ABSTRACT

Freshwater wetlands are an important natural resource; on a local scale they function to buffer hydrological and geochemical processes, and on a global scale they are an important sink/source of atmospheric carbon due to their high carbon density. The purpose of my PhD research was to study the thermal regime of northern peatlands and to study the impact of wetlands on surface water quality in a semi-urbanized watershed.

Heat and hydraulic head data measured in the peat of a large bog in Minnesota was modeled to assess how heat is transported from the land surface to the base of the peat column. I found that the major controls over heat transport through the peat profile are thermal conduction and heat loss and gain caused by the latent heat of ice during freezing and thawing in the upper part of the peat profile. To properly model the heat transport, I modified the US Geological Survey SUTRA groundwater and energy transport model to incorporate freezing and thawing, and prepared benchmark simulations for subsequent comparison. With respect to evaluating wetland functions on water quality on a regional scale, I studied what processes control the overall water quality of over 80 wetlands in the Croton Watershed (New York State) that provide drinking water to the City of New York. The focus of my study was to evaluate how wetlands control water quality and color to the Croton Reservoir.

Four synoptic samplings measured water chemistry and coloration parameters in almost all catchments with wetlands. The $g_{440}$ color of wetland surface waters is related to the dissolved organic carbon concentrations (DOC) and the percent of wetland area within catchments. The concentrations of sodium and chloride in wetland waters are directly correlated to the length of roads per wetland watershed area. The remainder of the major dissolved solids in the wetland waters is mostly derived from simple dissolution of carbonate minerals in the glacial drift mantling the watershed.

The dissertation also includes additional research on the water quality and source of springs used as domestic water source in Southern Ethiopia.
WETLAND GEOCHEMICAL AND THERMAL PROCESSES AT THE WATERSHED SCALE

by

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DISSERTATION

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INTRODUCTION AND SUMMARY OF FINDINGS
Introduction

Freshwater wetlands are an important landform that impact and regulate hyrological and ecological surface processes. Freshwater wetlands can be broadly divided into three groups based on their hydrologic setting: bogs, fens, or riverine (Figure 1; Mitsch and Gosselink, 1993). Wetlands are important in both the local hydrologic cycle and on a global carbon budget scale.

Freshwater wetlands provide many important functions in watershed hydrology. They can remove and retain nutrients, process chemical and organic wastes, and reduce sediment loads. During storm events, wetlands store water, attenuate floods, and temper soil erosion. Additionally, wetlands are usually productive habitats for wildlife (Tiner, 1997).

Northern peatlands store $10^{17.7}$ g of organic carbon (Figure 2 and 3; Gorham, 1991), equivalent to ~100 years of current fossil-fuel combustion (Moore et al., 1998). The interaction of peatlands with the Earth’s atmosphere is dynamic and complex: on an annual basis, peatlands are a source of methane to the atmosphere, but on a longer time scale, they may become repositories of carbon dioxide (Roulet et al., 1994). The response of peatlands to change in climate is uncertain (e.g. Waddington et al., 1998).
although many studies attempt to quantify carbon cycling in peatlands (Roulet et al., 1994; Siegel et al., 2001), the results are qualitative at best because the basic processes controlling peatland hydrogeology are poorly understood (Gorham, 1991; Moore et al., 1998).

Although freshwater wetlands are important, the wetland coverage in the United States and globally has diminished greatly in the past 150+ years. From pre-settlement to the 1980s, the total wetland area of the continental United States has decreased by ~50%; from ~80 million hectares to ~40 million hectares (National Research Council (U.S.); Committee on Characterization of Wetlands., 1995). In New York State, the decrease in wetland coverage is even more drastic – from ~1,040 hectares to ~410 hectares, equivalent to a 60% decline (Mitsch and Gosselink, 1993).

The “classical” assumption that water in peat soils is stagnant in deeper layers of peat (catatelm) and that where it moves, it moves unidirectional and decoupled from regional groundwater flow (e.g. Ingram, 1982) has been challenged in the last decade.
The current paradigm of porewater movement in peat soils is much more dynamic.

Porewater flows horizontally throughout a wetland soil profiles and can move downwards and upwards, recharging and discharging regional groundwater flow systems respectively. “Flow reversals,” a situation where the vertical direction of porewater movement changes seasonally have been well documented in many peatland morphologies and locations (Devito et al., 1997; McKenzie et al., 2002; Siegel et al., 1995).

Research

Considering the importance and value of freshwater wetlands, the purpose of my PhD research is to study, in a broad sense, the hydrogeology of wetlands. In particular, the focus is on in situ processes that may control both biological and hydrochemical processes. The research is in two field areas:

1. Understanding and modeling heat transport within a bog in the Glacial Lake Agassiz peatlands (GLAP). The GLAP cover Northern Minnesota and Southern Manitoba, and are a 7000-km² expanse of sub-boreal patterned peatlands (Glaser et al., 1981).
2. Understanding how freshwater wetlands in the Croton Watershed, New York, affect water chemistry and coloration. In the Croton Watershed over 100 wetlands cover about 6% of the Croton watershed (Tiner, 1997), and the rest of the land area is covered by forested uplands, housing complexes and towns, and lakes and reservoirs.

Research Chapters

Following is a brief description of the chapters included in this dissertation, including the primary findings of the research.

Chapter 1: Heat Transport in the Red Lake Bog, Glacial Lake Agassiz Peatlands

In Northern Peatlands, an important driving force in the carbon cycle is the temperature regime. Warmer temperatures favor the consumption of carbon by anaerobes, and lead to increased methane production. Temperature profiles collected over a two-year period from the Upper Red Lake Bog in the Glacial Lake Agassiz Peatlands, Minnesota were numerically modeled and it was found that heat transfer within the bog is primarily by conduction, as opposed to by convection. The largest deviation between my numerical model and the measured field data occurred during the spring melt, where the model was not able to model the latent heat effects of the frozen pore water. Chapter 1 is a collaborative effort with Donald Siegel, Donald Rosenberry, Paul Glaser, and Clifford Voss.

Chapter 2: Ground-water flow with energy transport and water-ice phase change: numerical simulations, benchmarks and application to freezing in peat bogs

The purpose of Chapter 2 was to evaluate if an improved model would be able to capture the variable thermal properties associated with ice formation in the subsurface. A new model is used, SUTRA-ICE, that is a modification of the SUTRA (Voss and
variable density, saturated-unsaturated US Geological Survey code. The modified model successfully matched the heat transport within the entire peat profile. The latent heat of formation of ice was critical in modeling the heat transport, more so than the variable thermal properties because of ice formation.

The SUTRA-ICE code was also successfully tested against a full analytical solution for freezing in a porous medium (Lunardini, 1985) – possibly the first numerical model of freezing to do so as other numerical models matched against partial or inexact analytical solutions. In addition, two possible benchmark problems for comparison with other numerical groundwater models that incorporate porewater freezing are presented. The research in Chapter 2 is a collaborative effort with Clifford Voss and Donald Siegel.

Chapter 3: Characterizing Wetland Surface Color and Water Quality in the Croton Watershed, New York: Natural and Anthropogenic Controls

Chapter 3 reports the results of a study of the Croton Watershed. The fieldwork included four synoptic samplings of sub-catchments that contain wetlands and detailed site experiments at using peepers, a passive diffusion sampling technology. Water coloration was found to be related to both dissolved organic carbon concentrations, and the relative wetland coverage in the sub-catchments. Concentrations of sodium and chloride identify road salt contamination to Croton wetland watersheds, and the amount of contamination is directly correlated to the length of roads per wetland watershed area.

Chapter 3 is the result of a very large collaborative effort to study the Croton Watershed, including Martin Otz, Donald Siegel, James Hassett, and Ines Otz. Martin Otz was responsible for the research focused on fluorescence.
Chapter 4: A geochemical survey of spring water from the main Ethiopian rift valley.

Southern Ethiopia: Implications for well-head protection

Chapter 4 is unrelated to the main topic of the dissertation, but is included, at the encouragement of my committee because it was a significant portion of research during my time as a PhD student.

The chapter focuses on water supply and water quality in Southern Ethiopia, where only 15% of the rural population has access to safe drinking water. A suite of spring and surface water samples were collected from the Arba Minch region of Southern Ethiopia, and were analyzed for major ions, nutrients, and the stable isotopes of water. It was found that springs in the region were the result of relatively short flow paths, and were dominated by precipitation water. The paper is published, and was a collaborative effort with Donald Siegel, Bill Patterson, and Jonathon McKenzie (McKenzie et al., 2001).

Future Research

My research has shown that the interaction of solutes and energy with freshwater wetlands is complex. Wetlands within the Croton Watershed color surface water through the addition of DOC, and are extensively impacted by road salt. In the future, it might be interesting to look at other developed watersheds that are used as drinking water reservoirs. For example, the Catskill reservoirs may be of comparative interest to the New Croton reservoir because it is less developed, and has different geology.

In the GLAP, the transport of energy in peat is controlled not only by conduction, but by the latent heat effects of ice freezing and melting. Advection of heat by ground water is slower than conduction of heat. Future work in this area may include looking at
the impact of future climate change not only on the thermal regime of the peat, but also on biological activity such as anaerobic methane production. Additionally, the modified SUTRA model could be further adapted to include both unsaturated ice formation and combining solute and energy transport.

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CHAPTER 1: HEAT TRANSPORT IN THE RED LAKE BOG,

GLACIAL LAKE AGASSIZ PEATLANDS
Abstract

We report the results of an investigation on the processes controlling heat transport in peat under a large bog in the Glacial Lake Agassiz Peatlands. For two years, starting in July 1998, we recorded temperature at 12 depth intervals from 0 to 400 cm within a vertical peat profile at the crest of the bog at sub-daily intervals. We also recorded air temperature 1 m above the peat surface. We calculate a peat thermal conductivity of 0.5 W m$^{-1}$ C$^{-1}$ from the rate of heat dissipation with time and model the vertical transport of water and heat through the peat using SUTRA, a numerical model of groundwater flow coupled to heat transport. The model was calibrated to the first year of collected heat data, and then validated with the second year of collected heat data. The model results suggest that advective porewater flow is not necessary to transport heat within the peat profile and that most heat is transferred by thermal conduction in these water logged soils. Changes in local climate and resulting changes in thermal transport still may cause non-linear feedbacks in carbon emissions related to the generation of methane at depth within the peat profile as temperatures deep in the peat profiles increase.
Introduction

Peatlands, which are dominated by the accumulation of waterlogged peat soils more than 40 cm deep (National Wetland Working Group, 1997), constitute a major global carbon sink. Northern peatlands store $\sim 5 \times 10^{17}$ g of organic carbon (Gorham, 1991), equivalent to $\sim 100$ years of current fossil-fuel combustion (Moore et al. 1998).

The interaction of peatlands with the Earth’s atmosphere is dynamic and complex. Annually, peatlands provide large inputs of methane and carbon dioxide to the atmosphere but on a longer time scale, they may be repositories of atmospheric carbon dioxide (Roulet et al., 1994).

One way by which peatlands interact with the atmosphere is by releasing methane generated by anaerobic bacteria at depth. The transfer of methane from depth within the peat profile occurs either by episodic releases of large volumes of methane gas associated with the lowering of peatland water tables (Rosenberry et al., 2003, Windsor et al., 1992; Moore and Roulet, 1993) or by continuous diffusion through the peat soil. In some peatlands the generated methane can form pockets of free phase, over-pressured methane that causes the surface of the peatland to rise and fall due to the buildup and episodic release of the gas (Glaser et al, 2004; Rosenberry et al, 2003).

Numerous factors control the overall production of organic matter in a peatland, including the availability of nutrients, the hydrologic regime, the climatic regime, and temperature. Temperature is important because it controls the rate at which biological and chemical processes take place. Bridgham et al. (1999) found from empirical greenhouse studies that increased surface radiation produces significant changes in methane and carbon dioxide production rates in peat. Respiration rates and the
development of anaerobic conditions strongly depend on temperature (Lewis, 1995).

Decreases in soil temperature lowers the rate of decomposition and increases the rate of peat accumulation (Fox and Van Cleve, 1983). Chapman and Thurlow (1996) calculated for a Scottish bog that an increase in surface temperature of 4.5°C might double CO₂ emissions and increase methane emissions by 60% based on observations of 2 peat sites in Scotland. Rappoldt et al. (2003) proposed that near surface waters (less than 35 cm depth) in the peat column freely convect. In their study, water moved primarily because of daily density differences driven by diurnal temperature changes. However, free convection only applies to the very open, upper fibric portions of peat columns where the distinction between pure surface water and water in porous media is blurred. Below this fibric zone, humified peat in peatlands can be many meters thick.

Few studies report the results of investigations on heat transport through entire peat profiles in non-permafrost regions (e.g. Wilson, 1939). Thermal investigations of peatlands generally do not cover the deeper (> 3m) portions of a peat profile because seasonal temperature oscillations are most pronounced within 1-2 m of the peat surface. Moore (1987) measured temperature from the land surface to 200 cm depth in peat at 7 depth intervals from six peatland sites in northern Quebec and found that both surface temperatures and depth of freezing were controlled by the depth of snow cover. In a Minnesota bog, Brown (1975) found the temperature of surface peat closely followed that of air temperature, but at depths of 2-m there was a multi-month lag between surface temperature and temperature at depth. The chronology of the seasonal freezing cycle is important because the highest diffusive methane release from peatlands occurs from a
a few months to nearly 6 months after snowmelt, when soil temperatures reached their
annual maximum (Boeckx and van Cleemput, 1997; Duval and Goodwin, 2000).

Surface waters at bogs move downward into the peat profile because of local
water table mounds that develop under bogs, and in many cases, groundwater in larger
scale flow systems can move into or out of the base of peat profiles (Siegel et al., 1995).
Vertically moving peat porewater is an important process controlling the distribution of
solutes within the peat profile (e.g. Romanowicz et al., 1993; McKenzie et al., 2001).
“Flow reversals,” a situation where the vertical direction of porewater movement changes
episodically or seasonally, have been well documented in many peatland types and
settings (e.g. Siegel et al., 1995; Devito et al., 1997, McKenzie et al., 2001) and also in
non-peatland settings (Phillips and Shedlock, 1993; Rosenberry and Winter, 1997).

In a solid matrix and pore water system, heat is transferred by conduction through
the water and the solid matrix, and by advection (convection) of porewater through the
interconnected pore space. The one-dimensional transfer of heat by conduction alone, \( q_h \),
is described by Fourier’s law (Carlsaw and Jaeger, 1959):

\[
q_h = -k_m \left( \frac{dT}{dz} \right)
\]  

(1)

where \( k_m \) is the thermal conductivity of the medium, \( T \) is temperature, and \( z \) is the
distance in the vertical direction. Assuming a temperature range where neither ice nor
gas will form, the governing equation for heat conduction and advection through
isotropic, homogeneous, saturated soils is (Bredehoeft and Papadopulos, 1965):

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} - \frac{c_f \rho_f}{k} \left[ \frac{\partial (v_x T)}{x} + \frac{\partial (v_y T)}{y} + \frac{\partial (v_z T)}{z} \right] = \frac{c_f \rho_f}{k} \frac{\partial T}{\partial t}
\]  

(2)
where $T$ is temperature, $x$, $y$, $z$ are Cartesian coordinates, $c_f$ and $\rho_f$ are the specific heat and density of the fluid, $v_x$, $v_y$, $v_z$ are components of fluid velocity, $c_{fs}$ and $\rho_{fs}$ are the specific heat and density of the fluid-solid system, and $k$ is the thermal conductivity of the solid-fluid complex.

Considering the importance of heat in surface and deeper biochemical processes, we report here the results of a study to evaluate the detailed thermal response of a peat bog in the Glacial Lake Agassiz Peatlands (GLAP). We address the following questions: 1) what are the sources of heat to the deeper depths of peat, and in particular to depths of maximum methane production, 2) what are the thermal processes controlling the thermal regime of the peatland and 3) what are the relative influences of advection and conduction on heat transfer through the peat surface? We hypothesize that the primary control on heat flux into the peat profile is the peat surface temperature, and that heat moves primarily by thermal conduction, not advection.

**Study Area**

The Glacial Lake Agassiz Peatlands (GLAP) in Northern Minnesota and Southern Manitoba, are a 7000-km$^2$ expanse of sub-boreal patterned peatlands (Glaser et al. 1981; Figure 1). The surface waters of bogs in GLAP have total dissolved solids (TDS) less than 15 mg L$^{-1}$ and a pH less than 4.0 (Glaser et al. 1981). The primary source of water to the bog is precipitation, although there is a significant amount of groundwater discharge into the base of the peat profile.

The vegetation assemblage of the raised bogs is dominated by *Picea mariana*, *Carex oligosperma* and ericaceous shrubs with a continuous mat of *Sphagnum* (Heinselman 1970, Glaser et al. 1981). The average peat thickness is 2 to 3 m, reflecting
~ 5000 years of accumulation (Glaser et al., 1981). The study site in the Red Lake Peatland is situated along the bog crest in watershed II (Glaser et al. 1981) where the peat depth is 4.3 m. The upper 3 meters of peat consist of oligotrophic bog peat derived largely from *Sphagnum* moss and wood. The upper ~50 cm is fibric in texture, grading to dark brown hemic peat below. There is no sapric peat in the peat column. Beneath the bog peat is 60 cm of fen peat, also hemic. Within the peat column are discontinuous layers of wood and occasional ash layers (Janssens et al., 1992).

Average precipitation in the peatland ranges from 64 cm in the eastern part to 56 cm in the west (Glaser et al., 2004). The peatland straddles a north-south trending divide where average annual evapotranspiration is equal to average annual precipitation. Consequently, the peatland is highly sensitive to the regional climate and east-west shifts of the precipitation and evapotranspiration divide caused by droughts or wet periods. The peatland is typically covered by at least 15 cm of snow for 70 to 100 days per year (Glaser et al., 2004) and subject to extreme multiyear droughts (Glaser et al., 2004).

**Methods**

**Fieldwork**

We intensively instrumented the Red Lake Bog site for long-term hydrometric analysis. At the crest of the Red Lake Bog thermocouples were installed at depths of 0, 25, 50, 75, 100, 125, 150, 200, 250, 300, 350, and 400 cm and pressure transducers at 100, 200, and 300 cm depth. Temperature and atmospheric pressure were measured approximately 1 m above the land surface. The data are stored in a solar powered data logger connected to a mobile phone for remote data-access. From June 18, 1998 to August 18, 1998, temperature data were averaged at a minimum of every 5 minutes and a
maximum of an hour per day. The remainder of the data was measured every 1 to 6 hours.

The instrumentation was installed at the hydrologic divide on the crest of the Red Lake Bog where hydraulic head measurements and the hydrogeologic setting indicate that porewater mostly moves in the vertical plane (Rosenberry et al., 2003). Here, because of dimensionality reasons (Anderson and Woessner, 1992), moving heat and water can be simulated as vertical, one-dimensional flow.

**Thermal Diffusivity and Conductivity**

We determined the thermal diffusivity of the peat from the temperature data, and used it to calculate thermal conductivity. Fourier Transforms to calculate the yearly amplitude of the annual temperature fluctuations at each measured depth and the decrease in amplitude with depth was used to calculate the thermal diffusivity, \( k \), (Carslaw and Jaeger, 1959; Smith, 1989):

\[
k = \frac{\omega (\Delta y)^2}{2 \ln \left( \frac{A_z}{A_{z+\Delta z}} \right)}
\]

Where \( \omega \) is the angular frequency of the fluctuation in radians/unit time (\( \omega = 2\pi f \)) where \( f = 1/\text{period} \), \( A_z \) and \( A_{z+\Delta z} \) is the amplitude of the annual temperature changes at two depths and \( \Delta z \) is the distance between these depths. The thermal diffusivity, \( k \), was calculated for each measured depth relative to the peat surface, and we used an average of values from all depths in our modeling experiments. The range in thermal diffusivities we measured was only \( \sim 35 \text{ cm}^2 \text{ day}^{-1} \), and so we feel using the average value was appropriate. Amplitudes that were less than 1 °C were not included to eliminate potential thermocouple error.
Modeling

The heat transport simulations were modeled with the Saturated- Unsaturated Transport model (SUTRA), a fluid density-dependent groundwater flow and heat transport code (Voss, 1984). The Argus ONE Open Numerical Modeling Environment and the USGS Graphical User Interface (Voss et al., 1997) were used as pre- and post-processors for the SUTRA model. The model is a hybridization of finite-element and finite-difference methods; finite-element methods are used to simulate fluxes of fluid mass and finite-difference methods are used for all other non-flux terms, such as solute mass and energy (Voss, 1984). Groundwater flow is simulated with a numerical solution of the fluid mass balance equation for saturated flow and variable fluid density (Voss, 1984). Energy transport is simulated through numerical solutions of an energy balance equation that assumes the solid matrix and pore water are locally at equal temperature, and that fluid density and viscosity are variable (Voss, 1984).

The model simulates vertical one-dimensional flow, appropriate for the hydrologic conditions at the bog crest. We used a constant head boundary for the top boundary (Dirichlet condition; Bear and Verruijt, 1987), representing the water table, and no-flow boundaries on the lateral sides of the model (Neumann conditions; Bear and Verruijt, 1987). The elevation of the groundwater table was held constant at the land surface because the elevation of the water table only fluctuated a small amount (< 10 cm) over the period of record used. The hydraulic portion of the model was set at no flow, and then the heat flux model was run transiently. To model heat transport, we applied specified temperature boundaries to the top and bottom of the model (Dirichlet condition; Bear and Verruijt, 1987). The time step for the model was 1 hour, and the input
temperature values for the heat boundaries were changed daily based on mean daily
temperature values taken from the field measurements of air temperature at the peat
surface and water temperature at the bottom of the peat column. We calibrated the model
using one year of data, starting in July 1998. The model was calibrated by varying the
porosity and thermal properties of the soils. The model was calibrated to mean daily-
recorded temperatures at all depths. The model was validated by verifying that model
results during the subsequent year (starting in July 1999) adequately matched measured
data.

Sensitivity analysis was done to assess the relative effect of individual parameters
on the model results. The model was run with each calibration parameter changed
individually. The calculated root mean squared statistic compared measured versus
modeled values for heat data for all depths, and from these data we calculated a
normalized sensitivity coefficient (Zheng and Bennett, 2002):

\[ X_k = \frac{S_{a_k+\Delta a_k} - S_{a_k}}{\Delta a_k / a_k} \]  (5)

where \( X_k \) is the normalized sensitivity coefficient for parameter \( k \), \( S_{a_k+\Delta a_k} \) and \( S_{a_k} \) are the
root mean squared calibration statistics for the base case and the perturbed case
respectively, and \( a_k \) and \( \Delta a_k \) are parameter \( k \)'s value and the small change in the
parameter respectively.

**Results**

*Description of heat*

Heat data in the peat from the raised bog shows both seasonal and daily cycles,
both of which are predominately controlled by temperatures at the surface of the peat
profile (Figure 2). The temperature at the base of the peat profile is nearly constant at ~ 4.8 °C. The mean air temperature for the five years prior to the experiment and the two years during the experiment was 3.4 °C (from the NCDC-NOAA data for the Waskish weather station). Commonly, the average temperature of deeper soils is assumed to be the average air temperature plus 1 °C (Soil Survey Division Staff, 1993).

The surface peat temperature fluctuates widely from –34.1 to 25.9 °C over the two-year data collection period, and the pattern of fluctuations is a subdued replica of the local air temperature. The greatest deviation between the temperature of the peat and the local air temperature (measured ~ 1m above the peat surface) occurred during the winter. For example, in January and February of 1998 the average daily air temperature repeatedly dropped below –15 °C but the temperature at the peat surface ranged between 0 and –5 °C (with the exception of Jan 12, 1999 when the average daily surface temperature was –34.1 °C and the average daily temperature of the peat surface was –7.9 °C).

The temperatures in the shallow peat fluctuated daily (Figure 3). Seasonally, a similar pattern of fluctuation of temperature was observed, except the surface temperatures were transmitted to a significantly deeper depth because of increased amplitude of surface temperatures. Seasonally, the vertical direction of the thermal gradient reverses. During the summer, the surface of the peat profile is warmest, and the coolest temperatures are at the base of the peat profile. During the winter and early spring, the warmest temperatures are at the base of the peat profile and the coolest temperatures are at the surface of the peat profile (Figure 2).
From summer through fall the temperatures at near surface depths (≤ 100 cm) closely mimic the periodicity of temperature at the surface (0 cm) and air temperatures. During spring, there is a lag of 35 days between the rise in surface air temperature and the near surface temperatures (≤ 100 cm) within the bog.

Figure 4 shows our calculated Fourier transform amplitude spectrum diagrams for each depth that had calculated amplitudes greater than 1 °C. The average thermal diffusivity of the peat is ~110 cm² day⁻¹. Assuming an average humified peat density of 0.85 g cm⁻³ (e.g. Clymo, 1984) and a peat heat capacity of 4576 J Kg⁻¹ C⁻¹ (Moore, 1987) the thermal conductivity of the peat-water system is ~0.5 W m⁻¹ C⁻¹.

Calibration results

The parameters used in the calibrated model are in Table 1. The calibration was based on the average temperatures each day and for each measured depth. For the whole model, the mean absolute residual between measured and modeled temperatures, the root mean squared residual error, and the linear correlation coefficient are 0.34, 0.59 and 0.99 respectively (for 3450 data points). Figure 5 shows the results comparison between measured and modeled temperatures graphically and Figure 6 shows a calibration plot for temperature data at all depths. For individual depths, the greatest error occurred at the 25 cm depth (root mean squared residual error of 1.31) and decreased with depth.

The greatest deviation from the measured and modeled temperatures occurred during April and May. Excluding April and May, the mean absolute residual error and the root mean squared error of the SUTRA model improve to 0.29 and 0.38 respectively.
**Sensitivity analysis**

Sensitivity analysis ranked the relative impact of model parameters on the model output. The model was most sensitive to the thermal conductivity of the peat, followed by the porosity, the specific heat capacity of the peat, the density of the peat. Considering that the model is primarily modeling heat conduction, it is not surprising that the most sensitive parameter is the thermal conductivity. The total porosity is also a significant factor because porosity controls the ratio of liquid water volume to solid peat volume.

**Validation**

The model was validated by running the calibrated model for the next year of data, from July 1, 1999 to June 20, 2000. The model validation (Figure 7 and 8) had a mean absolute error of 0.9 °C, a variance of residual errors of 1.3 °C, and a root-mean-squared error of 1.2 °C for the measured data at all depths versus the modeled data. The validation model deviates from the measured heat data during the spring melt, similar to that of the calibrated model.

**Discussion and Conclusions**

We feel that the calibrated model was a good analogue for 1-D vertical heat transport in the Red Lake Bog. The calibrated model and the spectral analysis methods determined values for saturated peat thermal conductivity of 0.4 and 0.5 W m$^{-1}$ C$^{-1}$ respectively, similar to values calculated by other researchers (e.g. Moore, 1987; Williams and Smith, 1989).

At the study site, small amounts of groundwater flow upward into the base of the peat profile and downward from the surface of the peat. Pockets of methane at depth
within the peat profile also create transient, hydraulically over pressured zones (Rosenberry et al., 2003). Our model results and field data both suggest that advective heat transport is not required to explain the observed temperature distributions, and that the primary method of heat transport is conductive. To test this hypothesis, the Peclet Number for heat transport, $P_e$, can be used (Domenico and Palciauskas, 1973):

$$P_e = \frac{\ell \bar{v}}{\alpha}$$

where $\ell$ is the characteristic length, $\bar{v}$ is the vertical linear velocity of porewater, and $\alpha$ is the mixed thermal diffusivity – the thermal conductivity of the solid-fluid complex divided by the product of the density and specific heat of the fluid. If the Peclet Number is much less than 1, the system is conduction-dominated; if the Peclet Number is much greater than 1 the system is convection-dominated.

We calculated the Peclet Number under vertical advective flow condition in the upper 2 m of the vertical profile of the Red Lake Bog. Rosenberry et al. (2003) report the largest head gradients at this depth, and we measure the greatest heat changes across this interval. The calculated Peclet number for the peat is 0.1, indicating heat transport is primarily by conduction.

The most significant problem with our numerical model of heat transport was the lag in the increase in modeled and measured temperatures during the early spring. The lag may be the result of melting ice in the near surface peat, when energy that would normally be transported downward into the bog is consumed by the latent heat of fusion of the ice. Evidence for this energy consumption is recorded in the heat data at 25cm depth. During winter, the temperature at 25 cm drops below freezing and, given the very low total dissolved solids of the pore waters, it can be assumed that ice forms to at least
this depth. In northern Minnesota, frost typically extends to about 50 cm in mineral soils (Minnesota Department of Transportation, 2004). In the spring, the surface temperature (0 cm depth) and the air temperature rose, but the subsurface temperatures at 25 cm and below stay constant and did not mimic the air temperature profile. Only after the temperature at 25 cm began to rise did the temperature at deeper depths begin to rise.

We tested the hypothesis that the heat of fusion associated with melting ice in the shallow peat caused the temperature deviation, by estimating how much heat was required to melt the ice and the resulting lag in the timing of the peat-temperature rise (Hall et al., 2003). Assuming a unit area of ice, 1 m$^2$, and an ice depth of 25 cm (based on the measured heat data), a peat total-porosity of 90%, an ice density of 916 g/cm$^3$, and a latent heat of 333,700 J/kg, it would require ~ 69 MJ to melt all of the ice. Using the heat conduction equation, we estimated the amount of time it would take to melt all of the ice to 25-cm depth. The total heat conduction, $H$, is:

$$H = \frac{kA(T_2 - T_1)}{L}$$  \hspace{1cm} (7)

where the thermal conductivity, $k$, is 1.225 W m$^{-1}$ C$^{-1}$, an average of the thermal conductivities of ice and water. The average value for $k$ is reasonable considering that the ice will be melting, $T_1$ is 0 °C, $T_2$ is the temperature at 0-cm depth, taken as 4.3 °C, the average temperature at 0-cm for the lag periods in 1999 and 2000, $A$ is the cross sectional area, 1 m$^2$, and $L$ is taken as the total depth for heat transport, 30 cm. Using Equation 7, the total heat conduction is calculated as 1.8 MJ day$^{-1}$.

Assuming that the springtime ‘lag’ in temperature increase at depth is caused by the latent heat of fusion, we estimated the time to melt the ice from when the temperature at the 0-cm depth rose above 0 °C to when the temperature at 25-cm depth rose above 0-
cm. The average measured time for temperatures at 25-cm depth to start rising from when surface temperatures began to rise was ~35 days. The time we calculated from our heat conduction and latent heat of fusion calculations, based on equation 7, was very close: 38 days. The similarity in calculated and observed times for the melting of ice confirms that the lag in temperature rise at the 25-cm depth is most likely caused by melting ice.

Our results may have implications on the generation of methane at depth within the peat profile. A common assumption is that soil temperatures below 50 cm depth (Lewis, 1995) are relatively constant. We found that temperatures fluctuated significantly at depths far greater than 50 cm, including a range of ~ 4 °C at a depth of 200 cm. This is the depth at which free phase methane is formed by anaerobes in this bog (Siegel et al. 1992; Rosenberry et al. 2003; Glaser et al., 2004). Temperature fluctuations at this depth affect the generation of methane, which depends in part on temperature (e.g. Chapman and Thurlow, 1996). In contrast, ice below the peat surface inhibits warming of deeper peat, because surface energy in the spring is used for melting. The ice melting - temperature conduction lag may help explain the observed delay in the onset of methanogenesis from bogs in the spring (e.g. Boeckx and van Cleemput, 1997).

We propose that changes in the surface heat regime, because of short and long term climate change, could have significant and non-linear impacts on the heat regime at the critical deeper depths where methane is generated in peat profiles in peatlands. With increased global warming, the temperature of the regional ground water that discharges into the base of some peat profiles could be warmer, and the additional heat within it conducted upwards during the winter would increase temperature at the base of the
methane generation zone. Warmer temperatures at the surface of the peat would translate into warmer temperatures at depth, and would also potentially decrease the amount of ice formed in the winter in the upper peat and/or increase the rate at which the ice melts. Warmer surface temperatures would also promote greater transport of both methane to the atmosphere and dissolved organic carbon to surface waters from these large carbon reservoirs.

**Acknowledgments**

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### Tables

Table 1 – Parameter values used in calibrated model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value(s)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Specific Heat</td>
<td>4182 J Kg^{-1} C^{-1}</td>
<td>Fixed</td>
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<tr>
<td>Thermal Conductivity of Fluid</td>
<td>0.6 J s^{-1} m^{-1} C^{-1}</td>
<td>Fixed</td>
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<tr>
<td>Specific Heat Capacity of Peat</td>
<td>3500 J Kg^{-1} C^{-1}</td>
<td>Calibrated</td>
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<tr>
<td>Thermal Conductivity of Solid Grain</td>
<td>0.4 J s^{-1} m^{-1} C^{-1})</td>
<td>Calibrated</td>
</tr>
<tr>
<td>Porosity</td>
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<td>Calibrated</td>
</tr>
<tr>
<td>Density of Peat</td>
<td>850 kg m^{-3}</td>
<td>Fixed</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1 – Map of the Glacial Lake Agassiz map showing the location of the Red Lake Bog.

Figure 2 – Daily average of heat data collected at all depths. Numbers refer to depth within peat profile in centimeters. The air temperature is measured ~ 1 m above the land surface directly above the location where the heat data are collected.

Figure 3 – Two-day focused view of the measured heat data. The numbers on the figure refer to depths at which the measurements were made, in cm.

Figure 4 – Results of Fourier Transform analysis of daily average temperature values over two-year period. The largest peak for each depth corresponds to 365 days, as would be expected. The numbers beside each line correspond to the depth of measurement in centimeters. The 0-cm depth represents the temperature at the peat surface.

Figure 5 – Comparison of the measured and modeled temperature results versus time for the calibrated SUTRA model (1998-1999) at twelve observation depths.

Figure 6 – Comparison of the measured versus modeled temperature results for the calibrated SUTRA model for the entire year (1999; note the deviation of spring data from 25 cm and deeper from the modeled results), and for part of the year (with spring values removed).

Figure 7 – Comparison of the measured and modeled temperature results versus time for the validated SUTRA model (1999-2000) at twelve observation depths.

Figure 8 – Comparison of the measured versus modeled temperature results for the validation SUTRA model.
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Figure 8
CHAPTER 2: GROUND-WATER FLOW WITH ENERGY

TRANSPORT AND WATER-ICE PHASE CHANGE: NUMERICAL SIMULATIONS, BENCHMARKS AND APPLICATION TO FREEZING IN PEAT BOGS
Abstract

In northern peatlands, the freezing of water in the subsurface is an important process that can control heat transport, hydrogeologic systems, and biological activity. Temperature was measured over one and a half years in a vertical profile in the Red Lake Bog, Minnesota. In order to successfully simulate the transport of heat within the peat profile, the U.S. Geological Survey’s SUTRA computer code was modified. The modified code simulates fully saturated, coupled porewater-energy transport, with freezing and melting porewater, and includes proportional heat capacity and thermal conductivity of water and ice, decreasing matrix permeability due to ice formation, and latent heat. The model is verified by correctly simulating the Lunardini analytical solution for ice formation in a porous medium with a mixed ice-water zone. The modified SUTRA model correctly simulates the temperature and ice distributions in the peat bog. Two possible benchmark problems for groundwater and energy transport with ice formation and melting are proposed that may possibly be used by other researchers for code comparison.
Introduction

The freezing and thawing of subsurface water in regions experiencing sub-zero air temperatures can directly affect numerous geological and biological processes, including the thermal regime, groundwater flow patterns, groundwater recharge and sub-terrain biological activity. Further, given the sensitivity of arctic regions to climatic changes (Serreze et al., 2000), understanding the processes that control the formation and extent of ice is important.

The interaction of near-surface water and ice with the regional groundwater regime also partly controls where and the rate at which subsurface ice forms. For example, in northern peatlands the thermal regime is controlled both by seasonal temperature fluctuations and also the advection of deeper, warmer water (Hunt et al., 1996; McKenzie et al., 2005). Ice in upper soils in these regions can involve groundwater flow in complex feedback mechanisms. For example, by forming a temporary confining zone, ice can both diminish upward discharge of groundwater and potential recharge of aquifers by precipitation (Romanovsky and Osterkamp, 2000; Woo and Marsh, 2005). The melting ice may itself be controlled to some extent by upward groundwater advection of heat (Kane et al., 2001). Ice also affects how contaminants may be transported in the subsurface (e.g. Grant and Iskandar, 2000). Thermal models in northern climates have been used to reconstruct and estimate climate change. For these reasons, it is important to establish models that simulate conduction, advection and water to ice phase changes.

The transport of heat in the subsurface is controlled by conduction due to a temperature gradient (Narasimhan, 1999) and heat transport can also be influenced by
advection of flowing porewater (e.g. Deming et al., 1992). Where there is seasonal or annual freezing of porewater in the subsurface, the formation and melting of ice will affect heat conduction because the bulk thermal properties of the soil change. Ice has a different heat capacity and thermal conductivity than liquid water and solid aquifer matrix (Farouki, 1986). The latent heat released as ice forms is at least ten times greater than that released by heat capacity alone (Williams and Smith, 1989).

The advection of heat is also affected by the formation of ice. Porewater velocities decrease with ice formation (Lundin, 1990) and the decrease in hydraulic conductivity in places may temporarily confine shallow groundwater flow systems. Finally, the rate of freezing and thawing of porewater may interact with groundwater flow systems and precipitation/snow melt at the land surface in complex feedback mechanisms (Kane et al., 2001).

Several numerical models incorporate freezing and thawing processes into porewater flow models. Possibly the first model to do so was by Hwang et al. (1972) for studying the interaction of surface structures on permafrost. Hansson et al. (2004) simulated water and vapor flow with a 1-dimensional model based on the HYDRUS-1D model (Simunek et al., 1998). Ippisch (2001) simulated water and vapor flow using a finite difference approach and found that, for permafrost situations, the flow of water in near freezing regimes is most important control on ice extent. Mottaghy and Rath (2005) used a finite difference model (Clouser, 2003) for saturated and unsaturated porewater flow with ice formation to show the importance of latent heat in reconstructing paleoclimate using borehole temperature inversions. The STOMP model (White and Oostrom, 2000) was designed for the transport of organic contaminants in the subsurface.
and includes the freezing and thawing of porewater. The TEMP/W (Krahn, 2004) model, a numerical simulation of the freezing and thawing of pore water where freezing is limited to a calculated freezing zone, is an add-on component for the geotechnical GEO-SLOPE modeling environment.

To effectively model heat transport in the subsurface for cold regions where ice formation occurs, one must therefore incorporate changes in thermal and hydraulic properties as a function of ice content. Presented herein is SUTRA-ICE, a numerical model that fully incorporates ice formation and melt as a modification to the SUTRA numerical solute, head, and water transport code (Voss and Provost, 2002) for the case of fully saturated flow. The modified model can simulate the phase transformation of porewater to ice over a range of sub-freezing temperatures (without ice segregation or layering), along with the associated changes in heat capacity, thermal conductivity, relative permeability, density, and the latent heat of formation. Although there are other numerical models that simulate similar processes, the model presented here is based on an already widely used numerical code, is fully 3-dimensional, and is easily modified by the user. The SUTRA-ICE model is verified by comparing its results to a closed-form analytical solution for ice formation (Lunardini, 1985). Two potential two-dimensional benchmark problems are suggested that incorporate both flowing porewater and ice formation. Finally, the modified code is applied to evaluate the impact of ice formation on temporal changes of the thermal profile in a large peat bog.
Methods

Numerical Model

The SUTRA computer code (Voss, 1984; Voss and Provost, 2002) is modified to incorporate freezing (without ice segregation) and thawing properties within the context of its energy transport model. SUTRA allows modeling of variable density, mass transport of fluid, solute and/or energy transport under saturated and/or unsaturated conditions, and it solves the set of governing equations for thermal energy and fluid and chemical mass transport through a combination of finite element and finite difference approximations. SUTRA is very powerful because it can be configured to represent a wide range of hydrogeologic conditions, and new processes can be easily added by the user.

The code is modified by changing the spatial properties of pore water that occur when temperatures at a specific model node or element are below the freezing point, 0°C. These properties include the effects of ice on the thermal conductivity, heat capacity, permeability of the porous medium, and the latent heat of formation of ice. Values of thermal conductivity and heat capacity change as a function of ice content, and are based on volume-weighted averages through the soil profile as a first approximation (Williams and Smith, 1989). It is assumed that the ice is immobile, the medium is non-deformable, and freezing point depression due to solute concentrations is negligible.

Thermal Properties

The bulk thermal conductivity, $\lambda$, including solid matrix, water and ice is calculated by a volumetric average approximation (Williams and Smith, 1989):

$$\lambda = \epsilon \lambda_w + \epsilon S_i \lambda_i + (1 - \epsilon) \lambda_s$$

Eq. 1
where $\varepsilon$ is the porosity, $S_w$ and $S_i$ are the saturation of liquid water and ice, and $\lambda_w$, $\lambda_s$, and $\lambda_i$ are the thermal conductivities of liquid water, the solid matrix, and ice respectively. If there is no ice, then Equation 1 simplifies to the original equation for thermal conductivity used in SUTRA, $\lambda = \varepsilon S_w \lambda_w + (1 - \varepsilon) \lambda_s$. The saturation of ice and water consists of their relative volumetric proportions within the pores. The SUTRA-ICE model presented herein assumes fully saturated conditions and therefore:

$$S_w + S_i = 1 \quad \text{Eq. 2}$$

$$\frac{\partial S_w}{\partial T} = - \frac{\partial S_i}{\partial T} \quad \text{Eq. 3}$$

An apparent heat capacity, $C_a$, is used (Goodrich, 1982; Hansson et al., 2004) that incorporates both the heat capacity of ice and the latent heat:

$$C_a = \varepsilon_w \rho c_w + \varepsilon_i \rho_i c_i + \varepsilon_s \rho_s c_s + \varepsilon_s L_f \frac{\partial S_w}{\partial T} \quad \text{Eq. 4}$$

where $\varepsilon_w = \varepsilon S_w$, $\varepsilon_i = \varepsilon (1 - S_w)$, and $\varepsilon_s = (1 - \varepsilon)$ and are the liquid water, ice, and solid matrix fractional volumes respectively, $\rho$, $\rho_i$, and $\rho_s$ are the densities of liquid water, ice and the solid matrix respectively, $L_f$ is the latent heat of formation of ice, $S_w$ is the saturation of ice, $T$ is temperature, and $\varepsilon \rho_i \frac{\partial S_w}{\partial T}$ is the mass of water per volume porous medium that is produced by melting as $T$ increases.

Assuming fully saturated conditions, the apparent heat capacity is:

$$C_a = \varepsilon (S_w \rho c_w + S_i \rho_i c_i) + (1 - \varepsilon) \rho_s c_s - \varepsilon_s L_f \frac{\partial S_i}{\partial T} \quad \text{Eq. 5}$$
Soil Freezing Functions

In soils, porewater freezes over a range of temperatures below freezing (Williams and Smith, 1989). As soil temperatures decrease below the freezing point for pure ice, there is a slight freezing point depression because of dissolved salts in the porewater. Once ice starts to form, ice does not immediately crystallize, but forms only gradually because of capillary and absorbtive forces that are amplified as more water is converted to ice (Williams and Smith, 1989) because more of the remaining fluid exists in the form of thin films. Even when most of the soil water is frozen, there remains a small amount of super cooled, unfrozen soil water – the residual saturation, $S_{w_{res}}$. The residual unfrozen water consists of water molecules attached to grain surfaces and water that has a significantly decreased freezing point from increased dissolved solids that are excluded by ice formation. The freezing function for water-saturated soils is similar in shape to the saturation function for unsaturated soils, but depends on temperature instead of pressure (Figure 1).

There are numerous functions used to describe the freezing of a soil. Figure 2 shows two commonly used functions (without hysteresis) and derivatives of them. The freezing function should be smooth and easily differentiated, because the derivative $\partial S_w / \partial T$ is used to determine the apparent heat capacity in Equation 5. The simplest freezing function is a linear function:

$$
S_w = mT + 1 \quad \text{if } S_w > B_T
$$

$$
S_w = S_{w_{res}} \quad \text{if } S_w < B_T
$$

Eq. 6
where \( m \) is the slope of the freezing function, \( T \) is the temperature, and \( B_T \) is defined as the temperature at which the linear freezing function attains residual saturation, \( S_{\text{wres}} \), defined as:

\[
B_T = \frac{S_{\text{wres}} - 1}{m}
\]

Eq. 7

The derivative of the linear freezing function (Equation 6) is:

\[
\frac{\partial S_w}{\partial T} = m \quad \text{if} \quad T > B_T
\]

Eq. 8

\[
\frac{\partial S_w}{\partial T} = 0 \quad \text{if} \quad T < B_T
\]

Another possible freezing function is a one-parameter exponential function (Lunardini, 1988):

\[
S_w = \exp \left[ -\left( \frac{T - T_L}{w} \right)^2 \right] \quad \text{if} \quad S_w > S_{\text{wres}}
\]

Eq. 9

\[
S_w = S_{\text{wres}} \quad \text{if} \quad S_w \leq S_{\text{wres}}
\]

where \( T_L \) is the liquidus or freezing point, usually \( 0 \) \(^\circ\)C, and \( w \) is a fitting parameter. The derivative of the exponential freezing function with respect to temperature is:

\[
\frac{dS_w}{dT} = -\frac{2(T - T_L)}{w^2} \exp \left[ -\left( \frac{T - T_L}{w} \right)^2 \right]
\]

Eq. 10

**Permeability**

Ice that forms in pore space will decrease the permeability as it clogs open pores and restricts the movement of water. To represent this decrease, a relative permeability, \( k_r \), is used, where the effective permeability is the product of the fully saturated
permeability and the relative permeability. The relative permeability is less than unity for ice saturations greater than zero. The relative permeability cannot equal zero, or the flow equation cannot be solved; however, a very small minimum value can be set.

The simplest function to changes in the relative permeability with ice formation is a linear decrease in $k_r$ for temperatures between freezing and the temperature at which the residual saturation, ($B_T$; Equation 7) is reached. At this point, an arbitrary small minimum value ($10^{-6}$) of $k_r$ is assigned:

$$\begin{align*}
    k_r &= \left( \frac{10^{-6} - 1}{B_T} \right) T + 1 & \text{if } T > B_T \\
    k_r &= 10^{-6} & \text{if } T < B_T
\end{align*}$$

Eq. 11

An impedance factor can also be used to calculate the relative permeability $k_r$ (Jame and Norum, 1980). Again, the minimum relative permeability is limited at $10^{-6}$.

$$\begin{align*}
    k_r &= 10^{-\Omega Q} & \text{if } 10^{-\Omega Q} > 10^{-6} \\
    k_r &= 10^{-6} & \text{if } 10^{-\Omega Q} \leq 10^{-6}
\end{align*}$$

Eq. 12

where $\Omega$ is the impedance factor, and $Q$ is defined as the ice content, equal to $\varepsilon S_i$.

Hansson et al. (2004) use a different definition of $Q$: the ratio of the ice content to the total (minus the residual) water content.

The direct measurement of the freezing function for a given soil is difficult, and there is limited data available for most soil types (Farouki, 1986). Koopmans and Miller (1966) empirically found that for a given soil, the characteristic shape of the saturation function (for unsaturated soils) is the same as the shape of the freezing function for fully saturated soils (Figure 1). The relationship between the two similar functions depends only on the ratio of interfacial tensions between the air-water and water-ice interfaces.
(Spaans and Baker, 1996) and the water-air and ice-water pressures calculated using the Clapeyron Equation (Black, 1995). If the relationship between the two functions can be calculated, one can employ a known (e.g. laboratory-measured) unsaturated function for a soil as the soil’s freezing function. For example, Grant (2000) provides a method for using the unsaturated van Genuchten function (van Genuchten, 1980) for calculating the freezing function and relative permeability due to ice formation. However, this alternative approach is not used in the examples discussed herein.

**SUTRA-ICE equations**

The SUTRA governing equations (Voss and Provost, 2002) modified for fully saturated, heat transport with ice formation are:

\[
\left( S_w \rho S_{op} + \varepsilon \rho \frac{\partial S_w}{\partial p} \right) \frac{\partial p}{\partial t} + \left( \varepsilon (\rho_s - \rho) \frac{\partial S_i}{\partial T} + \varepsilon S_w \frac{\partial p}{\partial T} \right) \frac{\partial T}{\partial t} - \nabla \left[ \left( \frac{k k_r p}{\mu} \right) (\nabla p - \rho g) \right] = Q_p
\]

Eq. 13

and

\[
\left[ \varepsilon (S_w \rho c_w + S_i \rho_j c_j) + (1 - \varepsilon) \rho_s c_s - \varepsilon \rho_j L_f \frac{\partial S_L}{\partial T} \right] \frac{\partial T}{\partial t} + \varepsilon S_w \rho c_w \nabla \cdot \nabla \cdot \left[ \varepsilon S_w \left( \lambda_s \mathbb{I} + \mathbb{D} \right) + \varepsilon S_i \lambda_s \mathbb{I} + (1 - \varepsilon) \lambda_s \mathbb{I} \right] \nabla T \right] \\
= Q_p c_w \left( T^* - T \right) + \varepsilon S_w \rho \gamma_w^{\nu} + (1 - \varepsilon) \rho_s \gamma_s^{\nu}
\]

Eq. 14

where \( S_{op} \) is the specified pressure storativity (the volume of water released from saturated pore storage due to a unit drop in fluid pressure per total solid matrix plus pore volume), \( p \) is pressure, \( t \) is time, \( k \) is the permeability tensor, \( k_r \) is the relative permeability, \( \mu \) is the viscosity of liquid water, \( g \) is gravity, \( Q_p \) is porewater flow, \( \mathbb{I} \) is the identity tensor, \( \mathbb{D} \) is the dispersion tensor, \( T^* \) is the temperature of the source fluid,
and $\gamma_o^w$ and $\gamma_o^s$ are energy sources in the fluid and in the solid grains respectively.

Equation 13 describes the balance of water mass in variable density porewater as impacted by fluid fluxes due to both temperature and pressure gradients, and Equation 14 describes the balance of thermal energy as impacted by energy fluxes due to conduction, advection, and sources or sinks. The term $\varepsilon (\rho_i - \rho) \frac{\partial S}{\partial T}$ in Equation 13 derives from application of Equation 3. Equations 13 and 14 are the main governing equations and Equations 6 through 12 describe the freezing functions and permeability during freezing in the SUTRA-ICE code.

Comparison with Exact Analytical Solution

The SUTRA-ICE model is tested by comparison with the three-zone analytic solution presented by Lunardini (1985). This is an exact analytical solution for the propagation of sub freezing temperatures in a porous semi-infinite, initially non-frozen medium with time, $t$. The solution is similar to the Neumann solution (Carslaw and Jaeger, 1959) for the movement of a freezing front which consider only two zones: a frozen and a thawed zone. The Lunardini solution divides the problem into three zones (Figure 3) where zone 1 is fully frozen, with only the residual amount of unfrozen water, zone 2 is ‘mushy’, with both ice and water, and zone 3 is fully thawed. The Lunardini (1985) solution is given below:

\[ T_1 = (T_m - T_s) \frac{\text{erf} \left( \sqrt{\frac{\alpha_s}{\alpha_f}} t \right)}{\text{erf} \left( \frac{\gamma}{\sqrt{\frac{\alpha_s}{\alpha_f}}} \right)} + T_s \]  Eq. 15

\[ T_2 = \Delta T_m \frac{\text{erf} \left( \sqrt{\frac{\alpha_s}{\alpha_f}} t \right) - \text{erf} \left( \frac{\gamma}{\sqrt{\frac{\alpha_s}{\alpha_f}}} \right)}{\text{erf} \left( \frac{\gamma}{\sqrt{\frac{\alpha_s}{\alpha_f}}} \right) - \text{erf} \left( \frac{\varepsilon \sqrt{\rho_f \alpha_f}}{\Psi} \right)} + T_f \]  Eq. 16
\[
T_3 = (T_O - T_f) \cdot \frac{-\text{erfc}\left(x/2\sqrt{\alpha_3 t}\right)}{\text{erfc}\left(\gamma \sqrt{\alpha_4/\alpha_3}\right)} + T_O 
\]

Eq. 17

where \(T_1\), \(T_2\), and \(T_3\) are the temperatures at distance, \(x\), from the temperature boundary for zones 1, 2 and 3 respectively, \(\text{erf}\) and \(\text{erfc}\) are the error function and the complimentary error function respectively, \(T_O\), \(T_m\), \(T_f\), and \(T_s\) are the temperatures of the initial conditions, the solidus, liquidus and the boundary temperature respectively, \(\Delta T_m = T_m - T_f\), \(\alpha_1\), \(\alpha_2\), and \(\alpha_3\) are the thermal diffusivities of the three zones, defined as:

\[
k_1/C_1, \ k_2/C_2, \ \text{and} \ k_3/C_3 \ \text{where} \ C_1 \ \text{and} \ C_3 \ \text{and the volumetric bulk heat capacities of the frozen and thawed zones, defined as:}
\]

\[
C_1 = \varepsilon \rho_w c_w s_{wres} + \varepsilon \rho_s c_s (1 - S_{wres}) + (1 - \varepsilon) \rho_s c_s 
\]

Eq. 18

\[
C_3 = \varepsilon \rho_w c_w + (1 - \varepsilon) \rho_s c_s 
\]

Eq. 19

and \(k_1\) and \(k_3\) are the bulk thermal conductivities of the frozen and thawed zones, defined as:

\[
k_1 = \varepsilon \rho_w \lambda_w s_{wres} + \varepsilon \lambda_s (1 - S_{wres}) + (1 - \varepsilon) \lambda_s 
\]

Eq. 20

\[
k_3 = \varepsilon \rho_w \lambda_w + (1 - \varepsilon) \lambda_s 
\]

Eq. 21

where \(\alpha_2\) is the thermal diffusivity of the mushy zone, and for the solution presented here is assumed to be constant across transition region, \(\alpha_4\) is the thermal diffusivity with latent heat term included, defined as:

\[
\alpha_4 = \frac{k_2}{C_2 + \frac{\gamma \rho L_f \Delta \xi}{T_f - T_m}} 
\]

Eq. 22
where \( \gamma_d \) is the dry unit density of soil solids, \( \gamma_d = (1-\varepsilon)\rho_s \), \( \Delta \xi = \xi_O - \xi_f \) where \( \xi_O \) and \( \xi_f \) are the ratio of unfrozen water to soil solid mass for the fully thawed and frozen conditions respectively, and

\[
\xi_O = \frac{\varepsilon \rho_w}{(1-\varepsilon)\rho_s} \quad \text{Eq. 23}
\]

\[
\xi_f = \frac{\varepsilon S_{sw} \rho_w}{(1-\varepsilon)\rho_s} \quad \text{Eq. 24}
\]

For a time, \( t \), the region from \( 0 \leq x \leq X_1(t) \) the temperature is \( T_1 \), where \( X_1 \) is:

\[
X_1(t) = 2\psi \sqrt{\alpha_1 t} \quad \text{Eq. 25}
\]

and from \( X_1(t) \leq x \leq X(t) \) the temperature is \( T_2 \):

\[
X(t) = 2\gamma \sqrt{\alpha_1 t} \quad \text{Eq. 26}
\]

and for \( x \geq X(t) \) the temperature is \( T_3 \). The unknowns, \( \psi \) and \( \gamma \), are found by iteratively solving the following two simultaneous equations:

\[
\frac{(T_m - T_s)}{\Delta T_m} e^{-\gamma^2(1-\alpha_1/\mu_s)} = \frac{k_2}{k_1} \sqrt{\alpha_1/\alpha_4} \frac{erf(\psi)}{erf(\gamma) - erf(\psi \sqrt{\alpha_1/\alpha_4})} \quad \text{Eq. 27}
\]

\[
\frac{\Delta T_m}{T_O - T_f} \frac{k_2}{k_3} \sqrt{\alpha_3 / \alpha_4} e^{-\gamma^2(1-\alpha_1/\mu_s)} = \frac{erf(\gamma) - erf(\sqrt{\alpha_1/\alpha_4} \psi)}{erfc(\gamma \sqrt{\alpha_4/\alpha_3})} \quad \text{Eq. 28}
\]

The Lunardini (1985) analytical solution assumes that the thermal diffusivity of the mushy zone is constant, and in order to allow direct comparison of values, the SUTRA-ICE code was modified to disallow the usual variability of this parameter for this particular situation. The choice of relative permeability function for this case is
arbitrary, as no flow occurs. Verification of the model against this analytical solution was attempted for the two sets of parameter given by Lunardini (Lunardini, 1991): $T_m = -4 \degree C$ and for $T_m = -1 \degree C$ (Table 1). The SUTRA-ICE code results successfully match the analytical solution for these two sets of parameters (Figure 4). The maximum absolute error for the $T_m = -4 \degree C$ case was 0.01 $\degree C$ or 0.1% of the total temperature range, and for the $T_m = -1 \degree C$ case, the maximum absolute error was 0.1 $\degree C$ or 1% of the total temperature range. Thus, the SUTRA-ICE code properly represents the physics of soil freezing for a fully-saturated porous medium with static water.

**Sensitivity of Freezing Process to Freezing Function Shape**

The sensitivity of the shape of the freezing function and the latent heat was evaluated by simulating a Neumann-type problem using the linear freezing function and linear relative permeability function for three different parameter sets, $m = 0.25, 0.5, \text{ and } 1.0$, and for $m=0.5$ without latent heat. The simulation parameters are listed in Table 2 and the results are shown in Figure 5. Use of a steep freezing function results in a narrow freezing front having a small length distance between the liquidus (i.e. the freezing point, $0 \degree C$) and the solidus (i.e. the point at which the soil freezing function reaches the residual saturation). Using less-steep freezing functions results in a wider mushy zone. The difference in onset distances of freezing may be due to the large amount of latent heat released that hinders additional ice formation, and the amount of release is controlled by the slope of the freezing function.

Without latent heat, the temperature and saturation profiles are entirely controlled by heat capacities and thermal conductivities of the water and ice. The latent heat effect is much greater than the heat capacities, and as such it controls the distribution of
temperature, and hence the distribution of ice. The release of latent heat acts to ‘slow’ progression of the freezing front and to create a steeper temperature divide between the fully frozen and unfrozen regions.

**Benchmarking Suggestions**

Models that incorporate both mass and energy transport with ice formation are difficult to verify against analytical solutions, because there are few solutions that solve this problem. Solutions that are available (Lunardini, 1981, 1991) focus primarily on either ice forming and melting with static water, and are usually one-dimensional and only involve the formation or melting of ice, but not both. To the authors’ knowledge, none include the movement of water. Following are two suggested heat transport problems that may be used for comparison of model results among simulation codes that represent the freeze-thaw process.

*Frozen Wall Problem*

The “frozen wall problem” is a two-dimensional areal model with warm porewater ($5^\circ$C) flowing into a domain that is partially intersected by a region with a specified sub-freezing temperature ($-5^\circ$C). The simulation is in the horizontal plane, thereby negating variable-density flow. The parameters used in the problem are given in Table 2 and the configuration and boundary conditions are described in Figure 6. This configuration, although hypothetical, is chosen because it is similar to what is expected for frozen soil boundaries used in the remediation of groundwater contamination (Andersland et al., 1996). The modeled area is initially at a super-freezing temperature and water of the same temperature steadily recharges the area from one side. At the start of the simulation, a specified sub-freezing temperature is set within the hypothetical wall,
which is held at this temperature throughout the simulation. This may be considered as one half-section of a larger region containing a series of walls with uniform spacing that are perpendicular to the regional ground-water flow direction.

The simulation results of the frozen wall problem are shown in Figures 7 and 8. At the -5°C specified temperature boundary region (i.e., the wall), ice forms along the leading edge of the boundary and a wedge of ice is formed behind the boundary. The cold temperatures from the ice boundary are conducted both upstream and downstream. The ice forms an essentially impermeable barrier to flow, forcing porewater to flow around the wall at a higher velocity due to the decreased flow area. The ice distribution reaches steady-state conditions by 800 days. Figure 8 compares results for the linear and exponential freezing functions. The linear relative permeability function does not decrease in value as quickly as the exponential function, thereby allowing more water flow through the mushy zone and creating a wider ice forming zone and greater distribution of colder temperature water down gradient from the frozen wall. Numerical convergence experiments showed that the results of the simulation do not change appreciably for models with finer mesh spacing or with shorter initial and maximum time step size.

Hill Slope in Arctic Climate Problem

The 'hill slope’ problem is a typical cold region groundwater flow system, wherein water recharging the shallow groundwater within the hillside discharges to a surface water body at the base of the hill and the hill slope freezes during the winter cutting off recharge (Figure 9). The exchange of energy between the atmosphere and ground surface is represented in a simple manner using a thermal boundary layer. The air temperature is
described by a sinusoidal function with an amplitude of 10 degrees centered around an average annual temperature of 1 °C with a period of 1 year:

\[ T = 1 - 10 \sin \left( \frac{2 \pi t}{365.25} \right) \]  

Eq. 29

where \( t \) is the time in days, and \( T \) is the boundary layer represented as being 25 cm thick, with a thermal conductivity of 0.4 W/m °C and essentially zero permeability (\( k = 10^{-10} \) m²) and no heat capacity. This is modeled by specifying these thermal conductivity and permeability values for the top row of elements, with heat capacities in the top row of nodes set to zero. Just below the thermal boundary layer is a specified pressure boundary, with a pressure of zero representing conditions at the water table and any water that flows into the hillside has the same temperature as the air (Equation 29). The point of this combination of boundary layer and water recharge is that during recharge, the subsurface thermal regime is mainly impacted by the temperature of recharging water. During the no-recharge period, when ice blocks the pores, the air temperature is transmitted to the ground through the boundary layer.

The pressure along the bottom of the 4.75 m deep water-body is the hydrostatic pressure of the water column, set in the model as a depth-dependent specified hydrostatic pressure value at each node along the water body bottom. The parameters used in the hillside problem are given in Table 2 and the configuration and boundary conditions are described in Figure 9. The simulation was run for a total of one year using a 6 hour time step.

The simulated ground surface temperatures are in Figure 10 and the temperature and saturation results are shown in Figure 11. The hillside benchmark problem is
potentially more analogous to actual field conditions. Results show that there is a several
degree difference in air and ground surface temperature during parts of winter and
summer seasons due to the thermal boundary layer modeled. As temperatures at the
ground surface decrease below freezing, subsurface ice starts to form where there are the
largest downward porewater velocities near the hillcrest. As the sub-zero temperatures
propagate into the near surface layers of the model, the relative permeability decreases,
cutting off the downward vertical flow, and moving the zone of active groundwater
recharge downhill. Below the ice layer, the porewater velocities decrease sharply due to
the end of recharge from above, and a decreasing low flow only persists because of water
released from pore storage. Once the ice extends below the entire hillside, the porewater
velocities are low throughout the model.

During melting, when the surface temperatures are above freezing, the ice initially
melts at the downhill end of the model because slightly warmer water from depth
discharges to the water body even during the winter. The ice-free region progressively
grows up the hill slope, while at the same time, the ice zone melts from above. As the ice
melts, a flow cell, with recharge and discharge, occurs between the end of ice zone and
the water body. Above the melting ice zone, a very shallow flow system connects the top
and bottom of the hillside. At the hillcrest, the ice zone melts early (i.e., before the
downhill ice-free region reaches it), at approximately day 235, allowing deeper flow
throughout the hillside, except for within the remaining ice zone. At the end of the first
year cycle, a warm region of water is left underground that impacts ice formation the
following year and it takes several years to reach a dynamic steady state wherein the ice
evolution for each yearly cycle is the same (not shown).
Freezing in a Peat Bog

The field temperature data used to test the modified numerical model was obtained from an intensively instrumented bog in the Glacial Lake Agassiz Peatlands, Minnesota (Figure 13). At the crest of a large raised bog, thermocouples were installed at 0, 25, 50, 75, 100, 125, 150, 200, 250, 300, 350, and 400 cm depths (Figure 13). Temperature and atmospheric pressure were measured approximately 1 m above the land surface. The data are stored with a solar powered data logger connected to a mobile phone for data-access. From June 18, 1998 to August 18, 2000 temperature data were averaged at a minimum of every 5 minutes and a maximum of an hour per day. The hydraulic head data were averaged over 5-minute to 1-hour intervals (McKenzie et al., 2005).

The instrumentation was installed at the hydrologic divide on the crest of the Red Lake Bog where porewater mostly moves in the vertical plane (Rosenberry et al., 2003). Here, because of dimensionality considerations (Anderson and Woessner, 1992), moving heat and water can be simulated as vertical, one-dimensional flow.

There are cyclical seasonal and daily changes in the temperature profiles in the peat. The main control on the thermal cycles is temperature at the surface of the peat profile (Figure 13). The temperature at the base of the peat profile is nearly constant at ~ 4.8 °C. The surface peat temperature fluctuates from –34.1 to 25.9 °C over the course of the two-year data collection period, and the pattern of fluctuations is a subdued replica of the local air temperature.

To model the temperature profiles at the site with SUTRA-ICE, a specified pressure condition (p = 0 Pa) for the top boundary, reflecting the water table is used, and
no-flow boundaries on the lateral sides. The elevation of the groundwater table was held constant at the peat surface because the elevation of the water table only fluctuated a small amount (< 10 cm) over the period of record.

The energy transport model was run in transient mode with 2-hour time steps. Specified temperature boundaries were applied to the top and bottom of the model. The input temperature values for the heat boundaries were changed daily based on mean daily temperature values taken from the field measurements of air temperature at the peat surface and water temperature at the bottom of the peat column.

It was found that an important calibration variable was the shape of the freezing function, with a steeper function decreasing the ice zone’s extent. The freezing curve used in calibrating the model is based on the wide range of values for peat that are compiled by Farouki (1986). The porosity is also an important variable in calibrating the energy transport model. The calibrated model has a high porosity of 40%, not unrealistic considering that peat has a very high water content. The porosity affects the energy transport primarily in the winter; as ice forms, latent heat is released and the bulk thermal conductivity of the system changes as ratio of water to ice changes.

The SUTRA-ICE simulation nicely represents both the depth of ice and the measured temperature profiles at the Red Lake Bog, MN (Figure 14; Table 2). The measured and modeled results both show that the 0 °C isotherm did not penetrate below 25 cm depth during the winters of 1999 and 2000, indicating that the SUTRA-ICE code was able to suitably simulate the depth of ice formation. In addition to matching the temperature profiles well, the SUTRA-ICE model was able to correctly predict the timing of the rise in temperature in the spring due to melting of ice. For comparison, the same
The model was run without the ice routine (i.e. using the standard SUTRA code; McKenzie et al., in press), and for the latter simulation, spring temperatures warm too soon. This confirms that ice formation and melting is a process that must be considered when evaluating the thermal regime in cold climates.

**Conclusions**

In northern peatlands the formation and melting of near surface ice is an important process in the control of heat transport and microbial activity (McKenzie et al., 2005). The ice formation process in soils is analogous to the physics of the unsaturated zone, with ice forming over a range of a range of sub-freezing temperatures until only the residual water content remains. During the phase transition latent heat is released, a process that can be modeled using an apparent heat capacity. An existing groundwater flow and energy transport code was enhanced to include these freeze/thaw processes.

SUTRA-ICE, a new model built on the existing SUTRA framework, can simulate the formation and melting of ice. The model is successfully verified by comparing model results to an analytical solution and by matching field data. Further verifications or improvements will ideally occur by other researchers comparing their ice-forming model with the benchmark problems offered herein, or by suggesting additional benchmarks.

The shape of the freezing function is found to be very important in controlling the rate and extent of ice formation (Figure 5). As ice forms over a range of temperatures, latent heat is released in proportion to the slope of the freezing function. If more ice is formed over a shorter temperature interval, then more latent heat will be released over a smaller temperature range. The released latent heat has more energy content than the
heat capacities of ice and water, and during freezing, significantly slows further growth of ice.

Two possible benchmark problems are suggested that may be used to compare other groundwater and energy transport codes that incorporate subsurface freezing and thawing. The first problem is an areal model with a frozen barrier, deflecting porewater flow. The second problem is a hill slope cross-section with a yearly sinusoidally-varying air temperature that induces the formation of a freezing zone that decreases and eventually ends groundwater recharge to the hillside, before melting during spring thaw.

A simulator that considers freezing and thawing is found to be necessary to explain the time changes in the vertical temperature profiles in a peat bog in Northern Minnesota. The SUTRA-ICE model successfully matches both the temperature distribution within the peat profile and the timing of ice thaw in the spring.

The model applied here assumes, as a first approximation, that the thermal properties of ice are constant for all temperatures, whereas thermal conductivity and heat capacity of ice change with decreasing temperature. Furthermore, the current version of the SUTRA-ICE model does not represent freezing in the unsaturated zone or solute transport and the impact of solutes on freezing. It was noted that if the ratio of $k_r/S_w$ is greater than one, then the porewater velocity will increase with ice formation. It is not clear whether this is realistic and so here, it is assumed that with the formation of ice in pores, the porewater velocity will decrease, constraining the selection of functionality for relative permeability and ice saturation.

A code such as the SUTRA-ICE model can be used for a variety of cold climate applications. Northern peatlands are a major source of atmospheric methane, and the role
of ice formation affects the extent and timing of heat transport into the peat profile. The model can also be used to study the impact of near surface ice formation on regional hydrogeology, groundwater recharge, and (given the current code limitations concerning solute impacts on freezing) contaminant transport. Additionally, the two-dimensional and three-dimensional SUTRA-ICE model may be used as a standard groundwater flow model that includes the interaction of subsurface ice with regional groundwater flow patterns.

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Table Captions

Table 1 – Parameters used in analytical solution by Lunardini (1985).

Table 2 – Model parameters used in SUTRA-ICE simulations.
### Tables

#### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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* Model was run for two cases, $T_m = -4$ and $T_m = -1$
### Table 2

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<th>Frozen Wall</th>
<th>Hill Slope</th>
<th>Peat Bog</th>
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<td>840</td>
<td>840</td>
<td>1920</td>
</tr>
<tr>
<td>Solid Grain Conductivity (W m(^{-1})C(^{-1}))</td>
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<td>3.5</td>
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<td>2600</td>
<td>2600</td>
<td>1300</td>
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<tr>
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<td>0.1</td>
<td>0.4</td>
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<td>10(^{-10})</td>
<td>10(^{-10})</td>
<td>10(^{-10})</td>
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<tr>
<td>Longitudinal Dispersivity (m)</td>
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<td>5</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>Transverse Dispersivity (m)</td>
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<td>0.5</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Time Step Size (hours)</td>
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<td>*</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Total Simulation Time (days)</td>
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<td>19200</td>
<td>365.25</td>
<td>735</td>
</tr>
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<td>L(_{sw})</td>
<td>EXP, L(_{sw})</td>
<td>EXP</td>
<td>L(_{sw})</td>
</tr>
<tr>
<td>Freezing Function Parameters</td>
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<td>w=0.5, m=1</td>
<td>w=0.5</td>
<td>m=</td>
</tr>
<tr>
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<td>0.025</td>
<td>0.5</td>
</tr>
<tr>
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<td>L(_{kr})</td>
<td>IMP, L(_{kr})</td>
<td>IMP</td>
<td>L(_{kr})</td>
</tr>
<tr>
<td>Relative Permeability Parameters</td>
<td>N/A</td>
<td>(\Omega=100)</td>
<td>(\Omega=80)</td>
<td>N/A</td>
</tr>
<tr>
<td>Minimum (K_r)</td>
<td>10(^{-6})</td>
<td>10(^{-6})</td>
<td>10(^{-6})</td>
<td>10(^{-6})</td>
</tr>
</tbody>
</table>

EXP=Lunardini; L\(_{sw}\)=Linear Saturation Method; L\(_{kr}\)=Linear Relative Permeability Method, * Time step is variable: Initial time step = 1 hour; Multiplier for time step change cycle = 2; Number of time steps in time step change cycle = 6; Maximum allowed time step size = 12 hours.
**Figure Captions**

*Figure 1* – Schematic diagram showing the analogy between the soil characteristic function and soil freezing function for a given soil.

*Figure 2* – a) Examples of two possible freezing functions, the exponential and the linear, that can be used to describe the formation of ice with temperatures below 0 °C in soils, as described by equations. $B_T$ is the temperature where the linear freezing function intersects the residual saturation, $S_{wres}$. b) The change in saturation with temperature for the functions in Figure 2a. Inset Table: Parameters used for the shown three functions.

*Figure 3* – Design of the simulation for comparing the SUTRA-ICE model with the Lunardini solution. $X_1(t)$ and $X(t)$, the distance from the specified temperature boundary to the solidus, $T_s$, and liquidus, $T_l$, respectively increases with time, and can be calculated from the analytical Lunardini (1985) solution (Equation 15-28). Distances are in meters and the initial grid spacing is uniform with $\Delta x = 1$ cm and $\Delta y = 50$ cm.

*Figure 4* – Comparison of the results for the Lunardini solution to that of SUTRA-ICE, for $T_m = -4$ and $T_m = -1$.

*Figure 5* – Results from using three sets of parameters for the linear freezing function (a) with the model setup as show in Figure 5. b) and c) show the results for the saturation and the temperature with distance respectively.

*Figure 6* – Design of suggested frozen wall benchmark problem. The grid spacing was $\Delta x = \Delta y = 0.5$ m. $T_{IN}$ is the temperature of inflowing fluid. Distances are in meters.

*Figure 7* – Temperature, ice saturation and velocity results for the frozen wall benchmark problem at various time increments. The steady state results (800 days) are in Figure 8. The results are with the exponential freezing function ($w = 0.025$; residual = 0) and the
impedance relative permeability function ($\Omega = 8$). For the saturation of water results, the white area has a saturation of 1.

*Figure 8* – Comparison of the results of wall freezing problem at 800 days (steady state) for the linear freezing and permeability functions versus the exponential freezing function and the impedance relative permeability function. For the saturation of water results, the white area has a saturation of 1.

*Figure 9* – Design of a suggested two-dimensional flow with ice benchmark problem. The top 2 rows, from 0 to 750 m, simulate a boundary layer as described in the text. The sloped upper right corner of the model simulates a water body. The boundary layer is 25 cm thick, represented by a row of specified temperature nodes for the surface temperature and row of specified pressure nodes for the land surface. The lake bottom, represented by specified pressure nodes, is set to hydrostatic pressure and inflowing water has a temperature of 4 °C. Distances are in meters.

*Figure 10* – Temperatures across the boundary layer in the hill slope model.

*Figure 11* – Results of the hill slope model for temperature, saturation, and velocity. Day 162 is near the maximum ice extent.

*Figure 12* – Monthly observed temperature profiles for three observation wells in the hillslope simulation. Depth 0 is at the top edge of the model for each observation well, and the well locations are indicated on Figure 9.

*Figure 13* – Measured temperature data from the crest of the Red Lake Bog, Glacial Lake Agassiz Peatland, Minnesota. These data were simulated using the SUTRA-ICE model. The lower inset shows the location of the field site.
Figure 14 – Comparison of measured results for the Red Lake Bog temperature profiles with that of SUTRA-ICE for both with and without the ice-routine. The two simulations were run with identical parameters.
Figures

Figure 1

[Graph showing the relationship between saturation of water and decreasing pressure or temperature, with a residual saturation indicated.]
Figure 3
Figure 4
Figure 5

(a) Linear Freezing Function

(b) Saturation of Water (S=)

(c) Temperature (T)

- $m = 0.25 \ (1/C)$
- $m = 0.5 \ (1/C)$
- $m = 1.0 \ (1/C)$

No Latent Heat

Distance (cm)
Figure 6

Initial T everywhere = 5 °C
Figure 7

Temperature (C) vs Saturation of Water ($S_w$)

- 4.2 Days
- 24.2 Days
- 56.2 Days
- 100 Days
- 200 Days
- 400 Days
Figure 8
Figure 9
Figure 10
Figure 11

Saturation of Water ($S_w$)

Temperature (°C)

40 days

55 days

162 days

89
Figure 11 continued)
Figure 13

a)

b)
Appendix A – Modifications to SUTRA Code

The SUTRA code, included the described modifications, are in FORTRAN 90.

Following are the modifications made to the SUTRA code (Voss and Provost, 2002) for the incorporation of ice formation for fully saturated conditions. The model modifications assume that changes in the saturation of water are due to freezing and thawing, as opposed to desaturation. This assumption allows for the use of the water saturation term, $S_w$, already in the code for unsaturated situation, to be used for a decrease in saturation due to ice formation. Future changes to the model may include incorporating both unsaturated and freezing functions, and would require a more extensive reworking of the model code.

**NODAL and ELEMN Subroutine Modifications**

In the NODAL subroutine the pressure equation is modified to incorporate the presence of ice.

```fortran
C.....CALCULATE CELLWISE TERMS FOR P EQUATION.
C.....FOR STEADY-STATE FLOW, ISSFLO=2; FOR TRANSIENT FLOW, ISSFLO=0.
 220 AFLN=(1-ISSFLO/2)*
     1   (SWRHON*SOP(I)+POR(I)*RHO(I)*DSWDP(I))*VOL(I)/DELTP
  CFLN=POR(I)*(SW(I)*DRWDU + (RHOICE-RHO(I))*DSIDT(I))*VOL(I)
```

In the ELEMN2 and ELEMN3 subroutines, the calculation of the thermal conductivities are modified to account for the thermal conductivity of ice

```fortran
C.....IN-PARALLEL CONDUCTIVITIES (DIFFUSIVITIES) FORMULA
  6900   IF (ME.EQ.1) THEN
C..........FOR ENERGY TRANSPORT:
    ESE=ESWG*SIGMAW+
        1   PORG(KG)*(1.0-SWG(KG))*SIGMAI+(1D0-PORG(KG))*SIGMAS
```

**ICESAT Subroutine**

A new subroutine, ICESAT, is added to the USUBS-subprogram for user programming of ice functions. Following is a sample of the subroutine, using the linear
and exponential freezing functions, and the linear and impedance relative permeability,
where the user specifies both the parameters that describe the functions, and which
functions to use. The ICESAT subroutine is called when temperatures are below
freezing, and it is used to calculate water saturation, $\frac{\partial S}{\partial T}$, and relative permeability.

The subroutine can be modified by the user to have different freezing functions and
relative permeability functions.

```
C     SUBROUTINE        I  C  E  S  A  T
C
C *** PURPOSE : 
C ***  USER-PROGRAMMED SUBROUTINE GIVING:
C ***  (1) SATURATION OF WATER AS A FUNCTION OF TEMPERATURE BELOW 0 C;
C ***  (SW(TEMP))
C ***  (2) DERIVATIVE OF SATURATION WITH RESPECT TO TEMPERATURE
C ***  (3) RELATIVE PERMEABILITY AS A FUNCTION OF TEMP
C ***
C ***  CODE BETWEEN DASHED LINES MUST BE REPLACED TO GIVE THE
C ***  PARTICULAR UNSATURATED RELATIONSHIPS DESIRED.
C
C
SUBROUTINE ICESAT(SW,DSIDT,RELK,TEMP,KREG)
IMPLICIT DOUBLE PRECISION (A -H,O-Z)
COMMON/CONTRL/ GNUP,GNUU,UP,DTMULT,DTMAX,ME,ISSFLO,ISSTRA,ITCYC,
1   NPCYC,NUCYC,NPRINT,IREAD,ISTORE,NOUMAT,IUNSAT,KTYPE,IFREEZ
C
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C     EXAMPLE   CODING   FOR
C     ICE FREEZING FUNCTIONS FOR A:
C     (1) LINEAR FREEZING FUNCTION AND LINEAR DECREASE IN RELATIVE
C     PERMEABILITY, WHERE THE USER SPECIFIES THE SLOPE, M,
C     AND THE RESIDUAL SATURATION, RESIDUAL
C     (2) EXPONENTIAL FREEZING FUNCTION (LUNARDINI, 1985) WHERE THE
C     USERS SPECIFIES THE SHAPE OF THE FUNCTION, W, AND THE
C     RESIDUAL SATURATION, EXPRES
C     (3) IMPEDANCE RELATIVE PERMEABILITY FUNCTION (LUNDIN, 1990)
C     WHERE THE SHAPE OF THE FUNCTION IS DEFINED BY OMEGA
C
C DOUBLE PRECISION SLOPE, RESIDUAL, BREAKT, W, EXPRES, OMEGA
INTEGER SWMETH, KRMETH
C
C*********** ****************************************************
C**********************************************************************
C     DATA FOR SW - METHOD 1 (LINEAR):
C
C DATA FOR KR - METHOD 1 (LINEAR):
DATA SLOPE/1.D0/, RESIDUAL/0.025D0/
SAVE SLOPE, RESIDUAL
```
DATA FOR SW - METHOD 2 (EXPONENTIAL):
DATA W/0.5D0/, EXPRES/2.5D-2/
SAVE W, EXPRES

DATA FOR KR - METHOD 2 (IMPEDENCE):
DATA OMEGA/8.D0/
SAVE OMEGA

***SET SW METHOD HERE (LINEAR=1; EXPONENTIAL=2)***
SWMETH = 2

***SET KR METHOD HERE (LINEAR=2; IMPEDENCE=2)***
KRMETH = 2

C.....SECTION (1):
C     SW VS. PRES   (VALUE CALCULATED ON EACH CALL TO UNSAT)
C     CODING MUST GIVE A VALUE TO SATURATION, SW.
C
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C
C METHOD 1 - LINEAR METHOD
IF (SWMETH.eq.1) THEN
    BREAKT=DBLE((RESIDUAL -1)/SLOPE)
    IF (TEMP.LT.BREAKT) THEN
        SW=DBLE(RESIDUAL)
    ELSE
        SW=DBLE(1D0+( SLOPE*TEMP))
    END IF
END IF  ! METHOD 1

C METHOD 2 - Exponential METHOD
IF (SWMETH.eq.2) THEN
    SW=DBLE(EXP( -1*(TEMP/W)**2))
    IF (SW.LE.EXPRES) SW=DBLE(EXPRES)
END IF  ! METHOD 2

C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C**********************************************************************
C**********************************************************************
C
C IF(IFREEZ-2) 600,1200,1800
C**********************************************************************
C**********************************************************************
C.....SECTION (2):
C     DSIDP VS. TEMP, OR DSIDP VS. SW   (CALCULATED ONLY WHEN IUNSAT=1)
C     CODING MUST GIVE A VALUE TO DERIVATIVE OF ICE SATURATION WITH
C     RESPECT TO TEMPERATURE, DSIDT.
C     NOTE: DSIDT = -1*DSWDT
C
C 600 CONTINUE

C METHOD 1 - LINEAR
IF (SWMETH.eq.1) THEN
    BREAKT=DBLE((RESIDUAL-1)/SLOPE)
    IF (TEMP.LT.BREAKT) THEN
        DSIDT=DBLE(0D0)
    ELSE
        DSIDT=DBLE(-1D0*SLOPE)
    END IF
END IF !METHOD 2
C
C    METHOD 2 - EXPONENTIAL
IF (SWMETH.eq.2) THEN
    IF (SW.LE.EXPRES) THEN
        DSIDT=0.D0
    ELSE
        DSIDT=DBLE(-1*(-2.0*(TEMP)/(W*W))*SW)
    END IF
END IF  !METHOD 3
C
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
GOTO 1800
C**********************************************************************
C*************************************************************
C
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
GOTO 1800
C**********************************************************************
C**********************************************************************
C.....SECTION (3):
C     RELK VS. T, OR RELK VS. SW   (CALCULATED ONLY WHEN IUNSAT=2)
C     CODING MUST GIVE A VALUE TO RELATIVE PERMEABILITY, RELK.
C
1200 CONTINUE
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C
C    METHOD 1 - LINEAR
IF (KRMETH.EQ.1) THEN
    BREAKT=DBLE((RESIDUAL-1)/SLOPE)
    IF (TEMP.LE.BREAKT) THEN
        RELK=DBLE(1D-6)
    ELSE
        RELK=DBLE((-1+10D-6)*TEMP/BREAKT) + 1D0
    END IF
END IF
END IF
C
C    METHOD 2 - IMPEDENCE METHOD
IF (KRMETH.EQ.2) THEN
    RELK=DBLE(10**(-1*OMEGA*(1-SW)))
    IF (RELK.LE.1.D-6) RELK=1.D-6
END IF
C
C - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
C
C**********************************************************************
C*************************************************************
1800 RETURN

END
CHAPTER 3: CHARACTERIZING WETLAND SURFACE

COLOR AND WATER QUALITY IN THE CROTON WATERSHED,

NEW YORK: NATURAL AND ANTHROPOGENIC CONTROLS
Abstract

The Croton Watershed (New York) is a developed watershed that provides drinking water for the City of New York. The purpose of the research is to evaluate: a) the extent to which wetlands in the Croton Watershed color the surface water, b) the relationship between wetlands and surface water color, and c) the extent to which anthropogenic contamination can be identified in sub-watersheds that contain wetlands in the Croton Watershed. These issues were evaluated using four synoptic samplings of surface waters the discharge wetlands, and through intensive field experiments to determine where color is primarily formed in wetland soils.

The $g_{440}$ color of wetland surface water in the watershed is proportionally related to the concentration of dissolved organic carbon and the percent of wetland area within individual watersheds. Profiles of the relative intensity of natural fluorescence in water from the upper 50 cm of peat in a representative wetland indicate that the most intense water color occurs below the most active hydrologic zone (i.e. from the land surface to ~10 cm deep).

Concentrations of sodium and chloride, stochiometrically equivalent, indicate that there is road salt contamination in Croton sub-watersheds that contain wetlands. The amount of contamination is directly correlated to the length of roads per sub-watershed area. Dissolved carbonate minerals primarily contribute calcium, magnesium, and alkalinity to wetland surface waters, although some calcium may be removed by water-mineral or biological reactions. Septic systems discharge nitrogen into many wetlands in the Croton Watershed. The extent of denitrification by wetlands is equivocal because the synoptic samplings do not capture complexities in loading rates.
Introduction

The Croton Reservoir and Watershed system is part of the City of New York’s water supply, one of the most famous and extensive water supply systems in the world (Figure 1; Koeppel, 2001). Twelve reservoirs built on the Croton River and three controlled lakes provide 10% of the drinking water to the City (Galusha, 1999; Linsey et al., 1999). All discharge from the Croton Watershed flows to the New Croton Reservoir, the New Croton Aqueduct, and to maintain flow in the Croton River.

During the 1990’s the water quality in the Croton reservoir degraded, because of residential, commercial, and industrial development in the watershed (Scheader, 1991). Although the water is not filtered, it is chlorinated. By-products from the chlorination disinfection occasionally are present in the water and during late fall the water may even exceed drinking water standards (Ashendorff, 2000). Because of these issues, the New York City Department of Environmental Protection (NYCDEP) funded a research project to determine the spatial and seasonal changes in the Croton Watershed's water quality and to understand how land-use and topography affect nutrient and other chemical loadings to the reservoirs.

The research presented herein characterizes the spatial variability of surface water that discharges from many of the wetlands in the Croton Watershed. We tested the hypotheses that color and surface water quality can be systematically related to wetland type, sub-watershed characteristics, classification type, wetland area within watersheds, vegetative cover type, and extent of urbanization defined by mapped parameters.
Background

Over 100 wetlands cover about 6% of the Croton Watershed (Tiner, 1997), and remaining area is covered by forested uplands, urban development, lakes, and reservoirs. The wetlands discharge to reservoirs and streams that flow southward across the watershed. In our study, wetlands that are large enough to have continuous surface water discharge (~80% of the wetlands) are investigated (Figure 1). Almost all of these wetlands are palustrine, non-tidal wetlands covered by trees, shrubs, persistent emergent plants, emergent mosses, and lichens (Figure 2a; Cowarden et al., 1979). The remainder or the wetlands are combinations of emergent vegetation, scrub-shrub (sedges and shrubs), and forested (Figure 3). Most wetlands in the Croton Watershed are covered by organic soils and peat that is less than 50 cm in depth. The wetland surface vegetation forms complex hummocks and hollows defined by clumps of trees, shrubs and mosses. The percent of wetland area per sub-watershed area is usually less than 25%, with a mode of 10% (Figure 4; Unpublished data from N.Y. City Department of Environmental Protection).

Tiner (2000) found that hydrogeomorphologically the wetlands in the Croton watershed are almost entirely (85%) lotic wetlands that form in small watersheds and on larger floodplains. Approximately 9% of the wetlands are terrene, formed in small watersheds on slopes without streams, and the remainder of the wetlands are associated with dammed reservoirs and surface water impoundments (Figure 2b; Unpublished data from N.Y. City Department of Environmental Protection).

The quality of surface water discharging from the wetlands depends on the mineralogical composition of the upland and wetland soils, the residence time of the
water, the degree to which soil organic matter is humified, wetland landscape position, and the degree of urbanization. Wetland surface-water color depends on how light is reflected, absorbed and scattered in the water, and on the optical properties of dissolved and suspended material (Davies-Colley et al., 1993). Dissolved organic matter (DOC) in wetland surface water has a distinctive yellow color (Davies-Colley and Vant, 1987) due to the absorption of short wavelengths in the visible spectrum and sorption of reduced iron onto de-protonated organic acids (Thurman, 1985).

The inorganic solutes in wetland surface waters are from groundwater discharge from sandy and gravelly glacial till that covers most of the watershed. The till consists of minerals derived from the underlying bedrock, mostly silicate and aluminosilicate minerals that form igneous and metamorphic rocks (Asselstine and Grossman, 1955; Grossman, 1957; Prucha et al., 1968). Interspersed within the silicate bedrock are bands of marble, some siliceous sandstone, and some shale. The silicate minerals in the igneous and metamorphic rocks within the watershed dissolve slowly compared to carbonate minerals (Langmuir, 1997). Therefore, wetlands in the Croton watershed should have surface water with relatively low concentrations of total dissolved solids (~<150 mg/L; White et al., 1963). If the soils contain carbonate fragments and clasts, the concentrations of dissolved solids (mostly calcium, magnesium, and alkalinity) could be as high as ~400 mg/L (e.g. Langmuir, 1997).

The concentration of total dissolved solids area is greater wherever highly soluble road salt or septic field leachate enters wetlands. Septic field leachate also adds high concentrations of ammonium (that can be oxidized to nitrate) in addition to sodium and some chloride to groundwater (e.g. Wilhelm et al., 1994).
Methods

Synoptic Measurements

We used synoptic sampling (defined as data that is obtained nearly simultaneously over a large area) to measured a suite of geochemical parameters of surface waters that discharge from ~80% of the wetlands in the (Fig. 1) Croton Watershed. The sampling points were at the outflows of sub-watersheds that contained wetlands. The measured parameters include pH, specific conductance, and the concentrations of dissolved organic carbon, wetland color, natural water fluorescence, base metals, silicon, iron, major anions, and nitrate. Synoptic samplings were taken at four times: beginning of the growing season (June 13, 2000), leaf out (March 2, 2001), and baseflow before leaf fall (October 12, 2001) and in early winter (November 30, 2001). Through synoptic sampling, we substituted space for time as a sampling approach.

The watershed was in an extreme drought throughout most of the sampling. The hydrological conditions prior and during each synoptic sampling were determined from long-term data from the National Oceanic and Atmospheric Administration’s National Climatic Data Center (NOAA-NCDC) from the Yorktown Heights and Danbury meteorological stations (NCDC Cooperative Network Index Numbers 309670 and 61762 respectively), presented in Table 1.

The amount of precipitation prior to the first and second sampling was slightly above and below historical averages respectively. The hydrologic conditions before the third and forth samplings occurred when precipitation was well below average. The total rainfall for both October and November 2001 was less than 1.2 inches. The number of
samples collected during each sampling depended on the antecedent hydrologic conditions. For example, during the synoptic sampling on March 2001, there was no outflow from many of the smaller wetlands and the number of wetlands sampled had lower discharge than when spring snowmelt was more dominant.

Samples were collected within a 24-hour period for each synoptic sampling. The samples were stored on ice, and analyzed shortly after delivery to analytical facilities. Total concentrations of metals were analyzed by direct current plasma emission spectroscopy or atomic absorption spectroscopy, anions were measured by ion chromatography, and dissolved organic carbon was measured using a carbon analyzer. The pH was determined by selective ion probe. Alkalinity was measured for the first two synoptic samplings by acidimetric titration to pH of 4.5. Replicates, duplicates, and analysis standards indicate a precision of ~3% and accuracy of ~+/- 7% for these analyses. U.S. Geological Survey standard waters were analyzed as unknowns along with internal standards in ensure data quality consistency. The "gelbstoff" wavelength of 440nm of absorption (\(g_{440}\)), a standard indicator of the "concentration" of yellow producing organic matter in water, was measured for membrane filtered water.

We measured the natural fluorescence of wetland waters by synchronous fluorescence spectrometry at the 370 nm, 445 nm, and 510 nm wavelengths that generalize fluorescent fulvic acid (370 nm) and fluorescent humic acid (445 nm). Fulvic acid also sometimes shows an additional peak at 510 nm (e.g. Christman, and Ghassemi, 1966; Miano et al., 1988; Ghosh and Schnitzer, 1980). Replicates and comparison to known standards indicate a precision of ~1% and accuracy of ~+/- 2% for these analyses.
Data Analysis

Spatial data was compiled by the State of New York College of Environmental Science and Forestry in a Geographic Information System, ESRI ArcInfo, to delineate sub-watershed boundaries and areas, and to calculate housing density, total road length and wetland area and type for each sub-watershed included in the synoptic sampling. Bivariate plots and statistical characterization among chemical parameters, landscape factors, and color were analyzed.

Peepers

Passive pore-water samplers, named peepers, were installed at several places in the Fahnestock wetland, a partly anthropogenic affected, peat-covered, forested wetland (Figure 1). The peepers were used to determine, as a first approximation, where the most color is generated in the humified peat profiles. The Fahnestock wetland is part of a suite of New York State Department of Environmental Protection wetlands being monitored over a long-term basis for changes in water chemistry. The wetland was chosen for the peeper experiments because it contains many of the elements associated with wetlands in the Croton watershed: natural groundwater discharge at the margins, a pristine forested wetland interior, and parts of the wetland affected by anthropogenic contamination. Peepers were placed in the center of the wetland away from groundwater seepage at the edges, near the groundwater seepages, and next to where an excavated construction debris landfill was removed. The last site is next to a service road that routes road runoff into the wetland (Figure 5).

Peepers are a sequence of 30 vertical compartments, each with 5 cm$^3$ volume, that are drilled into a plexiglass plate with a point. Each compartment is filled with distilled,
deionized water in diffusive contact with and separated from the peat by a 0.2 micron pore size Gelman polyplastic membrane. The peepers, inserted into the upper 50 cm of saturated peat, were installed at the beginning of the fall, 2002 and were then removed approximately 2 months later after chemical diffusion across the membrane equilibrated each chamber with the pore water immediately adjacent to it.

Peepers were also used to preliminarily determine where most water moves in the decomposed peat in a typical Croton wetland. We chose the Rich wetland, located in the northwester part of the watershed, where a typical hummock and hollow structure extend up to 30 meters perpendicular from a first order stream (Figure 1). We instantaneously poured 5 g sulforhodamine G dye and 5 g sulforhodamine B in a small depression approximately 10 m from three peepers. After 3.5 months, the dye had spread and the pore water was in equilibrium with the peeper chambers. After the peepers where extracted we determined where in the upper peat profile the two dyes had moved. During the experiment, there were several storms in the watershed, providing increased head to move water in the peat towards the stream.

Results

Surface Water Chemistry

Concentrations of major solutes, selected trace elements, nitrate, chloride and dissolved organic carbon varied by factors to orders of magnitude substantively across the watershed (Table 2). Figure 6 shows that for surface water that is discharged from wetlands within the Croton Watershed, the major cations are calcium, magnesium, and sodium with smaller concentrations of silicon, potassium and iron. The major anions are
bicarbonate and chloride with smaller concentrations of nitrate and sulfate. The shapes of the curves defined by the semi-logarithmic plots for each sampling are similar.

The distribution of $g_{440}$ color of surface water from sub-watersheds that have wetland coverage is shown on Figure 7. Color in the samples was greater in the June, October and November sampling during lower discharge than in the March sampling during snowmelt.

*Peeper Solute Profiles*

For the Fahnestock wetland, profiles of peeper pore water fluorescence intensity at the wavelength diagnostic of humic matter are shown in Figure 8. The relative fluorescence intensity (RFI) of fluorescent peaks across the visible light spectrum at 370, 445, 510 nm define distinct profiles at each peeper site. The vertical distribution of RFI peaks at the 370 and 510 nm wavelengths at the landfill and groundwater seep sites were similar; higher values occur in water from the upper ~20 cm compared to those in the lower part of the peat column. At the conifer swamp, 370 nm peaks stayed about the same with depth whereas the 510 nm wavelength relative intensity increased monotonically with depth.

The largest differences in spectral profiles at the Fahnestock wetland were defined by the 445 nm peaks. The relative intensity of this peak at all sites was ~200 units in the upper 20 cm of peat at the groundwater and landfill site, and then abruptly increased two-fold at the former and up to 4-fold at the latter site with increasing depth. Spectral intensity was greatest in narrow zones, in particular at the groundwater site. Intensity of the 445 peak at the conifer swamp increased monotonically with increasing depth, similar to the intensity of the other wavelengths quantified.
At the dye tracing experiment at the Rich wetland, dye was only found from 5 cm to 17 cm depth in a peeper located 10 m from the injection point. Elsewhere in the peepers, dye was not found.

**Interpretation**

*Origin of water color*

The color of wetland water is usually related to concentrations of color-producing dissolved organic carbon and dissolved iron which forms colored complexes with the DOC (Thurman, 1985). A bivariate plot of DOC versus $g_{440}$ for the synoptic sampling confirms this common correlative relationship (Figure 9); $g_{440}$ increases with DOC concentrations. Most data fall on a uniform trend, although some data sampled during the drought in June 2000 appear to have greater color per unit value for DOC. One possibility is that enhanced biodegradation of organic matter during the drought released more colored organic components than normal moisture regimes.

Another possibility is that more iron complexed with DOC during the drought. Figure 10 shows a log-log plot of $g_{440}$ versus iron concentrations. Although there is a trend of increasing $g_{440}$ with iron concentrations, the data are in a diffuse cloud and there is no clear discrimination of June 2000 data from the remainder of the results. Therefore, it is probable that DOC is the main control on color of wetland surface waters in the Croton Watershed.

We also examined the possibility that the measurement of natural fluorescence, an inexpensive analysis, may be used to estimate DOC and $g_{440}$, a more expensive analysis. Plots of $g_{440}$ and DOC versus fluorescence at 370 nm, a wavelength diagnostic of that produced by fulvic acids that constitute the bulk of DOC, are shown in Figure 11. The
results are promising: natural fluorescence correlates strongly to DOC, well within the precision, accuracy, and natural variability of these parameters.

The color of wetland surface waters in the Croton watershed is essentially directly related to the concentration of DOC. We tested the hypothesis that the amount of color in wetland surface water must also be related to the percent of wetland soils per sub-watershed area, and that this relationship should be scale independent. Wetlands that cover a large area of their containing sub-watershed should contribute more DOC and color per unit area than wetlands that cover a smaller area in their sub-watershed because larger areas of continuous peat soils will have longer flow paths in the peat and greater opportunity for the dissolution of DOC due to organic oxidation and degradation. Most biodegradation processes follow first-order kinetics (Langmuir, 1997); biodegradation is fast during early organic decomposition when labile carbon compounds are degraded primarily in the topmost active portion of the peat column. With time, the percentage of refractory carbon to labile carbon increases as DOC, consisting mostly of colored organic acids, is flushed out. Longer flow paths should lead to a greater proportion of organic acids in DOC output per unit wetland area.

Figure 12 shows a semilog plot of $g_{440}$ versus the percent of wetland area per area of sub-watershed. Despite some data scatter, probably related to local geomorphology, upland soil types, and land use, the data suggest an exponential trend; wetland color increases with percentage of wetland area per sub-watershed area.

Wetland $g_{440}$ color is only a small portion of the total water color from wetland DOC. From our fluorescence analysis, we distinguished 6 different natural background patterns (Figure 13), of which pattern 1 (MS) and 2 (SM) are by far the most common.
(Figure 14). The other patterns are sub-patterns, 1 (MSSh, MSh) and 2 (SMSh, ShMS), that have a third peak on the fluorescence shoulder at higher wavelengths. Patterns MS and its sub-patterns consist of a primary peak at ~370 nm and a secondary peak at ~450 nm. In contrast, patterns SM and sub-patterns have reversed peak intensities; the primary peak is at ~450 whereas the secondary peak is at 370nm. The shoulder peak at ~530 nm is probably caused by DOC contributed by sewage contamination (Galapate 1998).

**Major and minor solute chemistry**

Heisig (2003) recently determined that chloride and sodium concentrations in the baseflow of first and second order upland streams in the Croton Watershed are related mainly to road salting, and that nitrate concentrations are related to housing density. We further tested this theory by using data from our synoptic sampling data. In the sampled sub-watersheds, we would anticipate that biochemical processing might decrease sodium concentrations by sorption to peat soil organic matter, and that nitrate may be partially denitrified by reduction to ammonia and nitrogen gas in wetlands.

Figure 15, a plot of chloride versus sodium concentrations in milliequivalance per liter agrees with Heisig's (2003) conclusions; sodium and chloride plot on or near the linear theoretical stochiometric line for halite dissolution. Sodium and chloride concentrations in water from the wetland containing sub-watersheds are directly related to the length of roads per unit watershed area (Figure 16), in agreement with the hypothesis that road salting contributes most of these solutes to the surface water.

In the Croton Watershed, nitrate concentrations measured by the synoptic sampling have a weak inverse relationship to water color (Figure 17). There is a poor relationship between sulfate and nitrate concentrations measured by the synoptic
samplings. Concentrations of nitrate were found to be much lower during the June 2000 sampling as compared to the other three samplings.

Concentrations of calcium and magnesium in the synoptically sampled surface waters are stochiometrically almost equivalent to concentrations of alkalinity, consistent with the theoretical dissolution or carbonate minerals (Figure 19). Every equivalent of (Ca+Mg) must be balanced by one equivalent of alkalinity when one equivalent of carbonate dissolves:

\[(\text{CaMg})\text{CO}_3 + \text{H}_2\text{CO}_3 \leftrightarrow (\text{CaMg})^{2+} + 2\text{HCO}_3^-\]

Our data indicate that there is about 20% more base cation charge than alkalinity, an excess which is most likely from some calcium chloride added to road salt. Additionally, the concentrations of calcium are \(~10\%~\) greater than magnesium in surface water discharged from wetlands (expressed in meq/L; Figure 20).

**Vertical Profiles of Pore Water Chemistry and Color**

The peeper profiles of fluorescence (370 nm wavelength) at the Fahnestock wetland are essentially a measure of "yellow" color. The vertical profiles show that color development in wetland waters is most pronounced in deeper humified peat, compared to the upper \(~15\) cm (Figure 8). The largest flow of water occurs in the upper 15 cm of the peat column where labile carbon may be moved very rapidly, as confirmed by our dye tracing experiment. In the deeper more humified peat, the DOC and resulting color accumulate and is released when water levels drop and the upper part of the peat column becomes unsaturated.
Summary and Conclusions

1. The $g_{440}$ color of wetland surface water in the watershed is strongly related to the concentration of dissolved organic carbon (DOC), which in turn is related to the percent of wetland area per sub-watershed area. Natural fluorescence of wetland water within the Croton Watershed at the 370 nm wavelength correlates well with $g_{440}$ and therefore provides an inexpensive tool to analyze for wetland water color in the "yellow" hue. Iron does not significantly affect water coloration in the Croton wetlands.

2. The greatest amount of color forms below the hydrologically active zone, near the top of the peat column, as is measured by the RFI of natural fluorescence at the ~370 nm wavelength in peat porewater at a representative Croton Watershed wetland.

3. Road salt contamination to Croton wetland watersheds is clearly defined by concentrations of sodium and chloride, stochiometrically equivalent to halite and is related to the length of roads per wetland watershed area.

4. Concentrations of calcium, magnesium, and alkalinity in wetland surface waters are consistent with dissolution of carbonate minerals, although some calcium may be removed by water-mineral or biological reactions.

5. Nitrogen loading from septic systems to the wetlands is apparent, based on ranges of nitrate concentrations. However, clear trends between nitrate concentrations and the numbers of housing units per sub-watershed are indistinct, probably because of the complexities in loading rates, potential denitrification, and hydromorphic position of the wetlands within the sub-watersheds.
6. Natural fluorescence distinguishes color and DOC from different wetlands in the Croton Watershed, potentially including the extent to which septic discharges affect wetland waters.

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Figure 1

a)
Figure 1b)
Figure 2

a) 

![Bar chart showing Cowardin Classification of sub-watersheds. The categories are Lacustrine, Unconsolidated Bottom, Palustrine Emergent, Palustrine Forested, Palustrine Forested/Scrub Shrub, Palustrine Scrub-Shrub, Palustrine Scrub/Emergent, Palustrine Unconsolidated Bottom, and Ponds. The bars indicate the number of sub-watersheds for each classification, with Palustrine Forested having the highest number at 50.]

b) 

![Pie chart showing Wetland Types (Based on Total Wetland Area Within the Croton Watershed). The categories are Lotic stream (61%), Lotc River (24%), Dammed Lake (4%), Natural Lake (2%), and Excavated Pond (<1%).]
Figure 4

Percentage Wetland Coverage

- < 5%
- 5-10%
- 10-15%
- 15-20%
- 20-25%
- > 25%

0 2 4 Kilometers
Figure 5

![Fahnestock Wetland Diagram]

- NYDEP Water Table Well
- Peeper Location
- Groundwater Seep
- Direction of Surface Water Flow
- Landfill
Figure 6

NOTE: pH, E.C., and HCO$_3$ were not measured for the October 12, 2001 and November 30, 2001 Synoptic Samplings
Figure 8

Relative Intensity

Landfill Road

Groundwater Seep

Conifer Swamp

Depth (cm)

0 200 400 600 800 1000

Depth (cm)

0 200 400 600 800 1000

Depth (cm)

0 200 400 600 800 1000
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14
Figure 15
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CHAPTER 4: A GEOCHEMICAL SURVEY OF SPRING WATER FROM THE MAIN ETHIOPIAN RIFT VALLEY, SOUTHERN ETHIOPIA: IMPLICATIONS FOR WELL-HEAD PROTECTION; PUBLISHED AS

Abstract

The report discusses the stable isotope values and major solute compositions of 16 springs and river water samples along a topographic gradient in the main rift valley of southwestern Ethiopia. Most of the springs used for drinking water supplies discharge from local flow systems at scales of only tens of meters. The $\delta^{18}O$ and $\delta D$ values of waters unaffected by shallow evaporation form a local meteoric water line of $\delta D = 8.1\delta^{18}O + 19.0$, almost identical to that for the eastern Mediterranean area. The $\delta^{18}O$ values show an altitude effect of -0.5 ‰ per 100-m elevation rise. Total dissolved nitrogen concentrations locally exceed 6 mg/l (as N), and phosphate concentrations were elevated above background levels in some springs, exceeding 0.2 mg/l $PO_4$, probably due to agricultural practices upgradient of the springs. Modest well-head protection should be considered to protect public health from the effects of pollution by agricultural waste, given the very local scale of the flow systems providing spring water to Ethiopian villages.
Introduction

Ethiopia has been devastated in the past 30 years by famines and a protracted civil war costing over one million lives. Despite the generally abundant water resources in Ethiopia, the impoverished rural population usually does not have access to a clean water supply. Although 36% of people in Sub-Saharan Africa have access to safe drinking water (Ethiopian Central Statistical Authority 1996), only 15% of the population of the Southern Region of Ethiopia has access to potable water. A survey of the rural population in the southern region of Ethiopia found that the vast majority of people rated water as the most important problem in their communities (Mangin 1991).

Many communities in southern Ethiopia rely on groundwater springs and seeps as potable water supplies. Many communities protect these sources of water by collecting and distributing the spring water; a practice commonly referred to as “spring capping.” Two potential problems with capped springs are groundwater contamination, and variable seasonal yields that diminish during the dry season. Seasonal variation in flow is an important consideration because the flow of some springs is as low as 0.2 l/s, and the slightest decrease can be catastrophic to the supply of potable water for local communities.

To better understand where springs are recharged and where "well-head" protection might be considered, water samples were taken from springs throughout the Arba Minch region (Fig. 1) and analyzed for major solutes and stable isotope values of water.
Study Area

The sampled springs are located in the Main Ethiopian Rift Valley (Nelson et al. 1992), approximately 300 km southwest of the capital, Addis Ababa. The Ethiopian Rift Valley consists of Cenozoic volcanics one to twenty four million years old (Baker et al. 1972; Chernet 1988). The bedrock in the region consists of basalt, trachyte, rhyolite and ignimbrite and the western edges of Lake Abaya and Lake Chamo are covered by approximately a 1-2 km-wide plain of lacustrine and swamp deposits (Chernet 1988). Throughout the valley, there are extensive north-south fault zones (Baker et al. 1972).

Figure 1 shows that the majority of samples were taken from Arba Minch and rural water supplies in three of the local communities: Chencha, Gerese, and Gidole. To the west and north of Arba Minch are steep hills where the three local communities are located. To the east of Arba Minch are two rift valley lakes, Lake Abaya and Lake Chamo, and extensive plains.

The towns of Chencha, Gerese, and Gidole are located 36 km to the north, 28 km to the southwest, and 44 km to the south of Arba Minch respectively. The city of Arba Minch is situated on a bluff 200 m above the lakes. To the east of the city, at the base of the bluff, are the high yield Arba Minch Springs.

Hydrogeologic Setting

The average rainfall in the region is between 1000-1500 mm/year, increasing with elevation (Chernet 1988). The majority of the precipitation occurs between April and September, and is heaviest in July and August (IAEA/WMO 1998). The eastern rivers and streams that enter Lake Chamo and Lake Abaya are intermittent, and have little to no flow during the dry season. The evapotranspiration potential for the region is approximately 2300 mm/year (Shahin 1985).
The volcanic aquifers are fractured, and yield modest amounts of water to wells and springs. Water wells usually have a specific capacity of about 0.5 l/s/m and the mean permeability of the aquifer is on the order of 2 m/day (Chernet 1988). The ground water has very low total dissolved solids, generally less than 500 mg/l (Chernet 1988).

Methods

Sample Collection

In summer, 1998, thirteen springs and three rivers were sampled in the Arba Minch Region (Fig. 1) as part of a water-supply development project sponsored by HOPE International Development Agency. All samples were stored in 125-ml Nalgene™ bottles with no headspace to limit sample evaporation until analysis was done at Syracuse University geochemical laboratories.

Spring water samples were obtained from capped springs used primarily for rural water supply. Capped springs collect water in an enclosed concrete apron and distribute it to a local community by gravity-flow water systems. The storage capability of the capped springs varies from negligible to approximately 8 m$^3$. The mean residence time of the waters in a capped-spring system ranges from minutes for systems without a reservoir, to a day for systems with a reservoir. The stored water in the reservoir system is usually completely drained daily. Based on the short residence times, there should be negligible evaporation from the developed spring system.

Field Measurements

In the field, concentrations of nitrate, nitrite, phosphate, and ammonium were measured in the field on spring water using Chemtrics™ VVR Photometric Water Analysis System kits. The measurements were made within 24 hours of sample collection, and the equipment was washed between each measurement with deionized
water. The pH of the samples was not measured because the pH meter broke in transit to the field site. The location and elevation of the sampling points were extrapolated from 1:50,000 scale topographic maps (Ethiopian Mapping Authority 1995). All water samples were clear and had minimal turbidity.

Laboratory Measurements

Cation concentrations were measured using direct-current plasma spectroscopy with a Beckman Spectraspan-V. The samples were analyzed three times each for Ca, K, Mg, and Na. Chloride and SO$_4$ were measured with High Performance Liquid Chromatography, HPLC, with Waters™ instrumentation and the Waters' Millennium™ data acquisition and processing software. Total alkalinity (the sum of the charged carbonate species) was calculated from the charge-balance equation (Drever 1997) because without accurate field pH measurements, it was not possible to speciate the dissolved inorganic carbon.

Values of $\delta^{18}$O and $\delta$D of water were measured with a mass spectrometer (Finnigan MAT 252, directly coupled to a HDO III water equilibrator), and are reported relative to the Vienna – Standard Mean Ocean Water (VSMOW).

Results

Field Tests

The results and summary statistics of the field testing for NO$_2$, NO$_3$, PO$_4$, and NH$_3$ are presented in Table 1. Nitrite concentrations were negligible in all samples; less than 0.040 mg/l as N. In contrast, phosphate ranges from undetectable (< 0.01)-0.650 mg/l. Ammonium ranges from 0.45-1.15 mg/l as N and the minimum concentration of nitrate is 0.09 mg/l as N. Concentrations of NO$_3$ in two samples (the Halaltawa and
Leate Springs) were greater than 5 mg/l of NO\textsubscript{3} as N, the maximum measurable
concentration with the Chemtrics™ kits for NO\textsubscript{3} as N, and therefore could not be
analyzed.

**Laboratory Measurements**

The results and summary statistics of the laboratory measurements of major ions
(Ca, Mg, K, Na, Cl, and SO\textsubscript{4}) are presented in Table 1. Calcium ranges from 2.7-100
mg/l, Mg ranges from 0.88-36 mg/l, K ranges from 0.14-3.8 mg/l, and Na ranges from
1.3-34 mg/l. Chloride ranges from 0.62-32 mg/l and SO\textsubscript{4} ranges from undetectable (<
0.1)-11 mg/l. Alkalinity, calculated by mass balance, ranged from 8.3 to 495 mg/l as
bicarbonate.

The values and summary statistics of the stable isotopes in water are presented in
Table 1 and in Figure 2. The d\textsuperscript{18}O values range from –4.4 - –1.5 ‰ VSMOW and the dD
values range from –21 – 4 ‰ VSMOW.

**Interpretation**

Figure 2 shows the major solute concentrations plotted on a Piper trilinear
diagram (Piper, 1944). Two geochemical groupings are defined: (1) Ca-Mg-HCO\textsubscript{3} type
waters with TDS values between 100-500 mg/l and (2) a weak trend with low TDS
plotting between the Ca-Mg-HCO\textsubscript{3} type water and a point mid way between the Ca-SO\textsubscript{4}
and Na-Cl type waters. The Ca-Mg-HCO\textsubscript{3} type waters are consistent with what is
expected from the water-rock interactions in basaltic terrain of the main rift valley
(Hounslow 1995).

Stiff diagrams (Stiff, 1951) (Fig. 2) demonstrate that seven of the samples are
very dilute and consist of precipitation that has reacted minimally with the aquifer
minerals (Kornel, Gerese, Washe, Babreal, Yohanes, and Aira Springs and River-3). The size of the Stiff diagram is related to the extent of geochemical evolution of the water by water-rock interaction and/or evaporation. Precipitation in nearby Uganda has concentrations of Na, K, Ca, and Cl of 1.7, 1.7, 0.05, 0.9 mg/l respectively (Berner and Berner 1987), slightly less than the respective concentrations in the most dilute Ethiopian spring waters.

In contrast, waters from the River-1, River-2 and Halaltawa Spring have TDS > 200 mg/l and the Stiff diagrams of the proportions of base cations and ligands are in the shape of an "arrowhead", typical of water found in basalt aquifers (Hounslow 1995). The Stiff diagrams of the remainder of the spring samples, Kete, Halaltawa, Leate, Borgo, Arba Minch, and River 1, have “hexagonal” shapes and TDS concentrations consistent with a mixture of water that has reacted with basalt and the less chemically evolved dilute waters (Hounslow 1995).

The concentration of TDS is generally inversely related to the elevation of the springs as shown in Fig. 4. TDS increases from 13 to 446 mg/l over a descent of almost 100 m. This decrease in TDS is consistent with the concept that recharge from precipitation at higher elevations moves downward and laterally to spring discharge points down-slope, resulting in the discharge downslope having the longest subsurface residence time.

*Arba Minch Meteoric Water Line*

The springs and rivers with low TDS best document the stable-isotope values of precipitation. If these samples are an analog for the precipitation chemistry, they form a local meteoric water line (MWL) for the Arba Minch Region (Fig. 3) with an equation of:
\[ dD = 8.1 \, d^{18}O + 19 \]  \hspace{1cm} (1)

and a coefficient of determination, \( R^2 \), of 0.70. The scatter of the data around the proposed MWL may be due to microclimatic changes between the sampling points. Additionally, it should be noted that the local MWL is nearly identical to the MWL for eastern Mediterranean waters (Gat and Carmi 1970):

\[ dD = 8.0 \, d^{18}O + 22 \]  \hspace{1cm} (2)

The Leate and Borgo Springs appear to fall on an evaporative trend with a lower slope than that of the Arba Minch MWL. The discharge at these springs is small, less than 0.2 l/s, suggesting that groundwater flow is focused in near-surface fractures susceptible to enrichment by evaporation from the water table. The River-2 and River-3 samples also fall on an evaporative trend with a slope lower than the Arba Minch MWL. These rivers, located in a more arid region of the study area, were sampled at low flow and, volumetrically, were more susceptible to evaporative enrichment.

**Elevation effect**

There is a significant inverse correlation between the isotope values of the water samples and the elevation of the springs. Assuming that the spring samples reflect the isotope value of precipitation, the region has an elevation effect of approximately -0.5 ‰ \( \delta^{18}O \) per 100 m rise as shown in Figure 5, near the high end of the globally observed range (Clark and Fritz 1997).

Some of the spring water does not plot closely to the inverse trend. For example, the \( \delta^{18}O \) values of water in the Arba Minch Springs is -2.2 ‰, about 2 ‰ more depleted than would be predicted from the inverse relationship. Spring samples with a \( \delta^{18}O \) value similar to the Arba Minch Spring water are found at an elevation approximately 800 m
higher, at approximately 2000 m. Therefore, it is conclude that the Arba Minch Springs discharge from flow cell that starts near an elevation of 2000 m in the hills west of the city of Arba Minch.

**Agricultural Contamination**

Some of the rural springs are contaminated with nitrate and phosphorous that are likely derived from agricultural waste. The Halaltawa and Leate springs have greater than 5 mg/l of NO$_3$ as N, probably the result of animal waste because the samples do not have elevated phosphate concentrations (Fig. 6) (Hem 1985). For comparison, the maximum contaminant level for NO$_3$ is 10 mg/l as N in the United States (Hem 1985). The Gerese, Babreal, Borgo, and Tebel spring samples have PO$_4$ levels above normal background levels of 0.1 mg/l (Hem 1985). Figure 6 shows that the source of PO$_4$ is probably agricultural because increasing PO$_4$ concentrations occur with only minor total N concentrations (Hem 1985).

The isotopic and geochemical analyses show that many of the spring waters consist predominantly of precipitation that moves along very short flow paths from infiltration areas to spring-discharge sites. Therefore, in order to prevent contamination from animal and fertilizer waste, it is imperative that the area directly upgradient of the springs not be used for livestock grazing or holding, and farming. Livestock could be kept away from the immediate upgradient area with fencing or thorn-bush hedges, thus protecting the spring-water source.

**Conclusions**

The major conclusions of this study are:
1) Assuming that some of the spring waters are equivalent chemically to precipitation, a MWL for the Arba Minch Region can be derived with the equation:

\[
\delta D = 8.1 \delta ^{18}O + 19
\]

2) There is a significant inverse relationship between the elevation of the spring site and the geochemical composition and isotope value of the spring waters.

3) The elevation effect can potentially be used to discern the scale of the flow paths; for example, the source of the water for the Arba Minch Springs is approximately 800 m higher in the catchment area.

4) Some of the spring waters contain some nitrate contamination derived from animal waste. In order to protect against this problem, animals must be restricted from entering the area immediately upgradient of the rural springs. Additionally, some springs probably are contaminated with PO$_4$ from agricultural fertilizers.

**Acknowledgements**

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**References**


Piper AM (1944) A graphic procedure in the geochemical interpretation of water analyses. American Geophysical Union Transactions 25:914-923


Figure captions

Figure 1. Map of the study area, including sampling sites, and spring names with elevations. The lines connecting the towns or cities are seasonal roads.

Figure 2. Piper trilinear diagram with TDS plotted as circles.

Figure 3. Plot of $\delta$D versus $\delta^{18}$O values overlaid with Stiff diagrams.

Figure 4. Bivariate plot of TDS versus elevation.

Figure 5. Plot of elevation versus $\delta^{18}$O values.

Figure 6. Plot of PO$_4$ vs. total Nitrogen, the sum of NO$_3$, NO$_2$, and NH$_4$ for the rural spring samples.
Figures

![Study Area Map]

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Figure 1
Figure 2
Figure 3

**Description of Stiff diagrams**

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- **Precipitation**
- **Non-evolved groundwater**
- **Well evolved, basaltic groundwater**

**Groundwater Mixing and Evaporation**

- **Arba Minch MWL**
  - $\delta D = 8.1 \delta^{18}O + 19$
  - $R^2 = 0.70$

Legend:
- **Rural Springs**
- **Rivers**
- **Arba Minch Spring**
- **Samples considered analogous to precipitation**
- **Arba Minch MWL (Based on assumption that samples are analogous to precipitation)**
Figure 4
Figure 5
Figure 6
# Tables

Table 1 - Concentrations of nutrients, and major solutes, and values of stable isotopes in spring water and river water from the Arba Minch region of Southern Ethiopia.

All measurements are in mg/l except for $\delta^{18}O$ and $\delta D$ values which are in $\%$. VSMOW.

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*Maximum* 0.04 0.65 1.15 > 5 32 11 100.00 36 3.8 34 495 -1.5 4

*Minimum* 0.01 < 0.01 0.45 0.09 0.62 < 0.1 2.7 0.88 0.14 1.3 8.3 -4.4 -21

*Range* 0.03 0.70 31.4 97.3 35.1 3.66 32.7 486 2.9 25

*Average* 0.02 0.17 0.78 1.8 7.1 2.1 20.1 9.3 1.4 10 117 -3.0 -8
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DATE OF BIRTH: June 3, 1974

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John James Prucha Award, Syracuse University, May 2001
Newton E. Chute Award, Syracuse University, May 2000
AGU Outstanding Student Poster Award, 1999 AGU Fall Meeting, San Francisco
International Honors Student, Phi Beta Delta, Beginning Spring 1999
Tuition Scholarship, Syracuse University, Fall 1997 to Spring 2005

PROFESSIONAL EXPERIENCE:

Head Teaching Assistant, Department of Earth Sciences, Syracuse University, 2002-2004; Spring 2005
Course Instructor, University College, Syracuse University, 2000-2001; Fall 2004
Laboratory Instructor, Department of Geosciences, Hobart and William Smith College, Spring 2001
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