>
<td>3.632 ± .038</td>
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<td>0</td>
<td>22</td>
<td>0.618</td>
<td>.671</td>
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<tr>
<td>2a</td>
<td>4.263 ± 0</td>
<td>0</td>
<td>-.008 ± .003</td>
<td>0</td>
<td>92</td>
<td>1.166</td>
<td>.199</td>
</tr>
<tr>
<td>2b</td>
<td>5.183 ± 0</td>
<td>0</td>
<td>-.006 ± .004</td>
<td>0</td>
<td>30</td>
<td>0.898</td>
<td>.223</td>
</tr>
<tr>
<td>3a</td>
<td>4.945 ± 0</td>
<td>0</td>
<td>0</td>
<td>-.011 ± .015</td>
<td>99</td>
<td>1.312</td>
<td>.020</td>
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<tr>
<td>3b</td>
<td>6.074 ± 0</td>
<td>0</td>
<td>0</td>
<td>-.021 ± .011</td>
<td>32</td>
<td>0.832</td>
<td>.306</td>
</tr>
<tr>
<td>4a</td>
<td>4.310 ± 0</td>
<td>0</td>
<td>-.008 ± .002</td>
<td>-.003 ± .007</td>
<td>92</td>
<td>1.171</td>
<td>.279</td>
</tr>
<tr>
<td>4b</td>
<td>5.643 ± 0</td>
<td>0</td>
<td>-.004 ± .004</td>
<td>-.016 ± .013</td>
<td>30</td>
<td>0.815</td>
<td>.383</td>
</tr>
<tr>
<td>5</td>
<td>3.345 ± .029</td>
<td>-.007 ± .003</td>
<td>0</td>
<td>68</td>
<td>0.826</td>
<td>.627</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.777 ± .028</td>
<td>0</td>
<td>-.019 ± .010</td>
<td>74</td>
<td>0.838</td>
<td>.612</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.517 ± .031</td>
<td>-.005 ± .004</td>
<td>-.013 ± .011</td>
<td>68</td>
<td>0.801</td>
<td>.654</td>
<td></td>
</tr>
</tbody>
</table>

(1) \(n\) = number of data points in regression.
(2) SEE = Standard Error of the Estimate.
(3) Regressions 1a, 2a, 3a, and 4a include all available data.
(4) Regression 1b includes only data with WRP < 5 mm.
(5) Regression 1c includes only data with 5 mm < WRP < 20 mm.
(6) Regressions 2b, 3b, and 4b include only data with \(T_{18} > 10^\circ\)C.

\* \(p < .01\).
\# \(p < .05\).
\† \(p > .05\).
\¶ 95% confidence interval.
4.5.5. Multiple Regressions

Temperature, DTWT, and recent precipitation are all simultaneously affecting the methane flux, so a multiple regression model should give a clearer picture. For example, when the effect of 18 cm temperature on flux is examined for "dry" periods (WRP < 5 mm) versus "moderately wet" periods (5 mm < WRP < 20 mm) versus "very wet" periods (WRP > 20 mm) very different relationships arise (Regressions #1a - 1c of Table 4.3). Also, as already mentioned, both flux versus DTWT and flux versus WRP had improved correlations when only the warm season data was included and so some of the temperature driven variability was removed.

Table 4.3 summarizes four multiple regressions tested (as well as the single regressions of the previous sub-sections, all assuming the form

\[ \ln(CH_4 \text{ flux}) = a + b \cdot T_{18} + c \cdot DTWT + d \cdot WRP. \]  

(4.25)

Since the effect of temperature is so strong, the multiple regressions of flux versus DTWT and WRP (Regressions #4a and #4b) give the poorest results, and explain less of the variability than peat temperature alone. The strongest relationship (highest \( r^2 \) and lowest SEE) is the multiple regression (#7) using all three variables,

\[ \ln(CH_4 \text{ flux}) = 3.517 + 0.128 \cdot T_{18} - 0.005 \cdot DTWT + d-0.013 \cdot WRP. \]  

(4.26)

Only slightly less strong are the multiple regressions using 18 cm peat temperature and DTWT (Regression #5)

\[ \ln(CH_4 \text{ flux}) = 3.345 + 0.114 \cdot T_{18} - 0.007 \cdot DTWT \]  

(4.27)

and peat temperature and weighted recent precipitation (Regression #6),

\[ \ln(CH_4 \text{ flux}) = 3.777 + 0.128 \cdot T_{18} - 0.013 \cdot WRP. \]  

(4.28)

The strongest of all correlations tested is the simple regression of flux versus 18 cm peat temperature when only the "dry periods" (WRP < 5mm) are included (Regression #1b). Clearly, though, some influence in addition to temperature is
needed to explain summer variability, and based on this data, DTWT and WRP help to about the same degree, singly or together. Both of these variables fluctuate aperiodically throughout the summer (especially WRP) and a weekly flux measurement experimental design will not be the best way to examine their effects. It is a common experimental design, however, and most seasonal flux estimates are based on weekly (or less frequent) measurements. If WRP is as important as this data suggests, design of field campaigns should take it into account. It is clear that, in systems like Sallie's Fen, one or a few flux measurements in a summer may give a very poor indication of what the season's integrated flux would be. And until this effect is better understood, it is difficult to say in which wetland systems it will be important and in which it will not.

4.5.6. Model Flux Estimates Compared With Field Data

The model of Section 4.4 can be used to estimate methane fluxes by using the simulated DTWT and 18 cm peat temperature, along with the actual WRP, in any of the regression relationships of Table 4.3. Because of the difficulty the model has in simulating DTWT for both 1991 and 1992, for the long term run in Chapter 5 below, the most reasonable model results will probably come from Regression #6 (Table 4.3). In this section I will use Regressions #6 to test model fluxes against field data. The results are very similar when Regression #7 is used.

As a first test of the model, Figure 4.21.a compares model estimated fluxes against field fluxes measured when the 18 cm temperature was not recorded (and therefore not used to develop the regressions). The model overestimates the low fluxes and greatly underestimates the high fluxes (flux ≥ 1000 mg m⁻² d⁻¹). When the model flux is compared to all fluxes measured during the simulation period (1 Apr 91 through 30 Sep 92) the relationship improves, but still the model underestimates the high fluxes and overestimates the low fluxes (Figure 4.21.b). The very anomalous
Figure 4.21 - (a) Model flux compared with field flux (using Regression #6, Table 4.3) for those days when field 18 cm temperature was not measured. These points were not used to develop the regression. The model under predicts the high fluxes and over predicts the low fluxes. (b) same as (a) but using all flux data.
overestimate (labeled "a" in Figure 4.21.a) occurs 10 days after Hurricane Bob. The model's WRP has decayed to zero at this point, while apparently the real effect of the hurricane is still strong. This is clearer in Figure 3.26 discussed below.

Field and model (using Regression #6) methane flux time series are presented in Figures 4.22, with the warm season fluxes shown in more detail in Figures 4.23.a (1991) and 4.23.b (1992). The dashed lines in Figures 4.23.a-b simply connect the field measurements and do not necessarily represent interim period fluxes. Again it is clear that the model cannot simulate methane fluxes above about 750 mg m\(^{-2}\) d\(^{-1}\) (600 mg m\(^{-2}\) d\(^{-1}\) for Regression #7, and 500 mg m\(^{-2}\) d\(^{-1}\) for Regression #5), although field values are occasionally much higher. However, the uncertainty in these high field flux values is also quite high. The model does simulate some of the summer season variability (it appears to be due, in part, to precipitation events). The model captures the flux season length quite well (except the low fluxes of late August and early September 1991, which may represent residual effects of Hurricane Bob). The model also captures the slope of flux increase in the spring, and, perhaps, the decrease in the fall (Sept. 1992 data and/or another year would clarify this). The model, when averaged over the summer, seems to represent reasonable, if slightly low, flux values when compared to the field data scatter either summer. Finally, the model simulates the low winter fluxes and the winter season length quite well.

Model fluxes, when integrated into monthly values, show quite different patterns for 1991 and 1992 (Figure 4.27). Fluxes rose much more quickly in the spring and early summer of 1991 (it was much warmer and only slightly wetter than 1992), while August and September are more nearly equal. This pattern is also apparent in the weekly field flux measurements shown in Figure 3.18. Both July and August 1991 were nearly 2°C warmer than July and August 1992, but July 1992 was wetter than July 1992 while August 1991 was wetter than August 1992. This difference in precipitation patterns causes the difference between 1991 and 1992.
Figure 4.22 - Model and field flux time series (using Regression #6, Table 4.3).
Figure 4.23 - (a) Model and field flux time series for the warm season of 1991 (using Regression #6, Table 4.3). The dashed line connecting the field data merely connects the dots, and does not necessarily represent interim flux values. (b) Same as (a) but for the warm season of 1992.
Figure 4.24 - Monthly integrated methane fluxes (g m$^{-2}$) produced by the peat climate model and Regression #6. Note the very different behaviors in spring and early summer, due to a very warm 1991. See also discussion in text.
fluxes to be much less in August than July, highlighting the importance of precipitation and/or soil moisture to fluxes. Temperature, however, appears to be the dominant influence.

4.6. Discussion

The model developed in this chapter captures much of the soil climate variability that controls methane flux rates from peatlands, both the strong seasonal temperature control, and a more rapidly varying hydrologic control. The temperature results are quite good, as is ice thickness, but not spring ice thaw from below. The model is able to capture the flux season length and shape quite well; these are the dominant temperature effects. A better representation of surface skin temperature, and a more complete meteorological data set, would probably improve the results, but at a cost in both data collection and computation time. This relatively small improvement is not likely to be worth the effort, at least at Sallie's Fen, given the importance of hydrologic controls.

Model depth to water table results were not able to reproduce the very different field results of 1991 and 1992, but when parameterized for 1992 the model gives good results. Flux dependence on depth to water table at Sallie's Fen is not strong, and so model flux results were not greatly hindered by this. Sallie's Fen depth to water table appears to be an expression of the larger local watershed, and so its water table behavior is more complicated than a one-dimensional bucket with run-on and run-off can capture. A more realistic representation, however, would require a much more complete hydrological data set, and a watershed model. There are on-going efforts at Sallie's Fen to improve our understanding of the hydrological balance. More ombrotrophic, hydrologically isolated bogs will provide a better test for the current model. The important effect of precipitation events on Sallie's Fen methane fluxes has been incorporated into the model in a preliminary manner, and seems to play an
important role in flux variability. In fact, a much simpler model, using just air
temperature and some form of precipitation effect, would probably be sufficient to
capture much of the seasonal and short term variability in methane flux at Sallie's
Fen. A similar approach, using just air temperature, was used at a Minnesota site
(Crill et al, 1988), and seemed to capture the seasonal flux signal. In the next
chapter, this model will be driven by sixty years of Durham NH weather data to look at
methane flux sensitivity to interannual climate variability.
CHAPTER 5

MODELING THE SENSITIVITY OF METHANE FLUXES TO CLIMATE VARIABILITY
IN BOTH SPACE AND TIME

5.1. Introduction

There is much uncertainty about the biospheric or ecosystem response to climate change and its potential as a climate feedback mechanism (e.g. Lashof, 1989). Northern peatlands and their trace gas fluxes offer an important ecosystem in which to investigate this issue. The physics of soil climate requires that it integrates the more variable surface atmospheric climate, damping out the high frequency variability and responding more strongly to trends. Wetland methane flux response to temperature and hydrological change is strong and rapid, as it is a change in process rates rather than a change in ecosystem structure. Northern peatlands may thus serve as an early warning indicator of significant climate change (Harriss and Frolking, 1992). In addition, predicted climate change is large for northern high latitudes, and there is an enormous carbon pool in boreal and tundra wetland soils (Gorham, 1991) so their potential as a greenhouse gas source is large. However, in order to create a strong signal in the global atmospheric methane budget, large regions of the boreal and arctic peatlands will have to simultaneously experience similar climate deviations. For example, a summer that is very warm over eastern Canada and very cool over the Siberian lowlands may have no net effect on the global methane budget.

Since there are as of yet relatively few measurements of methane flux from northern peatlands, none before 1969 (Clymo and Reddaway, 1971), and none at a given site for more than a few consecutive years (Whalen and Reeburgh, 1988; Dise, 1993), in order to get a broader view of the temporal and spatial variability of
methane flux we must resort to modeling. Measurements from northern peatlands have shown that both soil temperature and soil moisture, among other factors, have a strong effect on methane fluxes (see Section 4.2). The multi-year studies at a fixed site (Harriss et al, 1982; Whalen and Reeburgh, 1988; Dise, 1993) show variation in annual flux from one year to the next, which are due, in large part, to climate variability. Soil climate is driven primarily by the atmospheric climate, for which there is some record over the past century. There are also GCM climate predictions for the next 100 years or so. This chapter begins with a brief review of potential climate change in the boreal and sub-arctic regions, and a review of models of methane flux sensitivity to climate. Then two model studies are presented. In Section 5.4, the model developed in Chapter 4 for Sallie's Fen, is presented, using the daily weather data from Durham, NH for 1926 - 1986. This study examined the effect of climate variability on methane flux using a detailed climate scenario, and thus preserved the inherent variability at one site from day to day, month to month, and year to year. A simpler model of the effect of air temperature alone on methane fluxes, using monthly air temperature records (1900 - 1987) and empirical relationships between soil temperature and methane fluxes was also developed (Section 5.5). This model was applied to the eight large regions of peatlands north of 45°N, and thus developed a global scale estimate of variability, both in time and space. In both of these models, climate variability and change was characterized by the historical temperature record, as opposed to climate model predictions of future climate scenarios.

5.2. Potential Climate Change in Boreal and Sub-Arctic Regions

There is a general agreement among the current generation of Global Climate Models (GCMs) that increasing greenhouse gases in the atmosphere will cause a warmer climate, and that high northern latitudes will experience the greatest warming (Mitchell, 1989). Table 5.1 summarizes the boreal/sub-arctic zone.
(global 50-70°N) temperature change predictions of four GCMs for a doubling of CO2 in the atmosphere. As the table indicates, summer temperature changes are generally expected to be less than the annual average (as winter temperature changes are greater). An average GCM predicted summer temperature change for the boreal regions is about 3-5°C. As shown in Chapter 3, peat temperature tracks air temperature closely.

However, there is less agreement among the GCM models as to how precipitation will change for a doubling of CO2, especially for the summer months (see Table 5.1). Some models predict wetter summers and some predict drier summers (Mitchell, 1989). Wetland soil moisture and water table level are important controls on both methane production and oxidation (e.g., Sebacher et al, 1986; Moore and Knowles, 1989). Precipitation scenarios (timing and strength of rain events) seem to influence methane fluxes as well (see Section 4.5.4).

More important than global or latitudinal band climate change is potential regional climate change and climate variability in both space and time. Since the major northern wetland ecosystems are concentrated in several regions, methane fluxes from these peatlands will depend on regional climate change and climate variability. For example, will all regions warm uniformly (not likely) or will some regions warm more than others? Will the warmest regions correspond to the wetland regions? How will interannual variability be distributed among the major wetland regions: in-phase or out-of-phase? At present, though, there is no reliable method for predicting regional (hundreds of kilometers) scale climate change due to greenhouse gas warming (Giorgi and Mearns, 1991; Grotch and MacCracken, 1991). Because of this uncertainty in future climate scenarios, I have chosen to use the historical climate record. Variability in space and time is present in the historical record in a realistic way, while future scenarios cannot reliably make these predictions.
Table 5.1 - GCM predictions for boreal/sub-arctic average temperature (°C), precipitation, and soil moisture changes.

<table>
<thead>
<tr>
<th>model</th>
<th>summer temp. (JJA)</th>
<th>winter temp. (DJF)</th>
<th>annual temp.</th>
<th>Change in summer precip.</th>
<th>Seasonal soil moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>GISS</td>
<td>+2 to +4</td>
<td>+5 to +12</td>
<td>+4.2</td>
<td>+ 1</td>
<td>-2 to +2 (3)</td>
</tr>
<tr>
<td>GFDL</td>
<td>+4 to +8</td>
<td>+6 to +15</td>
<td>+4.0</td>
<td>- 1</td>
<td>-5 to +4 (4)</td>
</tr>
<tr>
<td>NCAR</td>
<td>+0 to +4</td>
<td>+6 to +10</td>
<td>+4.0</td>
<td>+ 1</td>
<td>up to +2 (5)</td>
</tr>
<tr>
<td>UKMO</td>
<td>+5 to +6</td>
<td>+8 to +10</td>
<td>+5.2</td>
<td>- -</td>
<td>-</td>
</tr>
</tbody>
</table>

1) mm/d for mid-continental interiors.
2) cm of soil water storage.
3) wetter in winter, drier in summer.
4) increases southern boreal, decreases northern boreal.
5) year round increases.
5.3 Models Of Methane Flux Sensitivity To Climate

The ice core record of atmospheric methane (Chappellaz et al, 1990) shows a strong positive correlation between methane concentration and air temperature over glacial-interglacial climate variations. With temperature changes of about 5°C, methane concentrations vary from about 320 ppbv (glacial or cold periods) to about 700 ppbv (interglacial or warm periods), indicating a strong effect of climate on atmospheric methane and/or of atmospheric methane on climate. Current concentrations are about 1780 ppbv and increasing at a rate of about 10 ppbv/y (Khalil et al, 1993).

Three models of the climate sensitivity of methane flux from northern wetlands have been reported to date, each considering the effects of future climate change using GCM-based predictions. Livingston and Morrissey (1991) estimate regional methane flux for the North Slope of Alaska by coupling field measurements of flux from "very wet", "wet", "moist", and "dry" tundra with remote sensing derived area estimates for each of these classes. They then consider the impact of climate change by (1) projecting temperature effects using their linear relationship between flux and 10 cm peat temperature, and (2) shifting one-third of each wetland class area one notch "up" or "down" the wetness scale to simulate possible wet or dry climate scenarios. A 2°C increase in air temperature or a wetter climate doubled methane flux, while a drier climate cut the flux in half.

Post (1988) summarizes a Dept. of Energy sponsored workshop on the effect of climate change on carbon cycling in boreal and tundra ecosystems. The workshop assumed a 5°C temperature increase and a zero or ten centimeter drop in water table (wetter and drier scenarios), and used their best guesses as to its impact on methane flux. They estimated methane fluxes to double under either the wetter or drier scenario from 220 Tg/y to 440 Tg/y. This seems to be a huge overestimate of the
current methane flux and an unreasonable lack of sensitivity of methane flux to moisture regimes.

Roulet et al (1992b) use a water balance model, where change in wetland water storage is equal to precipitation minus evapotranspiration. They assume net lateral water flow is zero. From the change in water storage, and peat properties of buoyancy and specific yield, they estimate the change in water table location resulting from changes in storage. Climate drivers are mean June, July, and August air temperatures, precipitation, wind speed, and relative humidity. Using a control run (present climate at five wetland sites in Canada) and a projected 2xCO2 climate (temperature increases 3°C, precipitation increases 1 mm/d, wind speed and relative humidity are unchanged), they estimate that changes in 10 cm peat temperature and depth to water table. They then predict changes in seasonal methane flux, using correlations between flux and peat temperature and flux and depth to water table derived from a study in Schefferville, Quebec. They estimate that the projected temperature increase will enhance fluxes by about 5-40%, and that the lowered water table (due to increases in evapotranspiration above increases in precipitation) will reduce the methane flux by 75-80%. The net effect would presumably be a significant drop in methane flux.

5.4. Modeling Temporal Variability and Sensitivity to Climate Variability

5.4.1. The Durham NH Weather Record

Daily precipitation and air temperature data have been collected at the National Weather Service (NWS) station at Durham NH since 1896, with daily maximum and minimum temperature (and hence a daily average) since 1926. The station has moved from behind the Thompson School (UNH) to the US Forest Service Building to the NH Fish and Game Department Building. The moves (less than 1 km) were ordered by the NWS, which considers all these sites as one site. The 1951-1980 monthly mean air
temperature and precipitation climatic normals are summarized in Table 5.2, along with the 1926 - 1986 means and standard deviations.

There are three large gaps in the air temperature record, as well as about ten missing days. For this study, 1948 was not used (3 months of missing air temperature data); January 1964 daily air temperatures (missing) were replaced by the 1926 - 1986 daily averages; and 19 Aug. through 1 Sep. 1949 daily air temperatures (missing) were replaced by the 1926 - 1986 daily averages. Using long term daily averages will certainly mis-represent a single season's weather, but January weather is not that important to methane flux and thirteen days in August is probably a short enough period to misrepresent, rather than lose the entire year. Missing single days (about 10) were replaced by interpolated values (nearest neighbors). Daily precipitation data were complete. Since no net radiation data is collected at the Durham weather station, model evaporative demand is calculated with the Thornthwaite Equation (Eq. 4.14) using the mean daily air temperature.

5.4.2. Model Flux Simulations

The model of Sections 4.4 - 4.6 was used with Regression #6 of Table 4.3

\[ \ln(CH_4 \ flux) = 3.777 + 0.147 \times T_{18} - 0.019 \times WRP \]

to estimate daily methane fluxes for 1926 - 1986. Regression #6 was chosen because of the apparent unreliability of the depth to water table results (see Section 4.4.6 above). The daily results were summed into monthly (Table 5.3) and annual fluxes (Figure 5.1). The model estimated mean annual flux rate for the simulation period was 83.7 g CH4 m\(^{-2}\), with a standard deviation of 9.6 (range = 62 - 112 g m\(^{-2}\); the highest year, 1949, is the year that was missing 13 days of summer air temperatures, and thus might be a spurious result). There is no apparent pattern to the variability in annual fluxes; it is driven by the variability in weather. Recall also the variability in field measured
Table 5.2 - 1951-1980 Durham NH Monthly Climatic Means\(^{(1)}\) and Model Period Means and Standard Deviations.

<table>
<thead>
<tr>
<th>Month</th>
<th>1951-80 Air Temp (°C)</th>
<th>1926-86 Air Temp (°C)</th>
<th>1926-86 Temp St. Dev.</th>
<th>1951-80 Precip (mm)</th>
<th>1926-86 Precip (mm)</th>
<th>1926-86 Precip St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>-4.9</td>
<td>-4.8</td>
<td>2.5</td>
<td>89.2</td>
<td>82.2</td>
<td>49.4</td>
</tr>
<tr>
<td>Feb</td>
<td>-3.7</td>
<td>-3.7</td>
<td>2.1</td>
<td>79.2</td>
<td>77.9</td>
<td>34.1</td>
</tr>
<tr>
<td>Mar</td>
<td>1.2</td>
<td>1.2</td>
<td>1.9</td>
<td>93.0</td>
<td>91.6</td>
<td>53.5</td>
</tr>
<tr>
<td>Apr</td>
<td>7.3</td>
<td>7.1</td>
<td>1.4</td>
<td>96.5</td>
<td>93.8</td>
<td>54.7</td>
</tr>
<tr>
<td>May</td>
<td>13.1</td>
<td>13.1</td>
<td>1.4</td>
<td>90.7</td>
<td>83.7</td>
<td>52.1</td>
</tr>
<tr>
<td>Jun</td>
<td>18.2</td>
<td>18.1</td>
<td>1.1</td>
<td>76.2</td>
<td>81.3</td>
<td>43.0</td>
</tr>
<tr>
<td>Jul</td>
<td>21.2</td>
<td>21.0</td>
<td>1.0</td>
<td>76.2</td>
<td>82.4</td>
<td>48.2</td>
</tr>
<tr>
<td>Aug</td>
<td>20.1</td>
<td>20.0</td>
<td>1.2</td>
<td>84.1</td>
<td>83.0</td>
<td>43.2</td>
</tr>
<tr>
<td>Sep</td>
<td>15.8</td>
<td>15.9</td>
<td>1.2</td>
<td>85.6</td>
<td>83.4</td>
<td>50.1</td>
</tr>
<tr>
<td>Oct</td>
<td>10.1</td>
<td>10.1</td>
<td>1.3</td>
<td>99.3</td>
<td>87.1</td>
<td>46.4</td>
</tr>
<tr>
<td>Nov</td>
<td>4.1</td>
<td>4.1</td>
<td>1.4</td>
<td>119.4</td>
<td>111.4</td>
<td>58.3</td>
</tr>
<tr>
<td>Dec</td>
<td>-2.6</td>
<td>-2.6</td>
<td>2.1</td>
<td>108.7</td>
<td>97.1</td>
<td>52.3</td>
</tr>
<tr>
<td>Annual</td>
<td>8.3</td>
<td>8.3</td>
<td>0.66</td>
<td>1098.</td>
<td>1055</td>
<td>316.4</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Source: Ruffner, 1985.
<table>
<thead>
<tr>
<th></th>
<th>1951-80 Flux (g/m²)</th>
<th>1926-86 Flux St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan</td>
<td>1.16</td>
<td>0.15</td>
</tr>
<tr>
<td>Feb</td>
<td>0.92</td>
<td>0.15</td>
</tr>
<tr>
<td>Mar</td>
<td>1.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Apr</td>
<td>1.37</td>
<td>0.27</td>
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<tr>
<td>May</td>
<td>3.63</td>
<td>1.39</td>
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<tr>
<td>Jun</td>
<td>10.1</td>
<td>2.81</td>
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<tr>
<td>Jul</td>
<td>18.6</td>
<td>3.06</td>
</tr>
<tr>
<td>Aug</td>
<td>19.9</td>
<td>3.17</td>
</tr>
<tr>
<td>Sep</td>
<td>13.7</td>
<td>1.84</td>
</tr>
<tr>
<td>Oct</td>
<td>7.58</td>
<td>0.99</td>
</tr>
<tr>
<td>Nov</td>
<td>3.66</td>
<td>0.64</td>
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<tr>
<td>Dec</td>
<td>1.87</td>
<td>0.44</td>
</tr>
<tr>
<td>Annual</td>
<td>83.7</td>
<td>9.55</td>
</tr>
</tbody>
</table>
Figure 5.1 - Model estimated annual methane fluxes for Sallie's Fen NH, based on 1926-1986 Durham NH weather data (1948 weather data incomplete). The mean flux rate is 83.7 ± 9.6 g m⁻². (Note that the vertical scale begins at 60 g m⁻²).
fluxes for 1990 - 1992 (Figure 4.18). This raises questions about the reliability of flux estimates based on a single season of measurements.

In order to address the question of how many years of flux measurements are necessary to characterize a wetland's annual flux, the 60 years of model results were sampled in a random sequence. For the second and each subsequent year, a mean annual flux was calculated, as well as the flux standard deviation. Six random sequences were tested (Figure 5.2) Within 5 years all means were within 5% of the 60 year mean.

The variability in annual fluxes will closely follow the variability in climate because of the strong controls climate has on flux rates. Precipitation is generally much more variable than temperature (see the standard deviations in Table 5.2) but, at least at Sallie's Fen, temperature exerts a stronger control. Flux variability at another wetland will thus depend on both the climate variability at that site and the degree of dependence of flux on climatic factors. This study would indicate that at least five years of data should be collected at Sallie's Fen to ensure reliable estimates.

June through September fluxes contribute about 75% of the annual total and are also most susceptible to high variability (Table 5.3). Climate change and variability in those months will thus be the most significant for changes in annual methane flux. Figure 5.3 shows the mean June through September air temperature (mean = 18.8°C) and the total precipitation for the four months (mean = 31.7 cm) for 1926 - 1986.

To examine the potential impact of a warm climate, I will focus on 1973 and 1975. The mean June through September temperatures are 19.8°C in 1973 and 19.2°C in 1975, both above the long term mean (Figure 5.4.a). Precipitation in the summer (JJAS) of 1975 was quite high (52 cm) while 1973 summer precipitation (25 cm) was below the long term mean (Figure 5.4.b). Despite its slightly cooler and much wetter summer, the annual flux rate of 88 gm$^{-2}$ in 1975 is a little greater than the 84 g m$^{-2}$ of 1973, and neither are much greater than the long term mean of 83.7
Figure 5.2 - Mean annual methane flux rates as the 60 years of model estimates are accumulated in six different random sequences. Within 5 years all means are within 5% of the final mean.
Figure 5.3 - June through September mean temperature and total precipitation for Durham NH.
Figure 5.4 - (a) 1973 and 1975 monthly mean air temperatures, compared with the 1951-1980 climatic normals. Note that both summers (JJAS) are warmer than normal. (b) 1973 and 1975 monthly total precipitation, compared with the 1951-1980 climatic normals. Note that the summer (JJAS) of 1973 is drier than normal while the summer of 1975 is wet.
Figure 5.5 - 1973 and 1975 monthly mean methane flux rates, along with the model 1926 - 1986 means. Both years are quite similar to the long term means, although the weather was not (Figures 5.4.a&b).
g m$^{-2}$ (Figure 5.5). This surprising result is likely to be due to the summer precipitation patterns—in 1975, fourteen of thirty-two significant rainstorms (greater than 2 mm) in June through September occurred during the first half of June or the last half of September (accounting for about 19 cm of precipitation), and much of August's high precipitation was in one storm (8.5 cm). In 1973 only six of thirty significant rainstorms (and only 4 cm of precipitation) occurred in early June or late September. The early and late summer storms have less impact on the annual flux because flux rates are lower at these times, due to generally cooler temperatures. The wetter summer of 1975 had a precipitation pattern (one big storm, early and late season rains, and almost 30 consecutive dry days from mid-June to mid-July) that attenuated its summer methane flux less than the precipitation patterns of the drier (in every month) and warmer summer of 1973. In contrast, the warmer summer of 1991 gave much higher fluxes than the cooler summer of 1992 (see Section 4.5). Thus, although temperature controls on methane flux rates are very strong, timing as well as strength of summer precipitation are crucial to determining annual fluxes in a peatland that behaves like Sallie's Fen.

5.5. Scaling Up Flux Variability Estimates To All Northern Peatlands

As an initial study of the large scale climate-induced variability of methane fluxes from northern peatlands, I consider the effects of temperature variability only (Harriss and Frolking, 1992). Northern peatlands are concentrated in eight large regions: the Siberian Lowlands, the Hudson Bay Lowlands, the Fenno-Baltic lowlands, the Alaskan North Slope, the Yukon-Kuskokwim Delta, the boundary waters area of Minnesota, Central Alaska, and Nouveau Quebec (see Figure 5.6). These regions represent much (but not all) of the freshwater peatlands in the boreal and arctic regions. They are also regions for which at least some methane flux studies have been
Figure 5.6 - The eight major boreal and sub-arctic peatland regions. Peatlands within these eight regions account for about 70% of all inundated land north of 45°N (Matthews and Fung, 1987).
reported (except for the Siberian Lowlands, which, because of the vast size, cannot be ignored).

For each of these regions, a total inundated wetland area is determined from the 1°x1° fractional inundation data set compiled by Matthews and Fung (1987), taking into account that the area of a 1°x1° grid cell goes as the cosine of its latitude. Each region is assigned a representative wet site methane flux and an estimated flux season length (see Table 5.4). The Siberian Lowlands, for which I can find no flux data, is assigned a flux equal to the mean of the other seven regions. Table 5.4 lists the regions, their delineations, inundation areas, representative fluxes, season lengths, and net regional methane flux for a year (the product of the previous three numbers). The total yearly methane flux for the eight regions is about 17 Tg CH₄, only about 53% of the current estimated source strength for boreal and sub-arctic peatlands. This total is smaller in part because not all northern peatlands are included. Other reasons may include that the regional areas may represent only those wetland areas in each region that are very wet (Matthews and Fung, 1987), while fluxes from drier wetland areas are not insignificant, and that winter fluxes are ignored by the season length constraint.

For a site in each of the eight regions, mean summer (JJA) air temperature anomaly curves are constructed from the temperature anomaly data of Hansen and Lebedeff (1987), for 1900-1987 (see Figure 5.7). Hansen and Lebedeff (1987) find that for high northern latitudes annual mean air temperature anomalies are well correlated for stations separated by less than about 1200 km and that the correlation improved as the station separation decreased (see their Fig. 3). This would indicate that, for these regions, any monthly temperature deviation that occurred would prevail over much of any one of these extensive wetland regions, and one site's data should be somewhat representative of the entire region. Most summer temperature anomalies are within about 1°C of the 1951-1980 summer normals, with occasional

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Table 5.4 - Northern Peatland Regions Data

<table>
<thead>
<tr>
<th>Region</th>
<th>Lat. range</th>
<th>Long. range</th>
<th>Area (1) (10^9 m^2)</th>
<th>Rep. CH4 flux (mg CH4/m^2/d)</th>
<th>Season length (2) (days)</th>
<th>Regional CH4 flux (Tg/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siberian Lowlands</td>
<td>55-73N</td>
<td>60-90E</td>
<td>723</td>
<td>80.2 (3)</td>
<td>120</td>
<td>7.0</td>
</tr>
<tr>
<td>Fenno-Baltic Lowlands</td>
<td>50-70N</td>
<td>20-50E</td>
<td>634</td>
<td>57.8 (4)</td>
<td>120</td>
<td>4.4</td>
</tr>
<tr>
<td>Hudson Bay Lowlands</td>
<td>50-60N</td>
<td>75-100W</td>
<td>342</td>
<td>24.0 (5)</td>
<td>120</td>
<td>1.0</td>
</tr>
<tr>
<td>Boundary Waters area</td>
<td>45-50N</td>
<td>85-100W</td>
<td>98.0</td>
<td>188.0 (6)</td>
<td>150</td>
<td>2.8</td>
</tr>
<tr>
<td>North Slope AK</td>
<td>68-71N</td>
<td>140-165W</td>
<td>71.2</td>
<td>103.0 (7)</td>
<td>100</td>
<td>0.73</td>
</tr>
<tr>
<td>Central AK</td>
<td>60-68N</td>
<td>140-155W</td>
<td>46.7</td>
<td>32.2 (8)</td>
<td>120</td>
<td>0.18</td>
</tr>
<tr>
<td>Yukon-Kusk. Delta, AK</td>
<td>55-65N</td>
<td>155-170W</td>
<td>56.5</td>
<td>86.5 (9)</td>
<td>120</td>
<td>0.59</td>
</tr>
<tr>
<td>Nouveau Quebec</td>
<td>50-57N</td>
<td>60-75W</td>
<td>30.5</td>
<td>70.0 (10)</td>
<td>120</td>
<td>0.26</td>
</tr>
</tbody>
</table>

1) Areas are inundation areas from wetlands data base of Matthews and Fung (1987).
3) No data available, value is mean of other 7 values.
4) Svensson and Rosswall 1984; Crill, unpublished data.
10) Moore et al 1990; Crill, unpublished data.
Figure 5.7 - Summer (JJA) mean air temperature anomalies from the 1951-1980 climatic normals for a site in each of the eight northern peatland regions (Hansen and Lebedeff, 1987). Note that the variability for each site is of the same size, and that variations at neighboring sites are nearly in phase (e.g., the top three sites in Alaska) while more distant sites are not necessarily in phase (e.g., the bottom two curves).
Figure 5.8 - The mean of the eight summer temperature anomalies of Figure 4.9, representing the eight major northern peatland regions. Variability is reduced from the single site values of 0°C - 2°C to generally less than 0.5°C. There is a significant warm period in the late 1930's and early 1940's.
2°C anomalies. No region has summer temperature behaviors greatly different from any of the others. Figure 5.8 shows the net summer temperature anomaly for the eight sites by taking their average; since the eight anomalies are not all in phase, the net effect is reduced to variations usually within 0.5°C of the norm. There was an extended warm period from about 1935-1945, with all but the Siberian Lowlands' site showing warm temperatures for most of this period.

Using the methane flux to temperature relationship of Crill et al (1988), the flux rate dependence on peat temperature is

\[
\frac{DF}{DT} = F \left( \frac{17893}{T_{10} + 273.2} \right)^2
\]

(5.1)

where \( F \) is the flux strength, and \( T_{10} \) is a representative peat temperature, and \( DF \) and \( DT \) are the changes in \( F \) and \( T \). Using 10°C as a representative \( T_{10} \) for most northern peatlands, this gives a relative flux change, for a one degree change in temperature, of

\[
\frac{(DF/DT)}{F} = 0.22
\]

(5.2)

By assuming that the 10 cm peat temperature anomalies are equal to the monthly air temperature anomalies (probably a slight overestimate), net methane flux change for each region is then given by

\[
DF = \left( \frac{(DF/DT)}{F} \right) (F_{rep}) (A) (SL) (DT)
\]

(5.3)

where \( A \) is the region's area (10^3 km^2), \( F_{rep} \) is the region's representative methane flux (mg CH4 m^-2 d^-1), \( SL \) is the region's season length (d), \( DT \) is the region's summer temperature anomaly (°C), and \( DF \) is the region's variation from normal methane flux (Mg CH4), or methane flux anomaly, for the year (see Table 5.3 for values for the variables). Figure 5.9 shows this methane flux anomaly for the eight northern wetland regions modeled. The greatest flux anomaly occurs in the Siberian Lowlands, due to their large area and assumed moderate representative flux strength. The large Hudson Bay Lowlands have a much smaller flux anomaly because of the reported low methane fluxes from this region (Moore et al, 1991). The Boundary Waters Area of Minnesota, Ontario, and Manitoba have large flux anomalies due to
Figure 5.9 - Mean annual methane flux anomalies (Tg CH\(_4\) y\(^{-1}\)) for the eight major northern wetland regions. Flux anomalies are based on summer temperature anomalies, season length, regional flux strength, and inundation area (see text and Table 5.4). Anomalies for the three Alaskan regions and Nouveau Quebec are all small because of relatively small areas, low flux strength (Nouveau Quebec), and a short season (North Slope, AK). Although its area is small, flux anomalies for the Boundary Waters Area are high because of high flux strength and long season length. The Siberian Lowlands and Fenno-Soviet Lowlands have high flux anomalies because of their huge areas.
their high reported fluxes (Crill et al, 1988; Dise, 1993) and their longer season length. In addition Dise (1992) reports significant winter methane fluxes in this region, although these are not accounted for in this model. The Fenno-Soviet Lowlands have a large anomaly due to their large area and moderate flux strength. As discussed above, all regions have roughly the same temperature variations (magnitude but not timing) so no one region's methane flux anomaly is enhanced or reduced with respect to the others due to climate variability.

Figure 5.10 shows the sum of these eight regional anomalies, or the net northern wetland modeled methane flux anomaly. Superimposed on this curve is a nine year running mean of the net flux anomaly to account for the integrating effects of methane's lifetime in the atmosphere. In an individual year the anomaly (positive or negative) can be as much as 5 Tg CH4, or 29% of the total normal flux of the model. Most variations are about 0-2 Tg, or 0-12% of the total model flux. The nine-year smoothed curve is usually within 1 Tg, or about 6% of the modeled normal flux. Scaling this up to the current estimate of 32 Tg CH4/yr from northern peatlands, the annual temperature-driven methane flux anomaly would be about 0-4 Tg. The nine-year smoothed anomaly would vary by up to about 0-2 Tg.

During the initial stages of a climate warming (i.e., perhaps now or soon) the air temperature anomalies can be expected to be variable (as they have been for the past century) and, for the northern peatlands regions, probably increase by only up to about 1°C. This model would thus predict a temperature-induced increase in methane flux from northern peatlands of about 0 - 10% or 0-4 Tg/yr. This is less than 1% of the total annual methane flux to the atmosphere, and less than 10% of the current rate of increase of methane in the atmosphere. Thus, northern peatland methane flux increases due to the initial stages of climate warming are not likely to cause a major feedback, a major acceleration of the rate of climate change.
Northern Wetlands Annual Methane Flux Anomaly and Nine Year Average

Figure 5.10 - The integrated northern wetlands annual methane flux anomaly (Tg CH₄ y⁻¹) is the sum of the eight regional anomalies of Figure 4.11. The heavy line is the nine-year running average, to represent the effect of methane's nine year lifetime in the atmosphere. Annual anomalies are generally less than 1.5 Tg methane, while the nine-year running mean anomaly is generally less than 0.5 Tg methane.
5.6. Discussion

Freshwater peatlands are a major source of global atmospheric methane, and these environments are concentrated in regions which may be subject to the extremes of climate change. Methane emissions from freshwater peatland ecosystems are influenced by variations in climate (especially temperature and precipitation). Changes in the emissions of methane from these regions may be a potential biospheric feedback process, which could influence the dynamics of the climate system.

Modeling has two roles in the study of issues like this. First, only models can take our current understanding of a system and project the future behavior of the system. Of course, these projections, at their best, are only as good as our current understanding. Second, and more important, the dialogue between modelers and measurers enriches our understanding of these systems by continually challenging the modelers to better represent the picture the data presents, and challenging field scientists to better measure the variables (which are often suggested by modeling studies) that paint the clearest picture.

The projections of this study (especially Section 5.5) indicate that methane flux from northern peatlands is not likely to be the mechanism for a strong biotic feedback to near-term climate warming at high latitudes. During near-term change, climate variability is likely to dampen any flux increase that a warming trend would imply. In addition, if many of the northern peatland systems behave similarly to Sallie’s Fen, with its apparently significant precipitation sensitivity, changes in precipitation amounts and timing, which are far more difficult to predict than generalized and probably even regional warming, will play an important role in future methane fluxes. Over the longer term, a significant climatic change (like those predicted by current GCMs for a doubling of atmospheric CO2) could cause a substantial change in the methane flux from northern peatlands. Of course, many other ecosystem factors may also change with long-term climatic change, such as fire
frequency, permafrost thawing, plant respiration and production rates, and even plant community structure, resulting in additional changes to the ecosystem carbon balance (Billings, 1987), and perhaps overwhelming direct climate change effects on methane fluxes.

The dialogue between modeler and measurer has been productive in this study. There are clear indications in the field data from Sallie's Fen that rain events influence methane fluxes, although the mechanism for this influence is not understood. The model of Chapter 4 and Section 5.3 empirically incorporated this behavior and examined its influence on methane flux rates. The influence is significant and may be a cause for much of the summer flux variability, and some of the interannual variability, that is observed. The model suggests that within about five years a reliable (±5%) estimate of long-term mean annual fluxes can be determined. In order to better understand this precipitation effect (even empirically) a much more detailed field study is needed, with frequent flux measurements around rain events, measurements of water flow through the fen, measurements of dissolved O2 and CH4 concentrations in the fen water. This improved understanding can then be built into a more complete model, allowing more reliable predictions; it might also help to devise an efficient and effective schedule for summer measurements to better characterize seasonal fluxes. And it will undoubtedly raise new questions.
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