Nitrate Transport in Snowmelt
A Simple Conceptual Model

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ABSTRACT

A simple conceptual model of nitrate transport in snowmelt in a small headwater upland forested catchment is presented. The model, SCATS (Small CAtchment Transport in Snowmelt), is developed in the object-oriented program format using STELLA and consists of three modules; snowpack, solum, and stream. The model is based on data obtained during the 1994 Spring snowmelt event on Mount Mansfield in northern Vermont during which the highest streamwater nitrate concentration observed occurred early in the melt event at relatively low flow and was initially construed to be possible evidence of chemical fractionation occurring within the snowpack thus creating an ionic pulse. However, SCATS simulations suggest that the solum is dominant in determining streamwater chemistry during Spring snowmelt and that the streamwater nitrate concentrations originally construed to be a result of chemical fractionation occurring within the snowpack were more likely the result of processes occurring within the solum. The observation could not have been derived from mass balance determinations alone, suggesting that relatively simple conceptual models using the STELLA format may provide a useful tool for researchers in the interpretation of nitrate transport in snowmelt.

Key words: nitrate, snowmelt, streamwater chemistry, conceptual model, STELLA.

INTRODUCTION

Modeling in Small Catchments

An important part of biogeochemical research in small catchments is the development of mathematical models of different types (Moldan and Cerny, 1994).

Modeling should receive greater emphasis as continuing field and laboratory studies provide a better understanding of the processes involved (Hornbeck, 1986). Modeling efforts also serve to increase the demand for greater quantity and quality of data collected and therefore contribute to the advancement of our knowledge and understanding of natural systems. These models may be used to test hypotheses, determine important mechanisms, make predictions based upon anticipated changes within the catchment and integrate information obtained within the watersheds.

Models describing natural processes occurring in small upland forested watersheds may be divided into two general categories based on intended application, 1) decision making, and 2) research or training. An essential difference between the two is that decision making models are focused on providing information while research or training models are focused on providing knowledge (Jackson, 1982). The model described in this paper may be classified as a research model with the focus on providing knowledge that will help identify which mechanism(s) may be of most importance in nitrate transport during Spring snowmelt.

Modeling Nitrate in Snowmelt: Chemical Fractionation

Nitrate is added to the snowpack surface prior to and during Spring melt in the form of dry and wet deposition. Because nitrate in the snowpack exists as a solute in snowpack water, knowledge of water flux is a necessity in determining nitrate flux. The greatest loss of nitrate from the snowpack is in snowmelt. The rate of nitrate loss in snowmelt is effected by processes such as *melt-freeze cycles, rain scavenging, preferential elution* and *chemical fractionation.*

Chemical fractionation has perhaps the greatest influence in meltwater concentrations. Gregory *et al.*

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(1986) simulated chemical fractionation within the snowpack in a lumped conceptual hydrochemical model by use of the equation:

$$\frac{l_2}{f_2} = c(o)X^{\frac{-m}{M}} \quad (1)$$

where

l_2 = dissolved load within snowpack (meq l^{-1})

f_2 = flux of water (l)

$c(o)$ = concentration of pollutant prior to melting (meq l^{-1})

X = concentration factor

m = fraction of the snowpack melted

M = constant

Morris and Thomas (1987) used the following empirical equation to simulate chemical fractionation occurring within the snowpack:

$$c(t) = E\,c(0)\exp(-m(t)/M) \quad (2)$$

where

$c(t), c(0)$ = concentration of snowmelt at time t, t = 0 (meq l^{-1})

$m(t)$ = proportion of snowpack melted

E, M = constants.

Equations 1 and 2 describe chemical fractionation in relation to fraction of snowpack melted, m and $m(t)$ respectively, and a similar approach is used in the snowpack portion of the model described in this work.

Modeling Nitrate in the Solum: Mobile and Immobile Water

Nitrate is a relatively mobile ion, highly soluble in water and involved in few physical and chemical reactions with the soil. However, nitrate leaching or transport through the soil is a physically complicated process. The basic processes involved during nitrate transport include *diffusion* (Fick's first law) which refers to solute flux in relation to solute gradient and *advection* (or mechanical dispersion), the mass transport of water with dissolved solute in it. Variations in pore size, the spatial distribution of pores, and their continuity contribute to the irregular movement of advected water through the soil profile. The combined actions of diffusion and advection that mixes the resident soil solution and the percolating snowmelt or rainfall is termed *hydrodynamic dispersion* (Burt and Trudgill, 1993).

The simplest concept of solute transport is that of leaching when one solution displaces another from soil pores with uniform displacement and no mixing (piston flow) and may be stated as (Addiscott and Wagenet, 1985):

$$Z_p = \frac{Q}{\theta} \quad (3)$$

where

Z_p = depth of penetration (cm) of displacing solution

Q = quantity (cm) of displacing solution

θ = volumetric water content

An important concept in understanding of nitrate transport through the solum is that of mobile and immobile nitrate stores. Water within the solum may be partitioned and this partitioning has been described in various ways by different researchers. One such description is that soil water may be subdivided into three parts, drainable water that may be removed by gravity, plant available water or capillary held water (from field capacity at about 330 kPa down to the wilting point at about 1500 kPa), and unavailable water which is mostly hygroscopic water held tightly in films about individual soil particles (Amerman and Naney, 1982). Another description suggests that mobile water may defined as water held between 5 and 200 kPa and immobile water as the water held between 200 and 1500 kPa. Slowly infiltrating water may cause "piston flow" in the mobile phase during which solute moves from layer to layer. When flow rate is reduced, solute movement occurs between mobile and immobile phases as a result of equalization or solute diffusion. Solute holdback is explained by assuming that equilibrium is reached between the phases upon the cessation of flow (Addiscott and Wagenet, 1985).

The general concept of mobile and immobile solum water and nitrate has been incorporated into a number of modeling approaches describing solute transport in the soil (Addiscott, 1977; Gregory *et al.*, 1986; White, 1985). Addiscott (1977) used the concept of mobile and retained phases of soil water and solute to model leaching in structured soils. During water movement only the mobile solute fraction is displaced. Gregory *et al.* (1986) used a lumped conceptual hydrochemical model to determine the effect of snowmelt on water quality in which the soil was divided into a slow store (representing deeper layers of the soil) and a fast store (representing the upper layers of the soil and pipe flow). White (1985) describes a two-domain mixing model for predicting nitrate leaching during unsteady, unsaturated flow through soil. The model assumes that infiltrating water mixes with a volume of soil water to produce a miscible volume in which solute is transported. An immiscible volume of water is separated from the miscible volume by an interfacial area across which solutes can diffuse. Model output is by drainage of the miscible volume. The concept of

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mobile and immobile water and solute is used in the solum portion of the model described in this paper.

Modeling Nitrate in Streamwater: Hydrograph Separation

Traditional methods of hydrograph separation have relied on arbitrary graphical methods to separate streamflow hydrographs into stormflow and baseflow by extrapolation of groundwater recession curves beneath the hydrograph peak (Pinder and Jones, 1969). Groundwater stage versus base flow rating curves has been used as a reliable method of determining the ground water contribution to streamflow but is cost and time intensive. A number of techniques based on mixing processes and mass balance considerations that have been introduced and have yielded satisfactory results when calculating hydrograph separations (Johnson et al., 1969). These include the use of specific conductance (Pilgrim et al., 1979), acid neutralizing capacity (Robson and Neal, 1990), end-member mixing analysis (Christophersen et al., 1990) as well as the use of naturally occurring tracers such as oxygen 18 (Pearce et al., 1986) and Si (Pinder and Jones, 1969; Hooper, 1986; Hendershot et al., 1992).

Silica (Si) is commonly present in mountain streams in the northeastern U.S. and is controlled by rock weathering (Vitousek, 1977). Hooper and Shoemaker (1986) note that dissolved silica has an advantage over other naturally occurring tracers in that it is consistently absent from meltwater. Si was chosen for the hydrograph separation in the streamwater portion of the model presented in this paper.

METHODS

Fieldwork

The fieldwork was conducted at a Vermont Monitoring Cooperative (VMC) study site located on the southwest slope of Mount Mansfield in the Green Mountains of northern Vermont (44°30' N, 72°51' W) from October, 1993 through February, 1995. The Spring snowmelt period which provided data for input into the model occurred between April 4 and April 23, 1994. Streamflow at the mouth of the catchment is monitored by a United States Geological Survey (USGS) weir. Dry and wet deposition inputs and ambient meteorological data were measured at the nearby (2 km) VMC air quality monitoring station located at approximately the same elevation (425 m) as the weir (445 m). Snowpack depth was recorded at the site of the weir by an ultrasonic snowpack depth sensor. The snowpack was sampled near the weir at a single site at three depths on March 21, 1994, two weeks before the start of the Spring snowmelt event. Soil pore-water was sampled

in riparian soil 10 m upstream of the weir and 2m from the stream in February, 1995. Streamwater was sampled at the weir twice daily during the 1994 spring snowmelt period. All samples were analyzed for NO_3, SO_4, Cl, Ca, K, Mg, Na, Al, NH_4 and Si. Fieldwork is discussed in greater detail in Daly (1995).
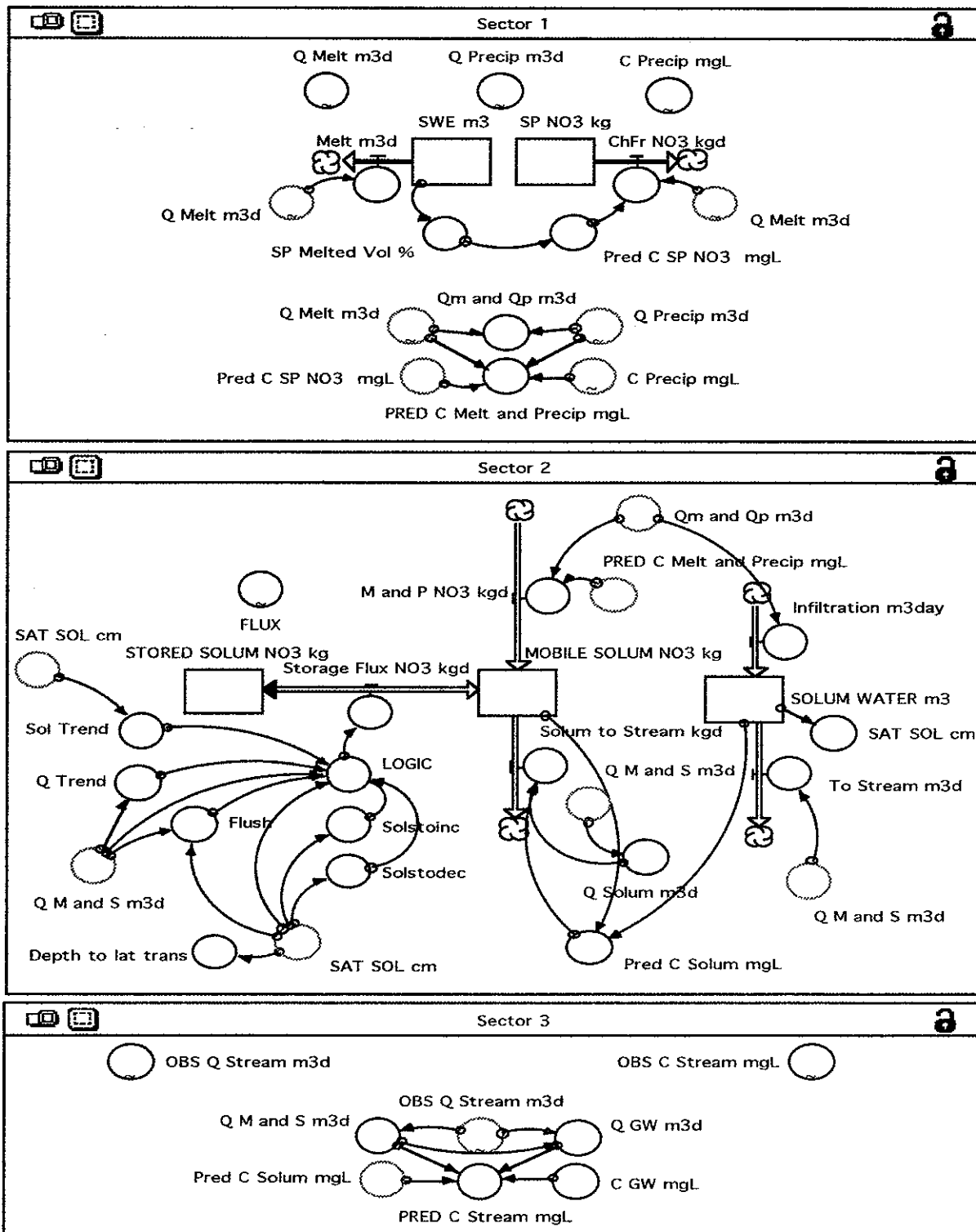
SCATS

SCATS (Small CAtchment Transport in Snowmelt; *Figure 1*) is a simple model. It has been said that where objectives and/or resources are limited, a simpler type of model is more cost effective, and in many cases, no less accurate (Johnes and Burt, 1993). For this study, a simple conceptual approach to modeling nitrate transport within the watershed was chosen because 1) the special application of this model and the limited field data available precluded the availability of statistic-based parameters for model input, 2) complex deterministic models usually make large requirements in terms of computing and data, are costly to develop and operate, and are difficult to calibrate because of the difficulties involved in collecting sufficient field data, and 3), the conceptual approach more clearly presents and identifies the important processes in development of initial or first generation models.

The software chosen to develop SCATS is STELLA, an object oriented program (OOP) that has greatly reduced human effort in modeling. Object-based programming may become the method of choice for modelers in the near future (Woodfield, 1988). The STELLA program has demonstrated usefulness as a modeling tool that can be rapidly adapted to verify the applicability of an equation or set of equations describing processes occurring in the natural environment and comprehensive and sophisticated models using STELLA have been developed (Cassell and Pangburn, 1990). STELLA can also be used as a very simple research tool capable of producing insights into very complex systems as is demonstrated here with SCATS.

The model is constructed using a combination of the four basic building blocks of the STELLA program; *stocks, flows, converters* and *connectors. Stocks* represent accumulations of material, in this case water and nitrate. *Flows* (fluxes) fill and drain the stocks. *Converters* change input to output by defining constants, calculating algebraic relationships, and storing logic statements, functions or graphs. *Connectors* provide the appropriate links (information/control) between model building blocks (Richmond and Peterson, 1992).

SCATS is divided into three modules; snowpack, solum and streamwater. Each module mixes inputs and calculates the quantity and concentration of resulting output which in turn is an input for the next module. The modules are located and function in the

Figure 1. *SCATS structural diagram in STELLA format. Sector 1 simulates meltwater nitrate concentrations from the snowpack. Sector 2 simulates the influence of the solum on meltwater nitrate concentrations. Sector 3 mixes variable solum water nitrate concentrations with a fixed groundwater nitrate concentration to simulate streamwater nitrate concentrations.*

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logical order that would be expected for a mass of water and nitrate moving through the catchment.

Snowpack Module

The snowpack module in (*Figure 1*, Sector 1) consists of two stocks, a snowpack water equivalent stock (SWE m3) and a snowpack NO3$^-$ stock (SP NO3 kg). The initial value for the SWE stock was estimated from the sum of the initial SWE and the snow that increased the SWE value during the simulation period. Q melt is calculated on a daily basis from the change in snowpack depth recorded at the weir. The initial value for the snowpack nitrate stock was the sum of the product of the mean of snowpack sample concentrations obtained prior to snowmelt on March 21 and the initial SWE stock, and the quantity of dry and wet deposition nitrate that occurred after snowpack samples were collected but prior to the commencement of the Spring melt event on April 4. Neither the SWE stock nor the nitrate stock have any inputs and the only output is due to snowmelt. The function of these stocks is to simulate the role of chemical fractionation in nitrate within the snowpack and the resulting nitrate concentrations in the meltwater.

Perhaps the simplest approach to modeling chemical fractionation within snowpacks, and the method used in SCATS, is based on an equation derived from experimental laboratory and field data presented by Johannessen and Hendriksen (1978). These data were used to develop a general relationship of the form (4):

$$y (NO_3^- CF) = 4.4699e^{-0.0466x(\% \text{ snowpack vol. melted})}$$

The concentration factor (*CF*) is the ratio of the solute concentration in meltwater to the original concentration in the snowpack. The mean concentration of NO3$^-$ in the Nettle Brook snowpack prior to snowmelt was 1.94 mg/l NO3$^-$. This mean value was then multiplied by the concentration factor in equation 4. This relationship of nitrate concentration vs. percent of snowpack melted is described in equation 5 and is embedded in the Pred C SP NO3 object (5):

$$y (NO_3^- \text{ mg/L}) = 8.6703e^{-0.0466x(\% \text{ snowpack vol. melted})}$$

Equation 5 describes chemical fractionionation in the snowpack for the first 50% of the snowpack melted after which snowmelt concentrations remain steady at approximately one half of the original mean snowpack concentration (0.89 mg/l).

Dry deposition into the research catchment during the simulation period is assumed to have accumulated during periods with no precipitation on the snowpack surface and to be subsequently mobilized by wet deposition. Combined dry and wet deposition nitrate is input to the snowpack module by the C Precip mgL object. Nitrate released from the snowpack during melt is mixed with wet and dry deposition nitrate in the PRED C Melt and Precip mgL object. Predicted concentrations of meltwater to the solum are calculated in the PRED C Melt and Precip mgL object by equation 6, a two-component mixing equation similar to that described by Pinder and Jones (1969):

$$C_{PRED} = ((Q_M \times C_M) + (Q_P \times C_P))/ Q_T \quad (6)$$

where

Q_T	=	total flow
C_{PRED}	=	predicted NO3$^-$ concentration of melt and precipitation
Q_M	=	Q melt
C_M	=	NO3$^-$ concentration of melt
Q_P	=	Q precipitation
C_P	=	NO3$^-$ concentration of precipitation (dry/wet deposition)

The predicted nitrate concentration is multiplied by the combined melt-precipitation water flux in the QM and Qp m3d object to simulate total nitrate flux from the melting snowpack to the solum.

Solum Module

The method used in the solum module (*Figure 1*, Sector 2) required that three stocks be used, one stock for solum water (SOLUM WATER m3 object) and two stocks for solum nitrate, mobile nitrate (MOBILE SOLUM NO3 kg object) and relatively immobile nitrate (STORED SOLUM NO3 kg object). Water input to the solum module is by the snowpack module melt and precipitation output (QM and Qp m3d object). Output from the solum water stock to the stream is controlled by the amount of solum flow (Q M and S m3d object) contributing to streamflow which is determined by the hydrograph separation in the streamwater module.

The initial value for the mobile solum nitrate stock was estimated by adjusting the initial stock quantity until the predicted streamwater nitrate concentration on day 0 of the simulation period coincided with the observed streamwater concentration on that day. The dry/wet deposition and meltwater nitrate quantity (M and P NO3 kgd object) output from the snowpack module provides nitrate input to the mobile solum nitrate stock. The nitrate concentration of the solum water is calculated in the Pred C Solum mgL object by dividing the mobile solum nitrate stock (kg) by the solum water stock water content (m3) and making appropriate conversions to yield mg/l. Nitrate output from the mobile solum nitrate stock into the streamwater module (Solum to Stream kgd object) is determined by multiplying the solum flow quantity

(m3) contributing to streamflow (Q M and S m3d object) and the simulated concentration of the mobile solum water contributing to the stream (Pred C Solum mgL object).

Equations based on flow through the solum (Q M and S m3d object) and on solum water content (SAT SOL cm object) were developed to control nitrate flux between the nitrate stocks. The equations were derived from mass balance calculations employing SWE, streamflow, and stream nitrate concentration data. Equation 7 (embedded into the Flush object) determines nitrate flux from the immobile nitrate stock (STORED SOLUM NO3 kg object) to the mobile nitrate stock (MOBILE SOLUM NO3 kg object) and was applied only when solum Q was increasing:

Flush =
$$(0.096(SAT\ SOL\ cm)+5.394)e^{0.001(Q\ M\ and\ S\ m3d)} \quad (7)$$

Equation 7 simulates the flushing of nitrate (kg) from the immobile stock to the mobile nitrate stock as a function of both the estimated height of solum water above the pre-melt level on day 0 (SAT SOL cm object) and the solum Q (Q M and S m3d object). Nitrate flux from the mobile nitrate stock to the immobile nitrate stock is determined by two equations, one applied when solum water height is increasing (Solstoinc object),

Solstoinc =
$$-0.0029(SAT\ SOL\ cm)^2-0.276(SAT\ SOL\ cm)-0.0007 \quad (8)$$

and the other applied when the solum water level is decreasing (Solstodec object),

Solstodec =
$$-0.0043(SAT\ SOL\ cm)^2-0.276(SAT\ SOL\ cm)-0.0042. \quad (9)$$

Equations 8 and 9 simulate storage of nitrate as a function of the calculated vertical height of water retained within the solum (Q M and P m3d - Q M and S m3d). The application of these equations is controlled by a logic statement in the LOGIC object that applies the equations as a function of increasing values for solum Q (Q Trend object) and increasing or decreasing values of stored solum water (Sol Trend object). Output of nitrate (kg/day) from the solum module to the stream module occurs in the Solum to Stream kgd object flow as the product of the predicted mobile solum concentration (PRED C Solum mgL object) and solum Q (Q M and S m3d object).

Streamwater Module

Estimating the relative contributions of soilwater and groundwater into the stream was accomplished in the snowpack module (*Figure 1*, Sector 3) using the method of Hendershot *et al.* (1992) which employs Si as a naturally occurring conservative tracer. The hydrograph separation was accomplished using the following equation allowing the closest fit between observed Si and predicted Si concentrations at Nettle Brook:

$$Q_s = 0.34(Q_t - 21)^{1.13} \quad (10)$$

where

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Q_s	=	flow through the solum (m3/day)
Q_t	=	total streamflow observed (m3/day)

The procedure used by Hendershot *et al,* (1992) was modified for this research in two ways. First, the Si concentration value for groundwater was determined at base flow (21 m3/day) from streamwater sampling, rather than from soil pore-water samples obtained from below the water table (the values were in close agreement, 2.72 and 2.76 mg/L respectively). Second, the Si concentration value for solum water was determined at peak flow (4801 m3/day) during the spring melt event from streamwater sampling, rather than from soil pore-water samples obtained from the solum above the water table.

Simulated streamwater nitrate (NO_3^-) concentrations were obtained by use of an equation similar to equation 6 in which a fixed groundwater nitrate concentration determined from soil pore-water samples obtained from the saturated zone (0.11 mg/l) was multiplied by the ground water component of the hydrograph separation, and the variable nitrate concentrations simulated in the solum module were multiplied by the solum water component of the hydrograph separation. The sum of the above was then divided by the total Q.

RESULTS

The hydrograph separation resulting from the use of equation 10 describing the solum portion of streamflow is presented in *Figure 2*. The negative groundwater contribution to streamflow at peak flow is a result of bankfull storage and is not uncommon during flood events (Pinder, personal communication).

Results of analysis of streamwater samples for NO_3-N and stream flow rate during spring snowmelt are presented in *Figure 3*. Streamwater had an average NO_3-N concentration of 0.430 mg/l during peak flow on April 16. The highest daily concentration of streamwater NO_3-N, 0.508 mg/l was recorded on April 6 at a substantially lower flow rate. Stream water nitrate concentrations typically increase with increased flow rates as a result of the high solubility (mobility) of nitrate in water and the relatively few reactions that occur between nitrate and the soil. The peak nitrate concentration on April 6 was initially
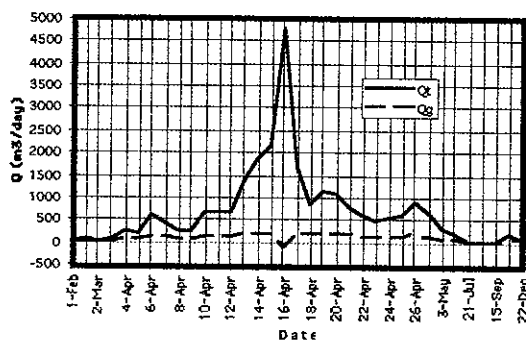
Figure 2. Nettle Brook Hydrograph Separation. Groundwater dominates the hydrograph at all but the highest flow rates as is observed during the Spring snowmelt event. Note that data points are primarily during the Spring snowmelt event.

considered to be possible evidence of chemical fractionation in the snowpack, a process that releases pulses of higher concentrations from the snowpack early in the melt period.

Simulated meltwater nitrate release from the snowpack (kg/day) using the equation derived from data presented by Johannessen and Hendriksen (1978) and the observed streamwater nitrate export determined from streamwater samples are plotted in Figure 4 as curves 1 and 2 respectively. The curves differ in the daily trend of nitrate flux (with the exception of day 13) and in the quantity of nitrate flux (nitrate is stored in the solum). These observations suggest that meltwater nitrate does not move directly to the stream but is stored and released as a result of processes occurring within the solum. To examine these processes and to determine the effect that nitrate stored in the solum has on streamwater nitrate, the SCATS model was run twice. In the first run the solum structure was modified so that the only operational stock or storage compartment in the solum was the mobile solum nitrate object (MOBILE SOLUM NO3 kg). In the second run the solum was structured so as to allow stored solum nitrate to function in two phases, mobile (MOBILE SOLUM NO3 kg object) and relatively immobile (STORED SOLUM NO3 kg object).

The first run, plotted in *Figure 5*, presents observed streamwater nitrate concentrations (OBS C Stream NO3 mgL) and predicted streamwater nitrate concentrations (PRED C Stream mgL) using only the mobile nitrate stock in the solum. When using only one stock no flux can exist between mobile and immobile nitrate stocks. Under these conditions predicted and observed streamwater nitrate concentrations differ considerably.

The second run, plotted in *Figure 6*, presents
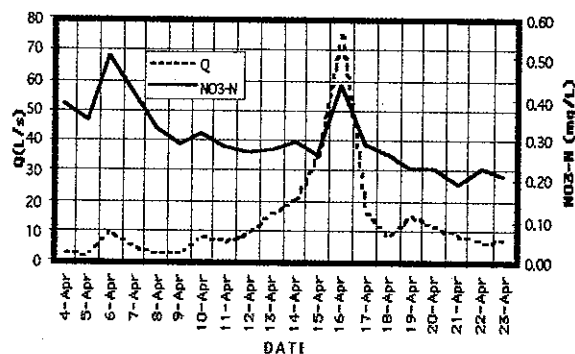
Figure 3. Nettle Brook nitrate during the 1994 Spring melt event.

observed streamwater and simulated streamwater nitrate concentrations using the two-stock solum structure and the flux controlling equations described above (Eqs. 7-9) which are based on varying flow through the solum (Q M and S m3d) and solum water content (SAT SOL cm), shown in *Figure 7*. An improvement in the fit between observed and predicted streamwater nitrate concentrations using the two-stock approach is apparent (*Figures 5, 6*).

DISCUSSION

Snowpack

Estimating snowpack meltwater runoff by the change in SWE from one time interval to the next is a method that has also been used successfully by Rasher et al. (1987). Meltwater is subsequently mixed with precipitation occurring as rainfall. The dominant form of precipitation during the Spring melt event at Nettle Brook was rain (11 days of the 20-day simulation period) and the only snow that fell on the snowpack occurred on April 7-8 which was rapidly converted to water by rain and warm temperatures. This precipitation pattern is common in the region. It has been observed that rain commonly accompanies Spring snowmelt in south-eastern Canada (Tranter, 1991) and in the nearby Adirondack Mountains (Peters and Driscoll, 1987).

Rainfall contains both dry and wet deposition nitrate in the SCATS model. This structure is based on the assumption that dry deposition inputs during the Spring snowmelt period are accumulated on the snowpack or soil surface and contribute nitrate to precipitation nitrate content during the first wet deposition event after a dry deposition period (Johnes and Burt, 1993).

The assumption of nearly complete mixing of precipitation (dry and wet deposition nitrate) with chemically fractionated nitrate from the snowpack

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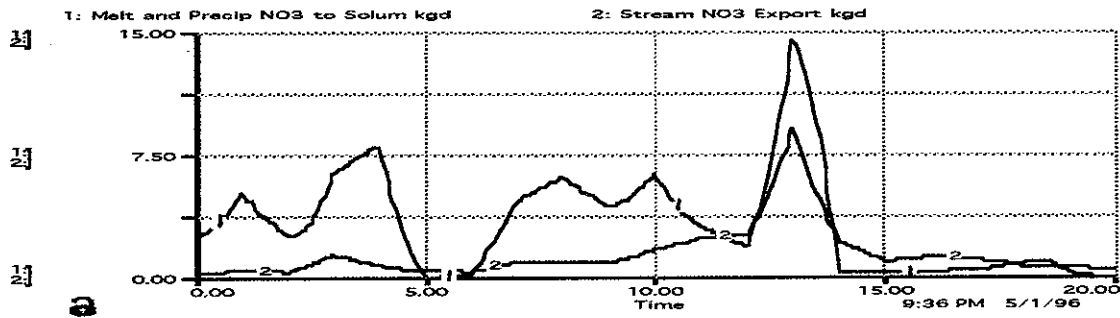
Figure 4. *Nitrate release from the snowpack (curve 1) is greater than observed streamwater nitrate export (curve 2) through most of the simulation period suggesting overall retention of nitrate within the solum. Cold weather and snow decreased meltwater nitrate export on day 5-6 and total snowpack ablation occurred on day 13.*
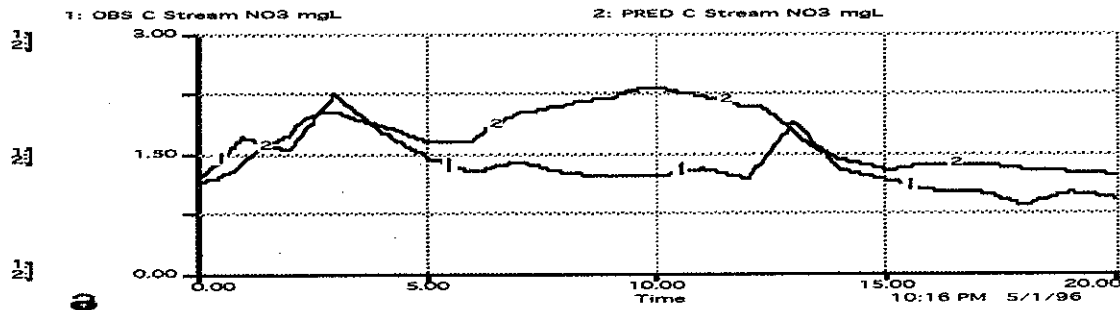
Figure 5. *First Run: One-Stock Solum. It is evident that when only one solum nitrate stock is used in the SCATS solum module that predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) do not fit observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) at Nettle Brook.*
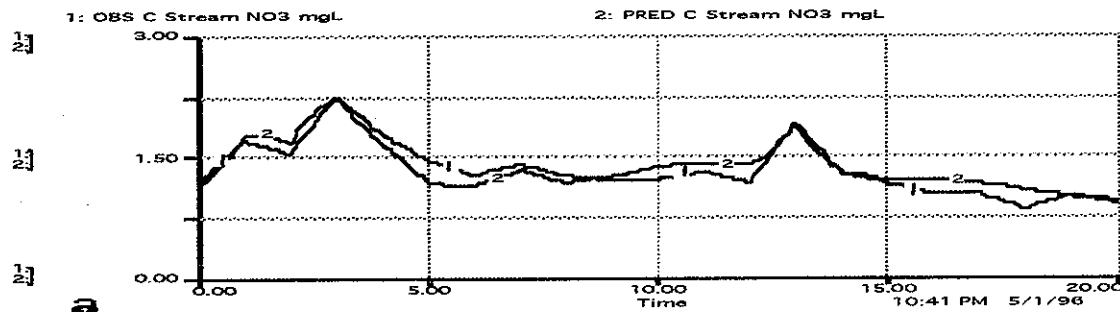
Figure 6. *Second Run: Two-Stock Solum. A considerably better fit was obtained between observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) and predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) using the two-stock solum approach and equations 7 - 9 to control nitrate flux between the stocks.*
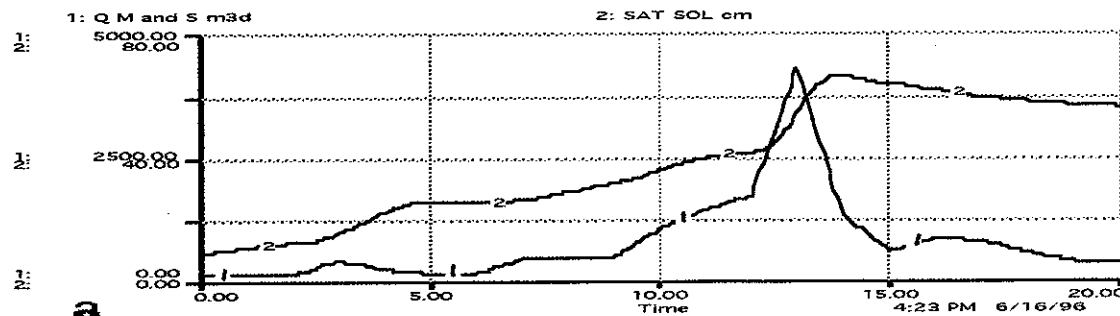
Figure 7. *Flow Rate (Curve 1) and Stored Water (Curve 2) Control Nitrate Flux Between Solum Stocks. Curve 1 represents flow through the solum (Q M and S object) and provides input for equation 7. Curve 2 represents the vertical height of water stored within the solum (SAT SOL cm object) and provides input for equations 7 - 9.*

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during the daily time step is based on the concepts that higher concentration chemically-fractionated solute is located on the exterior of individual snowgrains (Cragin *et al.*, 1993) and that meltwater and rain travels rapidly through the snowpack mixing with the chemically fractionated solute. Snowpack meltwater velocities ranging between 2-60 cm/min have been observed (Male and Gray, 1981). At these rates, precipitation water will have percolated through the snowpack and mixed with meltwater during the course of a daily time step. Using the slowest estimated meltwater velocity (2 cm/min) and the snowpack at its greatest depth during the simulation period (61 cm) water would take less than 31 minutes for percolation through the snowpack.

The litter and surface soil may contribute nitrate to the snowpack as a result of capillary action occurring at the base of the snowpack overwinter. SCATS assumes that this input is accounted for by the incorporation of the contaminated lower layer of the snowpack into the mean snowpack concentration prior to Spring snowmelt. During Spring melt it is assumed that the downward water flux renders further such contributions to snowpack nitrate relatively insignificant. Other potential sources of nitrate inputs to the snowpack include NH_4^+ inputs, particulates from the forest canopy, and photochemical or biochemical reactions. Ammonia oxidized to nitrate in the snowpack prior to March 21 is included in the initial snowpack nitrate load and other nitrate sources were assumed small and ignored.

Modeling chemical fractionation within the snowpack by correlating meltwater concentrations with the quantity of snowpack melted (reduction of SWE) was a method easily accommodated by the STELLA program. The use of equation 5 to simulate chemical fractionation within the snowpack was chosen over more sophisticated methods because of its simplicity and the fact that meltwater sample concentrations were not collected at the site with which to calibrate the results of a more sophisticated approach. Future work investigating nitrate transport in snowmelt using the approach presented in this paper should, if possible, employ a method of determining actual meltwater concentrations during the melt period.

Solum

Mixing of meltwater with mobile solum water in the solum module is assumed to dominate rather than "piston flow" because of the high flow rates that occur during Spring snowmelt events. The spatial and temporal heterogeneity of snowpack ablation rates and soil infiltration rates which occur throughout the catchment on a daily timestep basis also contribute to mixing of meltwater and solum water in the catchment solum.

The solum is treated as a "black box", but some

conjecture as to the possible significance of the equations required to control the nitrate flux between the mobile and immobile solum stocks may be of interest. Two natural phenomena that equation 7 may conceptually simulate on a catchment scale during a daily time step are; 1) differing nitrate release rates (nitrate movement from immobile to mobile water) resulting from the differing chemical and physical properties of differing soil horizons affecting solum water as lateral flowpaths change with fluxes in solum water storage (SAT SOL cm portion of the equation) and 2), increasing nitrate release from storage as the flow of water through the solum increases (Q M and S m3d portion of the equation). This would increase the effects of mechanical dispersion and advection and subsequent transfer of nitrate from the immobile phase to the mobile phase.

Equations 8 and 9 may be hypothesized to represent movement of nitrate into storage (nitrate movement from mobile to immobile water) on a catchment scale during a daily time step. Storage increases as the solum water height increases. A hysteresis effect was observed requiring separate equations for increasing and decreasing solum water content. More nitrate is stored or transferred from the mobile to the immobile nitrate stock as the solum water level rises than when the water level is decreasing. It seems reasonable that less transfer of nitrate would occur as water levels decrease because there would be less of a gradient between mobile and immobile nitrate concentrations as a result of previous nitrate transfer during the rising water stage. The dominant mechanism for the solum water related equations may be diffusion of nitrate from mobile to immobile water.

Stream

Inputs to stream channels can occur as direct precipitation to the channel, overland flow, subsurface stormflow (solum water) and groundwater. Precipitation to the channel is generally insignificant in small upland catchments (Higgins and Burney, 1982) and overland flow is rare in Vermont (Freeze and Cherry, 1978). Therefore, only solum water (Q M and S m3d object) and ground water (Q GW m3d object) were considered as inputs to streamwater in the SCATS stream module.

Leakage into and out of the catchment is usually assumed to be negligible but the extent of leakage is actually unknown in many studies (Johnson and Swank, 1973). Subsurface leakage may significantly affect water and nitrate mass balance calculations and is not accounted for in the SCATS model. Two major storage reservoirs within the catchment are soil pore water and groundwater. An estimation of the storage capacity and flux into and out of these reservoirs would be helpful when calculating water and solute budgets and should be considered in future

work at Nettle Brook.

Naturally occurring tracers provide a useful approach to hydrograph separations and at Nettle Brook was convenient because analysis of streamwater samples included Si. However, soil pore-water samples obtained at Nettle Brook did not yield sufficiently distinct solum and groundwater concentrations, 2.08 and 2.72 mg/l respectively, to separate the hydrograph into solum and groundwater components. Hendershot *et al.* (1992) successfully used concentrations of 2.2 mg/l and 3.9 mg/l respectively. The soil pore-water samples may not have been sufficiently distinct because they were obtained from riparian soils that are subject to considerable fluctuations of the saturated zone, thereby possibly transporting silica from groundwater to solum pore-water or diluting groundwater near the water table with solum water. Further, the concentration observed during peak flow, when flow is typically dominated by solum flow, was only 0.96 mgl. Hendershot *et al.* (1992) found that the low Si concentration observed during peak flow (2.2 mg/l) was close to observed concentrations from solum lysimeters (1.9-2.2 mg/l). The low Si concentration observed during peak flow may be the result of insufficient time for meltwater to come into equilibrium with solum water and/or dilution by meltwater flowing directly to the stream (overland flow) during peak flow. For this study, the high flow low Si concentration (0.96 mg/l) was used for the solum component, and the low flow high Si concentration (2.72 mg/l) used for the groundwater component of the hydrograph separation..

The use of Si as a naturally occurring tracer is based on the assumption that it behaves conservatively and the concentration remains fixed aside from dilution effects. However, Si concentrations are subject to change. The ability of silica in the soil to dissolve rapidly into meltwater, or of silica to be biologically consumed by diatoms may make silica unsuitable for some studies (Hooper and Shoemaker, 1986). Maule and Stein (1990) observed that the silica content of groundwaters varied with time and depth and that subsurface Si concentrations may not attain equilibrium with the substrate. Pearce *et al.* (1986) note that the soil water store may not be completely mixed bringing into question the validity of a simple two-component mixing model. In view of the difficulties encountered with the hydrograph separation in this study, it is suggested that further work conducted at Nettle Brook be based on a more comprehensive method such as was performed by Maule and Stein (1990) in which Oxygen 18 and Si together were used to partition stream water into four components.

CONCLUSIONS

SCATS simulations suggest that elevated streamwater nitrate concentrations observed early in the Spring melt event, initially construed to be the result of chemical fractionation occurring within the snowpack, was more likely the result of processes occurring within the solum. This is in agreement with the findings of other researchers. Peters and Driscoll (1987;1989) found the major control on the chemical composition of stream water to be a result of soil water and ground water contributions.

Another insight was gained by the observation that the SCATS solum module, using mobile and immobile nitrate stocks, was found to provide a structure capable of manipulating nitrate fluxes allowing satisfactory simulation of observed streamwater nitrate concentrations (*Figure 6*). This observation is construed to suggest that partitioning of nitrate into mobile and relatively immobile fractions may occur within the solum and is in agreement with the findings of other researchers (Addiscott, 1977; White, 1985).

These observations could not have been derived from mass balance determinations alone suggesting that relatively simple conceptual models using the STELLA format may provide an important tool for researchers in the interpretation of nitrate transport in snowmelt. It is proposed by the author that using actual snowmelt nitrate concentration data in the snowpack module, and confirming the hydrograph separation in the stream module may lead to development of useful empirical equations based on phenomena occurring within the solum. Equations similar to equations 7, 8 and 9 may be found capable of adequately describing catchment-scale transport of nitrate in the solum on a daily time-step basis at Nettle Brook, and perhaps in other similar catchments. Further, it should be noted that the biogeochemical nitrogen cycle should not be viewed in isolation (Rosswall, 1981). SCATS may also provide a template for modeling other ions, and ultimately, reveal relationships existing among diverse ions in the research watershed thus yielding further insights into streamwater chemistry.

Finally, considering the simple conceptual structure and the intended purpose of this model, the acquisition of knowledge and insights into nitrate transport in snowmelt, SCATS has performed satisfactorily. SCATS was found to be a non time-intensive, economic method which may be used with minimal field data to yield insights into nitrate transport in snowmelt during research conducted at Nettle Brook.

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