# NITRATE TRANSPORT IN SNOWMELT
# IN THE
# GREEN MOUNTAINS OF NORTHERN VERMONT

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# ABSTRACT

Mass balance estimation and modeling of nitrate transport in snowmelt during a 20-day 1994 Spring snowmelt period is presented. The work is based on research conducted at Nettle Brook, a small first order stream in the Vermont Monitoring Cooperative (VMC) research watershed located on Mount Mansfield in the Green Mountains of northern Vermont. Dry and wet deposition data were collected 2 km from the Nettle Brook research site at the Proctor Maple Research Center (PMRC). Streamflow on Nettle Brook was recorded at a weir installed by the United States Geological Survey (USGS). Streamwater samples were collected monthly, except twice daily during snowmelt. Snowpack and soil pore-water samples were also collected. All samples were analyzed for anions, $NO_3$, $SO_4$, Cl, cations, Ca, K, Mg, Na, Al, $NH_4$ , and for Si.

The data were initially interpreted to suggest chemical fractionation occurred within the snowpack during snowmelt. Preferential elution was not evident. Nitrate exported during snowmelt accounted for 33% of the annual export in streamwater. Calculations revealed a loss of 39% of snowpack nitrate prior to spring snowmelt. Calculations based on atmospheric nitrate inputs and observed streamflow nitrate outputs (December 1,1993 - April 23, 1994) indicated storage or loss of nitrate within the watershed of 60% . Similar calculations based on the water year October 1, 1993 - September 30, 1994 indicated a net storage or loss of nitrate within the watershed of 70%.

Development of a conceptual model based on the object-oriented STELLA program using data obtained at the Nettle Brook research site has revealed insights into mechanisms important in determining streamwater nitrate concentrations in snowmelt. The model consists of three modules; snowpack, solum, and stream. Chemical fractionation in the snowpack was modeled by use of an equation derived from data presented by Johannessen and Hendriksen (1978). Release and storage of nitrate in the solum was modeled using a technique similar to that described by Addiscott (1977). Hydrograph separation in the stream was determined using the method of Hendershot *et al.* (1992). Model simulation results suggested that the solum is dominant in determining streamwater chemistry during snowmelt. Streamwater nitrate concentrations originally interpreted as possible evidence of chemical fractionation within the snowpack were most likely the result of processes occurring within the solum. This observation could not have been derived from mass balance determinations alone suggesting that use of a relatively simple conceptual model such as is described here is of great assistance in the understanding of nitrate transport during snowmelt.

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# CHAPTER I

# INTRODUCTION

## 1.1. The Significance of Nitrate: Research Objectives

The first studies investigating nitrogen (N) cycling were conducted during the 18th and 19th centuries. In the middle of the 18th century, Lavoisier and co-workers named the gas "azote" and "nitrogene". In the mid-19th century von Liebig, Boussingault, Lawes and Gilbert engaged in a very active controversy which resulted in many excellent measurements including nitrate concentrations in rainfall (Paul, 1977). Nitrogen occurs in valence states from -3 to +5 and is considered to have one of the more complex biogeochemical cycles (Gundersen and Bashkin, 1994; Moldan and Cerny, 1994; Rosswall, 1981).

Nitrogen is very often the growth-limiting element in terrestrial ecosystems. Most nitrogen contributing to forest growth or exported in streamflow exists in the inorganic forms as nitrate and ammonium. Nitrate ($NO_3^-$) is highly soluble and is more mobile than ammonium ($NH_4^+$) primarily because it is not retained by soil cation exchange sites (Thorne, 1985). In northern Vermont, it has been estimated that 25-35% of annual precipitation occurs as snowfall and is responsible for generating about one-half of the total annual runoff within a 30-day period during spring snowmelt (Dunne and Leopold, 1978). Because of the high flux of water during spring snowmelt, the relatively high solubility of nitrate in water, and the relatively shallow hydrologic pathways dominating high flow events, spring snowmelt is hypothesized to be responsible for major nitrate export from upland forested catchments.

Nitrogen is a nutrient of major importance in the forest ecosystem but nitrogen compounds are also potential toxicants (Rosswall, 1981). Nitrate has been determined to be the most common contaminant found in groundwater (Freeze and Cherry, 1979) and may present problems in surface waters. In the Adirondack Mountains, New York, observed short term adverse effects of excess nitrate include the lowering of streamwater pH and elevated Al in the stream (Peters and Murdoch, 1985; Schofield et al., 1985). In the Catskill Mountains, New York, it has been found that high concentrations of meltwater nitrate usually coincide with low pH and high concentrations of aluminum during late winter and early spring, and appears to play a role in creating toxic conditions for stream biota and particularly fish (Murdoch and Stoddard, 1992; Galvin and Cline, 1978).

In recent times, the cycling of nutrients (i.e. nitrate) and the type and degree of ecosystem management in headwater forested watersheds have become issues of growing concern as a result of the potential effects on terrestrial productivity and water quality downstream of these catchments (Lawrence and Wigington, 1988). Stottlemeyer and Troendle (1992) note that the determination of factors responsible for regulating streamwater ion (i.e. nitrate) concentrations improves our understanding of these ecosystems and potential short and long term ecological problems. The current international global change research program has focused on three areas of environmental research; 1) monitoring of changes, 2) understanding of processes, and 3) development of predictive models (Dozier *et al.*, 1991). The focus of this study is similar to the focus of the global research program in that the monitoring of physical processes is succeeded by modeling of these processes in an effort to gain a better understanding of the processes.

It has been said that research may be roughly divided into two categories, experimental (monitoring) and modeling (Heathwaite *et al.*, 1993). This study incorporates both approaches to examine the hypothesis that spring snowmelt is responsible for major nitrate export from an forested upland catchment in the Green Mountains of northern Vermont. In the experimental phase a field reconnaissance was conducted at the Nettle Brook catchment during which appropriate physical data were collected and subsequently used in the modeling phase to develop a simple conceptual computer model. Specific research objectives were, 1) to estimate depositional inputs of nitrate to the snowpack, 2) to estimate nitrate outputs in streamflow during a spring melt event, 3) to estimate overwinter nitrate mass balance within the catchment, 4) to gain insights into the mechanisms important in the transport of nitrate in snowmelt by developing a simple conceptual computer model based on the field data.

## 1.2. The Small Catchment as a Research Tool

The small catchment is considered to be a basic unit of study in hydrology because it represents an area with an easily definable topographic boundary which, as a first approximation, defines the catchment boundary. In small headwater catchments with shallow groundwater and high relief, the topographic or hydrologic divide generally coincides with the groundwater divide (Jenkins *et al.*, 1994). Precipitation inputs for the catchment area can be readily estimated and surface outputs generally measured at one outflow point. It follows that the small catchment is also an important basic unit for ecosystem biogeochemical studies because element budgets are, in most instances, intimately associated with the catchment hydrology. Water provides a medium for reactions and a method of transport for many elements.

Research and monitoring of small headwater catchments may be used as early warning systems of long term local, regional or global ecological change because such catchments are considered to be sensitive indicators of ecosystem change (Christophersen *et al.*, 1990; Moldan and Cerny, 1994). For example, the increased leaching of nitrate, or changes in the seasonal pattern of nitrate export from a catchment may be early warning of disturbance in the nitrogen cycle. Adverse long term environmental trends such as the occurrence of *nitrogen saturation* in upland forested watersheds is one such issue of current concern. *Nitrogen saturation* has been defined as the declining ability of an ecosystem to retain added N (Aber, 1992) and is an effect that can, in many instances, be related to increased acid deposition resulting from anthropogenic inputs into the atmosphere. This phenomena that can be easily detected and measured by monitoring of streamwater nitrate concentrations. Such trends observed in the small catchment may then be compared to those of other similar catchments to determine if the observed changes are local, or part of a larger regional or global trend. Improved understanding of these ecosystems facilitates the making of informed management decisions that are necessary for the preservation of our natural resources.

## 1.3. Modeling as a Research Tool

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 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 developed during the course of this study is intended to be 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 at Nettle Brook. The model will focus exclusively on the nitrate ion although there are many important interactions between nutrient cycles and ions (Rosich and Cullen, 1982; Rosswall, 1981) as well as transitions involving other ions such as ammonium. It has been asserted that modeling the movement of major ions such as $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $NO_3^-$ and $SO_4^{2-}$ independently of each other should be possible during solute movement in percolating waters (Bales, 1991) and the model is based on this assumption.

## 1.4 Nitrate in the Ecosystem

Nitrate inputs to upland forested watershed ecosystems are dominated by dry deposition inputs (deposition with dry particulate matter), precipitation inputs (deposition with water), and nitrification. Nitrate outputs from these ecosystems primarily occur as hydrologic outputs in streamflow or groundwater seepage, and denitrification requiring the presence of reduced carbon in a low oxygen environment. The following sections discuss the movement of nitrate through the small forested upland catchment ecosystem.

### 1.4.1. Nitrate in the Atmosphere: Dry and Wet Deposition

Dry deposition may be defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation. The dry deposition of sulfur and nitrogen is estimated to supply between 30 and 50% of the total (dry and wet) deposition in the Eastern U.S. on an annual basis (Meyers *et al.*, 1990). These contaminants may originate from industrial emissions, sea spray, plants and wind-blown terrestrial dust. Transport from the source occurs in three steps, aerodynamic transport, boundary layer transport, and surface interaction (Davidson, 1989). Much of the NO and $NO_2$ that enters the atmosphere (primarily anthropogenic inputs) is ultimately removed as $HNO_3$ (Huebert *et al.*, 1983) which accounts for nearly all of dry deposited nitrogen (Meyers *et al.*, 1990). Dry deposition $HNO_3$ is removed from the atmosphere passively by gravitational sedimentation and dissolves according to the equation:

$$HNO_{3(gas)} = H^+ + NO_3^- \qquad (1).$$

Wet deposition refers to the active removal or scavenging from the atmosphere of gaseous and particulate material by rainout, washout or fog scavenging, and subsequent deposition to the earth's surface (Huebert *et al.*, 1983). Wet deposition generally provides the bulk of total deposition except where there is 1) low annual precipitation, 2) the presence of large particles (such as those emitted from volcanoes), or 3) deposition scavenging is minimized by the presence of unrimed snow (Cadle, 1991; Neubauer and Heumann, 1988). Nitrate ions along with sulfate ions in are the major contributors to rain acidity in the Northeast United States (Altwicker, 1983).

Rain drops or snow flakes are nucleated in the atmosphere by micrometer size particles. Rainout includes all processes occurring within clouds. In-cloud removal processes concentrate gaseous material inside dispersed cloud hydrometeors. Chemical processes occurring in this liquid phase often occur at rates much faster than in the gas phase (Carmichael *et al.*, 1983). Washout refers to processes occurring below the clouds. Washout mechanisms include Brownian diffusion, inertial interception and impaction, eddy turbulence and electrostatic and phoretic attraction. The primary scavenging mechanism for micrometer sized particles is inertial impaction (Cragin and Hewitt, 1993).

Snow has been found to be more enriched with nitrate than rain (Tranter *et al.*, 1987). Nitrite and nitrate concentrations in snow average nearly five times the concentration found in rain as a result of more efficient scavenging by snow (Cragin and Hewett, 1993; Huebert *et al.*, 1983). It is considered that, because both winter rains and snows originate from clouds at below-freezing temperatures, this difference in scavenging efficiency must occur below cloud level (washout) and be related, at least in part, to longer residence time in the atmosphere (Raynor and Hayes, 1983). In the Adirondack Mountains, NY, nitric acid was found to be the dominant chemical component in snowfall while sulfuric acid was the dominant component in rainfall (Peters and Driscoll, 1989).

There appears to be no consistent seasonal pattern of deposition of $NO_3$ and $NH_4$ (Meyers *et al.*, 1990; Edmonds *et al.*, 1991) but it has been observed that higher $HNO_3$ and $NO_3$ concentrations in wet deposition usually occurred in the winter (Meyers *et al.*, 1990). and the greatest input of $NO_3$ and $NH_4$ occurred during the spring at monitoring sites (Reynolds *et al.*, 1992). Deposition rates may also be influenced by local effects. The location of forested catchments in mountainous terrain is conducive to elevated atmospheric inputs from orographic precipitation, increased dry deposition as a result of increased wind speeds, and cloud immersion or fog (Ross and Lindberg, 1994).

### 1.4.2. Nitrate in Throughfall and Stemflow

Precipitation falls unmodified on only a small fraction of the forested watershed. Precipitation ion content in throughfall or stemflow may be modified as a result of interaction with plant surfaces in the forest canopy. Ions in throughfall are the sum of incoming precipitation, dry deposition, and foliar leaching (Ross and Lindberg, 1994) as well as being influenced by biological reactions. Nitrogen fixation (increasing $NH_4^+$ concentrations) and uptake (decreasing $NO_3^-$ concentrations) may occur within the canopy (Edmonds *et al.*, 1991). Lawrence and Wigington (1988) deduced that observed nitrate increase after precipitation interaction with the forest canopy may be a result of 1) evaporation of precipitation and subsequent wash-off of nitrate salts, aerosols, or particulates deposited within the canopy, 2) the nitrification of by-products from the decomposition of tissue, or 3) from foliar leaching of nitrogenous compounds.

Forest type and species greatly influence interactions with precipitation. Lawrence and Wigington (1988), in work done on a pine and mixed hardwood forest watershed in Oklahoma, found that oxidized nitrogen concentrations appeared to increase upon rainfall interaction with pine and to a lesser extent in hardwood canopies, and that these concentrations were inversely related to both rainfall and throughfall depth. Stevens *et al.* (1993), in research in a Sitka spruce forest catchment in North Wales, found that the passage of rain through the canopy generally enhanced nitrate concentrations. Edmonds *et al.* (1991), in a study in an old-growth coniferous temperate rain forest on the northwest Washington coast, found no significant difference between precipitation and throughflow nitrate concentrations.

### 1.4.3. Nitrate in the Snowpack

Fahey *et al.* (1986) emphasized the need to understand the role of nitrate storage and release from snowpacks, pointing to the fact that concentrations of anthropogenic N in ambient air of high-elevation areas in the U.S. have increased as much as 30-fold in the last several decades. An established snow cover, as a result of accumulated deposition, may represent the total chemical load on the environment integrated over several months.

However, this load is by no means static. Jones (1987) determined that forest cover is not a passive element in the ecosystem during snowpack evolution. Organic debris may act as a substrate for microbiological activity, which may flourish in snowpacks during snowmelt, and result in immobilization and the loss of $NO_3^-$ (Jones and Tranter, 1989). Almost as soon as snow crystals are deposited they begin to change as a result of metamorphism within the snowpack. Grain boundaries migrate during metamorphism, some grains grow while others are consumed thus affecting the location of solutes. Aside from solute relocation, solute concentration may change. Solutes that have accumulated in a snowpack may produce an ionic pulse during snowmelt. The initial 20-30% of meltwater may remove 40-80% of the solutes within the snowpack during an ionic pulse (Johannessen and Hendriksen, 1978; Cadle *et al.*, 1984; Bales *et al.*, 1989). Among the more important factors contributing to an ionic pulse are 1) *chemical fractionation*, 2) *preferential elution*, 3) *melt-freeze cycles*, and 4) *rain scavenging*.

*Chemical fractionation* refers to the increased release of a particular ion relative to the release of water from the snowpack during snowmelt. At the onset of major melt events, this phenomena has produced the highest concentrations of solute observed in snowmelt (Peters and Driscoll, 1989; Williams, 1993). Ice does not easily form solid solutions with many inorganic compounds and tends to exclude them during ice formation primarily for two reasons; 1) most molecules seem incapable of forming their own hydrogen bonds with the surrounding ice lattice, and 2) there is elastic strain associated with foreign molecules within the ice lattice which is mitigated if the impurities are forced to the edge of the ice molecule. The degree of elastic strain is influenced by differences in the size of ionic radii. In solution, water molecules form a hydrated shell around ions. Electrostatic forces are operative beyond the first shell of water molecules with additional layers having decreasing strength of attachment. The smaller the ionic radius, the larger the radius of hydration. Ions with larger hydrated radii are relatively immobile and are taken up first when the solution freezes. Some ions migrate to the air-ice interface and others to the bond regions between the grains. Recrystallization of snow crystals is believed to leave most of the solutes at the air-ice interface (Davis, 1991). The ionic strength of the surface liquid film formed as a result of exclusion may be quite high (Bales, 1991) and in dry snow may be as high as 10 molar concentration (Dozier *et al.*, 1991).

*Preferential elution* refers to the release of some ions in the meltwater before others (some ions are enriched more than others at any given time). The ions that are taken up before others when the ice crystal forms may then be released later than the other ions in an elution sequence when the ice crystal melts (Davies *et al.*, 1987). The elution sequence of major anions from melting snow has generally been found to be $SO_4^{2-} > NO_3^- > Cl^-$ (Peters and Leavesley, 1993; Brimblecombe *et al.*, 1987; Marsh and Pomeroy, 1993; Tranter *et al.*, 1986) but the sequence can vary. Johannessen and Hendriksen (1978) found that $Cl^-$ eluted prior to $NO_3^-$ in a Norwegian snow but $NO_3^-$ eluted out prior to $Cl^-$ in a Scottish snow. Davies *et al.* (1987) described the sequence as $SO_4^{2-} > Cl^- > NO_3^-$ but noted that elution sequences are variable and cited the need to maintain electroneutrality within the snowpack as one possible reason for this variability.

Tranter *et al.* (1986) propose that condensation nuclei ($Cl^-$ in sea salt aerosols) may be retained within the crystal while species scavenged during precipitation ($SO_4^{2-}$ and $NO_3^-$) are eluted first. Cragin *et al.* (1993) conclude that chemical fractionation and preferential elution are the result of ion exclusion during snow grain metamorphosis rather than chromatographic effects. Ion and chemical exclusion processes during ice crystal growth has been cited as the underlying mechanism by a number of researchers (Marsh and

Pomeroy, 1993; Bales, 1991; Davis, 1991). There seems to be considerable agreement that the snowpack is a multi-component system consisting of at least two components, a brine with a high concentration of solute at the boundary of ice grains, and a nearly pure ice containing low concentrations of chloride in the grain interior (Bales, 1991; Davies *et al,* 1987). The high initial concentrations found in meltwaters are thought to be the result of the leaching of these surficial brines by melt water at the onset of melting. The finding that preferential elution appears to be enhanced with time was construed to indicate that migration of ions into the brine continues with time (Brimblecombe *et al.*, 1987; Davies *et al.*, 1987).

Redistribution of impurities within the snowpack may also occur as a result of *melt-freeze cycles.* In a bench scale experiment, $NO_3^-$ was found to have the highest concentration factor following melt-freeze cycles (Bales *et al.*, 1989). Bales *et al.* (1993) found that melt-freeze cycles can increase ionic concentrations in meltwater several weeks after the initiation of snowpack runoff. It is believed that melt-freeze action increases solute concentrations at surfaces in contact with mobile meltwater as a result of polycrystalline and polygranular ice particles and grain growth. Williams and Melack (1991) found that a series of melt-freeze cycles that occurred after the initiation of snowpack runoff increased the concentration of solutes in the meltwater. Melt-freeze cycles concentrate solutes towards the bottom of the snowpack where they can be quickly removed by initial meltwaters (Colbeck, 1981). Finally, redistribution of impurities within the snowpack by *rainfall scavenging* may result from water flux driven by rainfall events. Nitrate is transported to sites closer to the base of the snowpack where it has the potential for rapid transport out of the pack (Bales *et al.*, 1989). It has been found that elution sequences are not fixed for all circumstances but depend on snowpack conditions at the onset of melt (Bales *et al.* 1989).

Chemical processes occurring within the snowpack are most likely to take place in association with the liquid phase at ice grain boundaries rather than within ice grains

(Brimblecombe and Shooter, 1991; Bales *et al.* 1989). These include gaseous re-emission, photochemical reactions, sublimation, and biological reactions or fluxes. Sunlight may penetrate the snowpack as much as 0.5 m, particularly in the spring when grain size is large (Dozier *et al.*, 1991). Neubauer and Heumann (1988), in a study conducted in Antarctica, observed that re-emission of $HNO_3$ after deposition in surface snow was probably a result of evaporation or photochemical decomposition. Jones *et al.* (1993), in a study conducted in Arctic snowpacks, found that solar radiation did not have an appreciable effect on the snow-atmosphere exchange of $NO_3^-$. In the same study, it was concluded that $NO_3^-$ was retained by snow grains during sublimation, probably as a result of retention in inter-grain boundaries or ice surface quasi-liquid layers. Sublimation may change pollutant concentration as a result of mass loss of the ice (Bales, 1991). Jones (1991), in a comprehensive survey of the influence of biological activity on snow chemistry, found substantial N depletion on litter substrates within forest snowpacks, as well as N additions as a result of the winter activities of vertebrates and invertebrates. Ammonium ($NH_4^+$) that has accumulated in the snowpack overwinter as a result of wet and dry deposition may contribute to streamflow nitrate concentrations during the spring snowmelt event. Ammonium in the snowpack may be oxidized to nitrate (Rascher *et al.*, 1987).

Finally, ion loss from the snowpack prior to spring melt may occur when soils remain unfrozen and infiltration from the snowpack base into the soil can take place. Stottlemyer and Troendle (1992) noted that solutes within a snowpack can migrate downward at temperatures 3-5°C below freezing possibly accounting for the loss of more than 50% of snowpack ions before significant spring melt occurred. However Cadle *et al.* (1984), in comparing snowpack loading of ions and cumulative wet deposition, found no evidence of ion loss before the spring rain/thaw period.

### 1.4.4. Nitrate in the Litter and Soil

Nitrate concentrations in meltwater are subject to change in the litter layer. Snowmelt may be enriched as it passes through the litter layer when soluble nitrate from atmospheric fallout which has accumulated on the litter/soil surface prior to the commencement of snowpack deposition is present (Colbeck, 1981). Rascher *et al.* (1987) found that forest floor processes resulted in a five-fold enrichment of $H^+$ and $NO_3^-$ over snowpack inputs. The researchers hypothesized that recent leaf-fall, forest floor decomposition and mineralization coupled with reduced biological assimilation contributed to the accumulation of solutes (N) on the forest floor during the winter. It has been suggested that decomposing heterotrophs are active during the winter months under a heavy snowpack and that the amount of the increase is influenced by C:N and C:P ratios (Gosz *et al.*, 1973). Microbial assimilation and denitrification may remove some nitrate from meltwaters percolating through the litter. Denitrification may occur if wetted litter develops anaerobic sites within the organic matrix, but snow meltwaters are well oxygenated and the existence of such sites is generally not favored (Jones, 1991).

Nitrate concentrations in meltwater may be further modified in the uppermost soil layers. Of the various forms of N present in soils, only the nitrate ion is leached out in appreciable amounts because it is not readily adsorbed and does not form insoluble nitrate compounds (Vinten and Smith, 1993). Stottlemeyer and Toczydlowski (1990) found that meltwater picked up nitrate from the organic and inorganic horizons of the soil as the water rapidly passed through macropores to the stream. Nitrification and decomposition of organic matter in unfrozen soils may be responsible for nitrate enrichment of meltwaters (Peters and Driscoll, 1989). Nitrate and moisture may move upwards in the soil in the winter and then downwards in the spring (Malhi and Nyborg, 1986).

Nitrate concentrations in meltwater may be further enhanced by oxidation of ammonium as it percolates through the forest floor (Williams and Melack, 1991; Rasher *et al.*, 1987). Ammonium in the snowpack will be eluted during melt and may exhibit preferential elution during the initial thaw (Stottlemyer and Toczydlowski, 1990). Autotrophic nitrifying bacteria obtain energy from oxidation of the eluted meltwater ammonium to nitrite ($NO_2^-$). Nitrite may then be oxidized to nitrate ($NO_3^-$) and contribute to concentrations of nitrate available for leaching.

Nitrate concentrations may be further modified in meltwater in the deeper layers of soil. Elgood (1990) found that soil clearly accounted for most of the increase in groundwater N content during melt events and that most of the water contributing to the rise in water table elevation was pre-event nitrate rich water displaced from the unsaturated zone and capillary fringe area.

### 1.4.5. Nitrate in Groundwater

Groundwater is often the largest water storage component in the catchment and therefore has the potential as a significant nitrate sink. Lysimeter studies suggest that the highest concentrations of nitrate leached from the soil into groundwater occur in the autumn and the early winter, this nitrate being derived from mineralization of soil biomass. The distribution of this nitrate within the aquifer is affected by factors such as the depth of the saturated zone, the saturated hydraulic conductivity of the aquifer, and lithological variations within the aquifer. A groundwater-dominated stream receives much of its streamflow from groundwater which typically has a lower nitrate concentration than precipitation dominated streamflow which has primarily traveled laterally in the upper soil horizons where nitrate may be available for leaching and transport (Burt and Trudgill, 1993). Aside from nitrate ($NO_3^-$), lesser amounts of dissolved N may be present in groundwater than in surface water in the forms of ammonium ($NH_4^+$), nitrite ($NO_2^-$), nitrogen ($N_2$), nitrous oxide ($N_2O$) and organic N.

Nitrate may be lost from groundwater by denitrification in the anaerobic conditions that commonly occur below the water table. Rhodes *et al.* (1986) found that groundwater in the Sierra Nevada had consistently low nitrate concentrations. Of 158 samples, 112 were below detection limits (< 0.001 mg/L). Denitrification most commonly occurs as a biologically mediated process, but may also occur chemically (chemoreduction in a low redox environment). $NO_3^-$ is first reduced to $NO_2^-$, then to $N_2O$, and finally to $N_2$ if complete reduction occurs. Biological reduction may be limited in groundwater by lack of a carbon substrate (Burt and Trudgill, 1993). There is greater potential for N loss as a result of denitrification where transport occurs laterally through a saturated zone containing a carbon substrate capable of maximizing biological activity (Heathwaite *et al.*, 1993).

### 1.4.6. Nitrate in Streamwater

Nitrate concentrations in streamwater typically vary in response to biological uptake. In the northeastern U.S. streamwater nitrate concentrations generally decrease during the growing season ( May - September) and increase during the dormant season (October - April). Streamflow nitrate concentrations during snowmelt are the result of contributions from at least one of the following four components (but most often is a mixture of two or more); 1) direct precipitation on stream channel or overland flow, 2) overland flow, 3) subsurface stormflow, and 4) groundwater discharge. The first component consists of "new" (event water) and the remaining three may contain various amounts of "old" (pre-event) and "new" water (Peters, 1994). At the catchment outlet, the changing mix of these waters with different chemical or isotopic signatures from various parts and depths within the catchment produces the observed chemical response through time (Moldan and Cerny, 1994). Important factors in determining water chemistry are stormflow (rainfall or snowmelt) quantity and quality, evaporation, mineral weathering, topographic relief, vegetative cover and biological activity (Semkin *et al.*, 1994).

The chemical composition of streamwater can vary substantially with discharge as a result of changing flowpaths as flow rates increase or decrease. At low flows streamwater more closely reflects the chemical signature of the catchment geology. Increasing flow generally produces a decline in alkalinity and pH, Si, Ca and Mg and an increase in organic C, K, Fe, Al and $NO_3^-$ as the ratio of lateral flowing water through upper soil layers to deeper waters increases (Moldan and Cerny, 1994).

Aside from changing flowpaths, time differences in the response of streamwater chemistry to catchment inputs as a result of antecedent moisture conditions has been observed (Walling and Foster, 1975). Soils further from the stream impact the stream later in the melt event. Swistock *et al.* (1989) concluded that the importance of soil water to streamwater chemistry increases as storm size and/or antecedent moisture content increases the chance for younger soil water from higher elevations to contribute. During low soil-moisture conditions the dry ground surface and upper soil horizons contain accumulations of readily soluble material (i.e. nitrate). As the variable source area expands, storm runoff will flush this material into the stream along with longer residence time soil-water which may also contain high solute concentrations. The streamwater solute content will reach a minimum towards the end of the storm as the supply of readily mobilized solutes has been depleted. Under high soil moisture conditions, the contributing area will be approaching its maximum extent and the readily soluble material in the upper soil horizons is likely to be depleted from previous percolation of storm waters. Solute concentrations will fall in response to the usually dilute nature of storm runoff that is traveling laterally towards the stream.

### 1.4.7. Nitrate Transport Processes

Water plays the most important role in nitrate transport within the catchment as well as functioning as a chemical solvent and catalyst (Likens *et al.*, 1995). An understanding of nitrate transport therefore requires an understanding of water movement. Snow and soil have voids or pore spaces between ice or soil particles which provide an opportunity for water to pass. Put in the most simple terms, water movement may be classified into three major categories, 1) *saturated flow*, 2) *unsaturated flow*, and 3) *by-pass flow*.

During saturated and unsaturated flow, water flows in response to the hydraulic gradient and is described by Darcy's law (Bedient and Huber, 1992);

$$q = -K(\theta)\frac{\partial h}{\partial z} \qquad (2)$$

where

$q$ = Darcy velocity *(depth/time)*

$z$ = depth below surface *(depth)*

$h$ = potential or head = $z + \psi$ *(depth)*

$\psi$ = tension or suction *(negative depth)*

$K(\theta)$ = unsaturated hydraulic conductivity *(depth/time)*

$\theta$ = volumetric water content

Unsaturated flow follows the same principles as saturated flow but is slower because hydraulic conductivity drops with decreasing moisture content. By-pass flow occurs with the preferential movement of water along specific pathways such as macropores in unsaturated media and pipe-flow in saturated media (Armstrong and Burt, 1993).

Mixing of solutes occurs as meltwater is transported through the snowpack or soil as a result of molecular diffusion and mechanical dispersion. Molecular diffusion increases as the liquid water content of the media increases. Mechanical dispersion increases with the speed of the flowing water and is highly affected by the geometry of snowpack pore spaces. The relative significance of these two dispersive mechanisms may be calculated by use of the Peclet number ($P_e$):

$$P_e = \frac{vd}{D} \qquad (3)$$

where

v = velocity of flowing water

d = grain size

$D$ = coefficient of molecular diffusion

This relationship may be used to estimate the relative importance of the dispersive mechanisms in solute transport. At lower flow rates molecular diffusion becomes more important allowing more impurities to migrate into the slowly moving water from discrete sources. This results in the removal of the largest quantity of impurity with the least amount of meltwater and can result in a higher concentration of impurity at less than maximum flow rates. For instance, the worst case scenario creating the strongest ionic pulse would be a series of melt-freeze cycles concentrating solutes at the base of the snowpack, followed by a slow melt greatly increasing the meltwater concentration as a result of the increased effect of molecular diffusion (Colbeck, 1981).

Nitrate transport processes occurring through the litter and soil include those discussed above but are further complicated by additional factors which may affect nitrate concentrations. These may be organized into physical, chemical, and biological categories, although considerable interaction and overlap occurs. Physical processes include advection, suspension or deposition, dispersion and diffusion. Chemical processes include sorption, ion exchange, crystallization, hydrolysis, oxidation-reduction and photochemical reactions. Finally, biochemical factors may effect reaction rates and directions as a result of the activities of specific microorganism populations (Frere *et al.*, 1982).

### 1.4.8. Nitrate Transport Processes: Spatial Variation

Nitrate in the atmosphere, throughfall and stemflow, snowpack, litter and soil, groundwater, and streamwater is subject to spatial variation. Increased precipitation, therefore increased wet deposition of nitrate, occurs with elevation increase as a result of orographic effects. However, Likens et al. (1995), in research conducted at the Hubbard Brook Research Forest (HBRF) in New Hampshire, observed significantly higher concentrations of $NO_3^-$ and $SO_4^{2-}$ in precipitation at lower elevations. The researchers conjectured that the increase may be related to greater human activity at lower elevations at monitoring sites. A contributing factor may be that precipitation falling on lower elevations has more time for atmospheric scavenging. An increasing quantity of lower concentration precipitation occurs with increasing altitude.

The snowpack may exhibit considerable vertical and lateral heterogeneity (Marsh and Pomeroy, 1993). Denudation or accumulation of snow as a result of transport by wind is a common occurrence. It has been observed that large portions of initial melt may be channeled into distinct flow paths resulting in reduced concentrations of impurities in the first melt fractions (Colbeck, 1981). On the scale of a large watershed, or even a small catchment, some areas may be melting while others are not. The concept of variable source areas is not new, but the effects of spatially distributed snow melt sources on chemical hydrographs are only recently being considered (Davis, 1991).

The distribution of soil type and soil thickness is perhaps the dominant spatial influence on streamwater chemistry. Differences in soil mineralogy, organic matter content, and density contribute to spatial soil chemistry differences. Soil horizons are responsible for vertical variability in soil chemistry. Vertical gradients in soil solution composition may directly affect the chemistry of streamwater as a result of variable contributions of soil horizons to lateral transport (Mulder and Cresser, 1994). As a result of variation of relief, drainage and vegetation (with symbiotic bacteria), soil may develop lateral variation resulting in sequences of different soil types (termed catena). Soils with leached horizons may develop on hillslopes or summits while soils in depressions may become gleyic or accumulate organic matter (Mulder and Cresser, 1994). There is greater potential for nitrate loss as a result of denitrification where transport occurs laterally through a saturated zone containing a carbon substrate capable of maximizing biological activity (Heathwaite *et al.*, 1993; Dowdell, 1976; Doner and McLaren, 1976) but denitrification can also occur in unsaturated soils in anaerobic microsites (soil aggregates) increasing with the size of the aggregates (Paul and Victoria, 1977). Variations in soil density may also affect oxygen availability.

Riparian soils may have the greatest influence on meltwater entering the stream (Hendershot *et al.,* 1992). Because of rapid equilibrium rates meltwater acquires the chemical signature of the riparian soil thus modifying soil water concentrations flowing from locations further from the stream. Denitrification may occur in the riparian zone if the soils remain waterlogged, thus reducing the diffusion of oxygen within the soil and resulting in an anaerobic environment. Oxygen availability determines whether aerobic or anaerobic microorganisms dominate and influences chemical species transformations. Redox potentials determining the progress of many inorganic reactions are also affected by oxygen availability. Spatial variations in soil or streamwater pH affect inorganic as well as organic reactions. The greatest ecological influence is considered to be pH because of the extreme $H^+$ sensitivity of microbes responsible for nitrification and denitrification (Mulder and Cresser, 1994).

### 1.4.9. Nitrate Transport Processes: Temporal Variation

Nitrate in the atmosphere, throughfall and stemflow, snowpack, litter and soil, groundwater, and streamwater may be subject to temporal variations of a long term scale (trend or anthropogenic effect) or short term scale (seasonal, diurnal, or event). Atmospheric inputs are a result of anthropogenic activities and natural phenomena. A primary atmospheric anthropogenic effect causing temporal variation of nitrate transport in upland catchments is the variation of dry and wet deposition nitrate rates resulting from changes in the generation of man-made aerosols. Increasing regulation of automotive and industrial emissions have resulted in decreases of airborne sulfate and nitrate concentrations, thereby decreasing deposition rates into catchments. Seasonal precipitation variability has a great influence on wet deposition nitrate inputs into the catchment. Foster *et al.* (1989) in a study of a deciduous forest watershed in Ontario, Canada, observed that precipitation during the dormant period was double that of the growing season (nitrate was the dominant anion in the precipitation). They also found that nitrate concentrations were higher in streamwater during the dormant period than during the growing season as a result of reduced biologic uptake, another example of temporal variability in response to seasonal changes. Seasonal precipitation variability further influences nutrient chemistry and cycling by affecting the level of the water table and the solute content (Semkin *et al.,* 1994). Throughfall and stemflow also exhibit variation in nitrate concentrations as a result of the effects on biologic activity exerted by seasonal changes to a degree dependent on the climate and vegetation type.

The snowpack may exhibit considerable temporal heterogeneity (Marsh and Pomeroy, 1993) influencing the hetrogeneity of meltwater quantity and quality during melt. At the onset of snowmelt, a significant proportion of meltwater may travel along impermeable layers at the base of the snowpack to the stream, thereby bypassing transport through the soil (Tranter *et al.*, 1987). There may also be considerable diurnal nitrate concentration fluctuation in meltwater as a result of changes of incoming light and heat (Rhodes *et al.*, 1986).

Soil horizon soil solution compositions may vary considerably during the year as a result of 1) variable composition of infiltration water, 2) variability in climatic conditions, and 3) variability in biological activity. The rate of mineralization of N generally increases with increasing soil moisture between the permanent wilting point (-15 bar) and field capacity (-0.05 to -0.1 bar) but decreases above field capacity because of restricted aeration (Vinten and Smith, 1993). Stevens et al. (1993) observed increased nitrate concentrations in streamflow with increased soil temperature up to approximately 7°C, followed by a decrease in concentration with increasing temperature. While the temperature range of 5°C to 40° will support most microbial activity, microbial activity has been observed at lower temperatures. The optimal temperature for nitrification by *Nitrobacter* is 23°C. The optimum temperature for denitrification to occur is above 25°C (De Laval and Remacle, 1976).

Short term temporal variation in the stream flow rates and chemistry in small catchments may be the result of 1) flashy stream discharge with streamflow subsiding rapidly once hydrologic inputs cease or 2) diurnal effects. Flashy stream discharge may be accompanied by rapid changes in runoff water flowpaths and soil chemical signatures. Streamwater nitrate export exhibits short term (diurnal) increases in concentration with increased discharge as well as longer term seasonal variation controlled by temperature dependent biologic processes. Stottlemeyer and Troendle (1992) at an alpine and subalpine catchment in Colorado, note that diurnal temperature fluctuations affect streamflow nitrate concentrations as a result of varying snowmelt rates. Diurnal changes in biological processes also occur in response to changing light conditions. De Leval and Remacle (1976) found that diffuse daylight did not modify the rate of nitrification but that intense light may inhibit the growth of nitrifiers by killing cells. Rhodes *et al.* (1986), during a study in the Sierra Nevada, concluded that nitrate uptake in the stream by periphyton can be significant in the warmer temperatures occurring at the end of spring snowmelt.

### 1.4.10. Nitrate Mass Balance in Small Catchments

Determination of nitrate input, output, and retention within the research catchment provides basic knowledge necessary for more in-depth research. Nitrate within the watershed is transported as a solute in water, therefore difficulties with tracing the transport of nitrate through the watershed may occur as a result of difficulties in quantifying water movement and storage. Given the lack of an impermeable boundary around a research catchment, mass balance calculation problems are compounded when there is a substantial component of groundwater discharge in the form of a spring or seepage into the stream that contains a significant quantity of water flowing from outside of the catchment. Groundwater losses from the catchment also present a problem. Detailed surveys of water table elevation and/or tracer studies must be undertaken to determine the groundwater contribution to streamflow and storage (Armstrong and Burt, 1993). Changes in basin storage (soil water, groundwater, or snowpack) need to be quantified to construct water budgets for shorter time periods such as months, weeks, and individual storms with shorter time periods requiring more detail in storage change (Peters, 1994).

Nitrate concentrations of water in transit through the catchment may be modified to a degree determined by the amount of time that the water resides in a specific location within the catchment. Transit times of water molecules entering the catchment from input to output may range from minutes, for channel precipitation and overland flow, to hours or days for shallow groundwater, to several years for deep groundwater. Transit times are determined by the velocity and pathways of the water particles which are determined spatially by hydraulic conductivity, porosity, topography and rate of groundwater recharge and temporally by storm duration, storm intensity, and antecedent moisture conditions (Moldan and Cerny, 1994).

Much variability exists among watersheds with respect to nitrate inputs and outputs. This variability is the result of many factors (i.e. climate, vegetation type and density, geology, topography, anthropogenic inputs, etc.) as well as the complexity of the interactions among these factors. This fact makes generalizations concerning relationships existing between nitrate deposition inputs and streamflow nitrate outputs difficult. Foster *et al.* (1989), in the Turkey Lakes Watershed (TLW) in Ontario, Canada, found that despite the large potential for nitrification in the soil during the growing season, less nitrate was exported from the basin in surface waters than entered in precipitation. Edmonds *et al.* (1991) in their research in an old-growth temperate rain forest on the northwest Washington coast, observed that the low nitrate concentrations in the soil solution indicated strong nitrogen retention in the ecosystem. In mid-successional deciduous forest ecosystems of the temperate zone N inputs in bulk precipitation are found to be greater than losses via leaching (Melillo, 1981). There appears to be a general agreement among researchers concerning the overall mass balance of nitrate cycling in undisturbed forest ecosystems. They conclude that the typical net result between inputs and outputs, regardless of the details of each, is that nitrate tends to be retained within the undisturbed watershed. A notable exception is the growing concern over the issue of *nitrogen saturation* which is evidenced by increasing nitrate export in a number of upland forested watersheds (Aber, 1992).

## 1.5. Modeling of Nitrate Transport

### 1.5.1. Nitrate in Snowmelt Modeling: Chemical Fractionation

Because nitrate in the snowpack exists as a solute in snowpack water, knowledge of water flux is a necessity in determining nitrate flux. Snowpack water mass is one of the more difficult inputs to quantify in natural hydrologic modeling. Aside from precipitation inputs, water may move into the snowpack upwards from the soil or laterally from outside of the catchment boundary. Upward water movement from the soil towards a freezing front is a phenomenon has been known for several decades that may add water to the snowpack water equivalent (SWE) of the snow cover. However, this mass flux rarely occurs to the extent that it would significantly affect the mass balance of the snow cover (Kuusisto,1986). Lateral transport of water (and solute) into the snowpack may occur as snow blown by wind into the watershed. This phenomenon is more of a consideration in upland watersheds (Cerny *et al.*, 1994).

Elevation differences within the catchment may also be an important factor in snowpack distribution. The World Meteorological Organization, in a report comparing models of snowmelt runoff (WMO, 1986), recommended the subdivision of river basins into elevation zones because of the strong elevation dependent gradients of temperature and precipitation in mountainous areas.

Nitrate is added to the snowpack surface prior to and during spring melt in the form of dry and wet deposition. 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 and has received considerable attention in snowmelt chemistry models, some of which are briefly described below.

Stein *et al.* (1986) coupled a quantitative snowmelt model (SNOW-17) with a simple conceptual model for snowmelt quality based on progressive leaching at the air-snow interface. Inputs for the model are snowpack water equivalent, the mean nitrate concentrations of the snowpack and rain, and k, the leaching coefficient of snow by meltwater. During a melt period without precipitation, the relationship between the nitrate concentration and meltwater quantity is given by the expression:

$$[C]_{i,i+1} = \frac{[C]_0}{\left(H_i - H_{i+1}\right)}\left[H_i e^{-k(H_0 - Hi)} - H_{i+1} e^{-k(H_0 - H_{i+1})}\right] \qquad (4)$$

where

$[C]_{i,i+1}$ = the concentration of the ion in a meltwater sample (mm) discharged during the melt period (μeq $L^{-1}$)

$[C]_0$ = initial concentration in the snow cover immediately before any ablation (μeq $L^{-1}$)

$H_0$ = initial water equivalent of the snow cover immediately before any ablation (mm)

$H_i$ = water equivalent of the snow cover prior to discharge of meltwater sample (mm)

$H_{i+1}$ = water equivalent of snow cover after discharge of meltwater sample (mm)

$k$ = leaching coefficient

The value of $k$ varied among different melt sequences and different ionic species during the same melt period. Jones (1987) commented that although the model described above performed satisfactorily, the model could not be used to predict meltwater quality at the practical operational level as a result of the coefficient $k$ being unknown prior to snowmelt. Stein *et al.* (1986) are studying the relationship between the value of $k$ and the physical and chemical nature of the snow cover.

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

$$\frac{l_2}{f_2} = c(o)X^{\frac{-m}{M}} \tag{5}$$

where

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

$f_2$ = flux of water (l)

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

$X$ = conc factor

$m$ = fraction of the snowpack melted

$M$ = constant

The problem of modeling the snowpack when rain input occurs during melt is addressed by adding rainfall quantity to the water flux in $f_2$ (Gregory et al., 1986).

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

$$\mathrm{c(t)} = E\,\mathrm{c(0)}\exp(-\mathrm{m(t)}/M) \tag{6}$$

where

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

$m(t)$ = proportion of snowpack melted

$E, M$ = constants.

### 1.5.2. Solum Modeling: Mobile and Immobile Water

Nitrate leaching or transport through the soil is a physically complicated process. The basic processes involved 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 action of diffusion and advection which mixes the resident soil solution and the percolating snowmelt or rainfall is termed *hydrodynamic dispersion* (Burt and Trudgill, 1993).

Not all water stored within the soil is affected equally by these processes. 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 1/3 bar down to the wilting point at about 15 bars), and unavailable water which is mostly hygroscopic water held tightly in films about individual soil particles (Amerman and Naney, 1982).

Aside from partitioning within the soil, solute flux varies between soils within the solum. Mulder *et al.* (1990) found that when catchment soils are close to water saturation subsurface translatory flow within organic horizons is an important process controlling stormflow hydrology and chemistry. Huntington *et al.* (1994) found surface soils play a primary role in the control of surface water chemistry. Shanley and Peters (1993) found that as soils become wetter, the upper soil organic horizons exerted more influence on streamwater chemistry. Although watershed runoff may be modeled effectively with little attention to actual flowpaths, understanding chemical transport requires knowledge of these paths (Frere *et al.*, 1982).

The release and storage of nitrate in the solum is a complex process that is not completely understood and remains in great part a "black box". An important concept in the understanding of nitrate transport through the solum is that of mobile and immobile nitrate stores. Mobile water is defined as water held between 0.05 and 2 bar, immobile water is defined as water held between 2 and 15 bar. Immobile water in the soil is primarily retained in the peds, from which nitrate can be transferred to the mobile phase across the mobile-immobile water interface. In addition to solutes being retained in peds because a portion of the water remains relatively immobile, there is additional retention of solute because diffusion between the inside and outside of the peds never reaches equilibrium. 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 by researchers (Addiscott, 1977; White, 1985). Addiscott (1977) used the concept of mobile and retained phases of soil water and solute to model leaching in structured soils. During movement of water in the soil, only the mobile 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).

A later version of the model (Addiscott and Whitmore, 1987) was modified such that equalization does not occur completely between phases (because of the mechanics of diffusion responsible for the movement) thus allowing greater holdback and the addition of a holdback factor to the model. The model is structured such that half of the vertical movement of water and solute occur before the transfer between phases, and half after. This is to take into account the fact that that phase transfer takes place in reality during, as well as after, the downward movement of mobile water. Solute moves downward through the mobile water only, but may also move laterally through the mobile and immobile water (Addiscott *et al.*, 1986). With each soil layer at field capacity, the ratio between the phases remains constant. This ratio is variable for different soils and soil layers. The main uncertainty in their model is considered to be the values assigned to the phases as well as the reality that there is no sharp discontinuity separating the mobile and retained phase. The model has been applied to winter leaching when the soil is at or near field capacity and evaporation is usually small.

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

$$Z_p = \frac{Q}{\theta} \tag{7}$$

where

$Z_p$ = depth of penetration (cm) of displacing solution

$Q$ = quantity (cm) of displacing solution

$\theta$ = volumetric water content

Another simple approach is the Burns (1975) equation, stated as (Addiscott *et al.*, 1986)

$$fh = \left[\frac{P}{P+\theta}\right]^h \tag{8}$$

where

$fh$ = fraction of solute applied at the surface

$h$ = penetration depth (cm)

$P$ = percolating water (cm)

$\theta$ = volumetric moisture content

Less successful portions of basically successful simulations have been attributed to the effects of preferential water movement and the effects of diffusion between mobile and less mobile water in the lower part of the soil profile (Addiscott and Wagenet, 1985).

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. There is also an immiscible volume of water separated from the miscible volume by an interfacial area across which solutes can diffuse. Output is by drainage of the miscible volume. The equations governing the conservation of water and solute within the miscible volume across an n$^{th}$ interval of time bounded by the times $t_{n-1}$ and $t_n$ are:

$$\left(V_n\right)+\left(V_i\right)_n+\left(V_r\right)_{n-1}=\left(V_m\right)_n=\left(V_r\right)_n+\left(V_e\right)_n \tag{9}$$

and

$$\left(C_0 V_a\right)_n+\left(C_i V_i\right)_n+\left(C V_r\right)_{n-1}=\left(C_m V_m\right)_n \tag{10}$$

where

$V_a$ = volume of water applied

$V_i$ = volume of original solution

$V_r$ = miscible volume remaining in soil

$V_m$ = miscible volume

$V_e$ = volume of effluent

$C_0$ = conc of solute in input water

$C_i$ = conc of solute in soil solution

$C$ = conc of effluent

$C_m$ = conc of solute in $V_m$ in the absence of diffusion

The equations describing diffusive transport between the miscible and immiscible volumes and the resulting change in concentration within the miscible volume are:

$$M_n=2A_i\bar{\theta}\left(C_m-C_i\right)_n\left(D_s\Delta t_n/\pi\right)^{1/2} \tag{11}$$

and

$$M_n=\left[\left(C_m-C\right)V_m\right]_n \tag{12}$$

where

$M_n$ = quantity of solute diffusing across interface $A_i$

$A_i$ = interface between miscible and immiscible phases

$\overline{\theta}$ = mean volumetric water content of the soil

$D_s$ = diffusion coefficient of solute in soil

$C_n$ = conc of solute in effluent

White (1985) suggested that because the size of the transport volume changes with time, especially during non-steady flow, a fixed separation between mobile and immobile phases based on soil-water suction or an assumed regular geometry of the immobile phase is inappropriate. White (1985) concludes by noting that a disadvantage of the model is that it requires values for the parameters $D_s$ and $A_i$ which are not easily determined.

Barry *et al.* (1990) in research at the Lac LaFlamme watershed in Quebec, Canada used portions of the HYFOR model (Fox, 1976) that simulated water flux through the soil. The watershed was divided into segments extending from the stream to the topographic divide. Segments were divided into elevation zones. The vertical soil profile was divided into four layers to simulate actual soil layering. The daily vertical flow of water in the soil profile is calculated as a fraction of soil moisture storage by use of the equation

$$F_V = (\theta_0 Z_1)KP \tag{13}$$

where

$F_V$ = vertical flux of water from a soil layer

$\theta_0$ = soil moisture content from previous day

$Z_1$ = soil layer thickness

$KP$ = fraction of total soil moisture ($\theta_0 Z_1$) draining to the underlying layer in one day.

Lateral flow occurs when the vertical flow gradient is low, as when the ratio of the initial soil moisture content in the overlying layer is equal to or greater than 1.25 times that of the underlying layer. Lateral flow is adjusted by the ratio of contributing area to total elevation zone area. The contributing area is calculated as the product of hydraulic conductivity and elevation zone boundary length. This modification simulates the variable source area concept because the contributing area increases as soil moisture content and hydraulic conductivity increase. Model inputs are 1) the daily amount of water reaching the soil surface (i.e. rain and/or snowmelt), 2) the initial soil moisture content of each layer, and 3) the initial lake or stream level. The model parameters are 1) the permeable deposit depth, 2) the saturated hydraulic conductivity, 3) water retention and unsaturated hydraulic conductivity relationships, 4) the average altitude, and 5) the boundary lengths for each elevation zone. Model outputs are 1) water outflow at the outlet, 2) subsurface flow contribution of each soil layer, 3) surface flow (including overland flow and pipe throughflow), and 4) soil moisture of each layer (Barry *et al.*, 1990).

### 1.5.3. Streamwater Modeling: 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 have been used as a reliable method of determining the ground water contribution to streamflow but is cost and time intensive. Mixing processes and mass balance calculations have been developed to determine hydrograph separations (Johnson *et al.*, 1969). With the advent of the use of naturally occurring or introduced conservative tracers to determine hydrograph separations it has been observed that water present in the watershed (old water) prior to an event (new water) can be responsible for more than half of the peak flow (Hooper, 1986). The graphical methods had typically resulted in a low estimate of the contribution of deeper waters (Pinder and Jones, 1969).

A number of techniques have been introduced that yield satisfactory results when calculating hydrograph separations without the cost and time intensity of installation and monitoring of observation wells. These include the use of specific conductance, acid neutralizing capacity (ANC), and end member mixing analysis (EMMA) as well as the use of naturally occurring tracers. Visocky (1969) used the electrical conductance method to estimate the ground-water contribution to storm runoff in north central Illinois. Pilgrim *et al.* (1979) also used specific conductance to estimate groundwater inputs near Stanford, California. The researchers concluded that simple mass balance chemistry methods based on dissolved solids for hydrograph separation may be misleading because contact time with soil pore water was found to affect conductance and it was determined that residence time of infiltrated water could be as short as a few hours. Robson and Neal (1990) used acid neutralizing capacity (ANC) as a naturally occurring conservative tracer in the Llyn Brianne area of Mid-Wales to separate the hydrograph into storm waters and baseflow waters where stormwater is considered representative of soil water and baseflow representative of deeper waters or groundwater.

End-member mixing analysis (EMMA) introduced a new concept into hydrograph separation techniques. EMMA is based on the premise that observed streamwater chemistry is dependent on observed soil water chemistry. This approach requires the identification of a sufficient set of temporarily invariant soil water end-members that mix conservatively. End-members are soil solutions that form the chemical boundaries of possible streamwater observations. Christophersen *et al.* (1990) found that at least three end members were necessary at the Birkenes and Plynlimon catchments. EMMA was unsuccessful for two catchments (Birkenes, Norway and Plynlimon, Mid-Wales) studied by Christophersen *et al.* (1990). However, this approach was successful in a study at Panola Mountain, Georgia in which Christophersen also participated (Hooper *et al.*, 1990). Potential difficulties with EMMA exist. These include the changing chemistry along flow paths as snowmelt or storm runoff progresses and the spatial heterogeneiety (both lateral and vertical) of the physical and chemical characteristics of soils. These characteristics may change substantially within a soil horizon (i.e. catena) and drastically across horizons and result in a tremendous set of possibilities for the resulting soil-water composition (Robson and Neal, 1990). Hooper *et al.* (1990) defend the conceptual validity of EMMA pointing out that although the static nature of such a model seems to contradict the importance of hydrological flowpaths in determining streamwater chemistry, that in fact, the importance of these flowpaths is evidenced in the mixing proportions indicated by EMMA. However, Hooper *et al.* (1990) cite as an issue of concern, the validity of choosing end-members, when, in reality, there exists a continuum of soil solutions with chemical compositions between the end members. Robson and Neal (1990) note that the results of EMMA should not be intended to provide exact mixing proportions, but rather the general nature of the findings are important (i.e. a conclusion such as the important role of deeper waters in storm events).

The use of naturally occurring tracers provides a useful approach to determining hydrograph separations. Pearce *et al.* (1986) in small, steep catchments in New Zealand, used oxygen 18 for a preliminary hydrograph separation. Results indicated that: (1) only 3% of storm runoff could be considered current storm water, (2) most of the mixing occurred on the hillslope and, (3) that subsurface discharge to the stream is an isotopically uniform mixture of stored water. Silica (Si) is present in mountain streams in the northeastern U.S. and is controlled by rock weathering (Vitousek, 1977). Si was one of a number of solutes used by Pinder and Jones (1969) to determine the ground water component at peak discharge. Hooper (1986) used dissolved silica as a conservative chemical tracer with satisfactory results. Maule and Stein (1990) successfully used Oxygen 18 and Si together to partition stream water into four components, 1) surface or meltwater that had never been in contact with mineral soil, 2) recent subsurface water or meltwater which recently entered the mineral matrix, 3) new plus old subsurface or a mixture of meltwater and old water, and 4) old water or pre-event groundwater. Hendershot *et al.* (1992) used Si successfully as a naturally occurring tracer in the Hermine catchment, Quebec, Canada, to separate streamwater into two components, solum water and groundwater.

# CHAPTER 2

# METHODS, RESULTS AND DISCUSSION

## 2.1. The Research Site: Nettle Brook

It has been stated that if snow scientists do not take a holistic approach in their research studies, they may misinterpret the processes driving the chemical changes within the snowpack (Jones, 1991). A fully integrated multi-disciplinary research catchment has the greatest potential for developing precise hydrological or chemical balance sheets. This holistic approach may provide insights into natural systems not obtainable by a highly focused view. While it is a tremendous challenge for scientists to organize themselves into multidisciplinary teams on one site, every opportunity should be taken to encourage this trend and to measure as many parameters as possible (Newbould, 1981).

The maintenance of such a site over a prolonged period of time presents important research opportunities. Annual mass balances are highly variable as a result of climatic variability and single-year data are insufficient to determine trends. This implies that research or a monitoring program should continue for a number of years. Gundersen and Bashkin (1994) suggested that in order to make valid conclusions regarding nitrate saturation and other ecosystem disturbances, long term monitoring (decades) is necessary. In recognition of the research potential available with this approach, the Vermont Monitoring Cooperative (VMC) has implemented a long-term integrated multi-disciplinary monitoring program and data base and maintains several environmental research sites in Vermont. This study was conducted on a VMC research site (Nettle Brook; *Figure* 1) and consequently the research results from this field reconnaissance will be incorporated into the data base being compiled by the VMC.

Nettle Brook, the study site, is located on the southwest slope of Mount Mansfield in the Green Mountains of northern Vermont (44°30' N, 72°51' W) during the period of

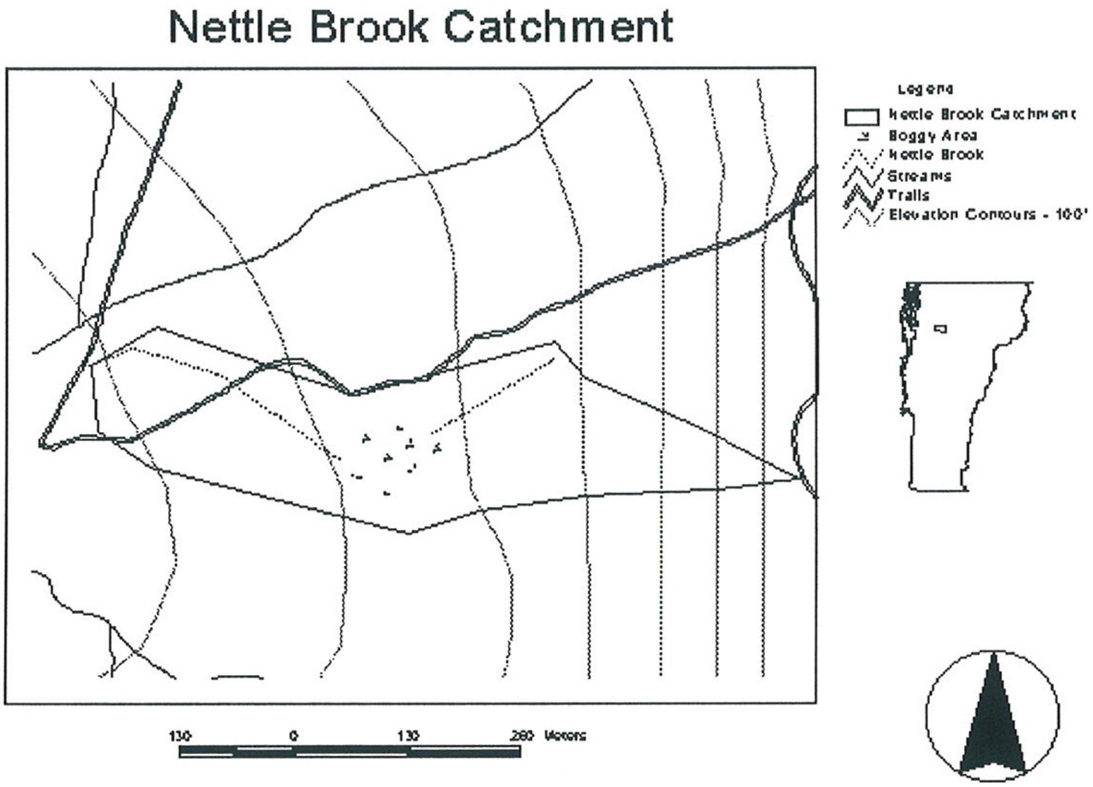

**Figure 1**. Nettle Brook Catchment. Geographical Positioning System (GPS) points were acquired at the catchment and superimposed on a Geographical Information System (GPS) coverage to estimate the catchment boundary and size. The data indicated a catchment area of 106,803.8 m$^2$ or approximately 10.7 hectares (11 hectares were used for mass balance calculations). Nettle Brook flows intermittantly feom east of the boggy area, and year round west of the boggy area. Nettle Brook is groundwater dominated except during flood events.

IN THE FINAL DRAFT I WILL USE A HIGHER DPI + SPELL CHECK, ETC.

October 1, 1993 through February 13, 1995. The drainage basin of the catchment has an estimated area of 0.11 $km^2$ and is drained by a small first-order stream, Nettle Brook. Nettle Brook is groundwater dominated and flows throughout the year below a boggy area and intermittently above the boggy area. The catchment elevation extends from 445 m to 665 m above sea level. Mount Mansfield receives a mean annual total of 1140 mm precipitation at the summit (1339 m) of which between 25 and 35% is snow. The bedrock is predominately mica-albite-quartz schist. The soils are dominated by Peru extremely stony loam, Marlow extremely stony loam, Cabot extremely stony silt loam and Lyman-Marlow very rocky loam. The forest canopy is 70% hardwoods, primarily sugar maple *(Acer saccharum)*, beech *(Fagus grandifolia)*, yellow birch *(Betula alleghaniensis)*. The remaining 30% are softwoods, primarily hemlock *(Tsuga canadensis)* and red spruce *(Picea rubens)* (Wilmot and Scherbatskoy, 1993).

Streamflow at the mouth of the catchment is monitored by a United States Geological Survey (USGS) weir that was installed on 28 September, 1993. Stage is recorded on a Campbell Scientific CR-10 at 5-minute intervals. Stream discharge was calculated from the stage above the 90° v-notch weir. Air, water, soil and snowpack temperatures as well as snowpack depth and reflected short wave radiation were also recorded at the site of the weir.

## 2.2. Nitrate in Deposition to Nettle Brook

Wet and dry 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). The wet deposition station is part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Dry deposition is monitored by the Dry Deposition Inferential Measurement System (DDIMS), part of the Environmental Protective Agency's National Dry Deposition Network (NDDN). Dry and wet depositional inputs of $NO_3^-$ into the catchment during the winter of 1993-94 are presented in *Figure 2*. Dry deposition into the catchment for the period Dec-Mar was 21.6 kg ($NO_3^-$) and wet deposition was 55.6 kg ($NO_3^-$) with a total deposition of 77.2 kg ($NO_3^-$) for the period. These inputs may be construed to approximate the atmospheric nitrate deposition or load to the snowpack prior to the commencement of the spring snowmelt event (April 4, 1994).

Annual dry deposition of $NO_3^-$ for the period October 1, 1993 - September 30, 1994 totaled 7.83 kg/ha ($NO_3^-$) or 86.08 kg ($NO_3^-$) in the 11 ha catchment. Annual wet deposition for the same period was 19.24 kg/ha ($NO_3^-$) or 211.66 kg ($NO_3^-$) into the catchment. Annual total deposition was 27.07 kg/ha ($NO_3^-$) or 297.74 kg ($NO_3^-$) in the 11 ha catchment for the period. Dry deposition accounted for 29% of the total annual input into the Nettle Brook catchment.

Annual total deposition ($NO_3^-$) at Whiteface Mountain in the nearby Adirondack Mts., NY, averaged 22.6 kg/ha for three years, 1985-1987 (Meyers *et al.*, 1990). At Whiteface Mountain, dry deposition accounts for 30% of the total annual deposition (Meyers *et al.*, 1990). Dry deposition of sulfur and nitrogen has been estimated to provide between 30 and 50% of the total annual deposition input (wet and dry) for all sites in the eastern U.S. (Meyers *et al.*, 1990). Meyers *et al.* (1990) note that an annual cycle is not evident in the time series of nitrogen deposition rates, although deposition rates appear higher during the spring period for nearly all sites in the monitoring network.

## 2.3 Nitrate in the Nettle Brook Snowpack and Soil

The snowpack was sampled near the weir at three depths on March 21, 1994, two weeks before the start of the spring snowmelt event. Snow samples were collected in polyethylene plastic bags which had been rinsed with deionized water. The melted samples were transferred to polypropylene plastic bottles which had also been rinsed with deionized water. Samples were stored at 4°C until analyzed for anions ($NO_3$, $SO_4$, Cl), cations (Ca, K, Mg, Na, Al, $NH_4$) and Si. Analysis of anions was conducted on a Dionex 2000i ion

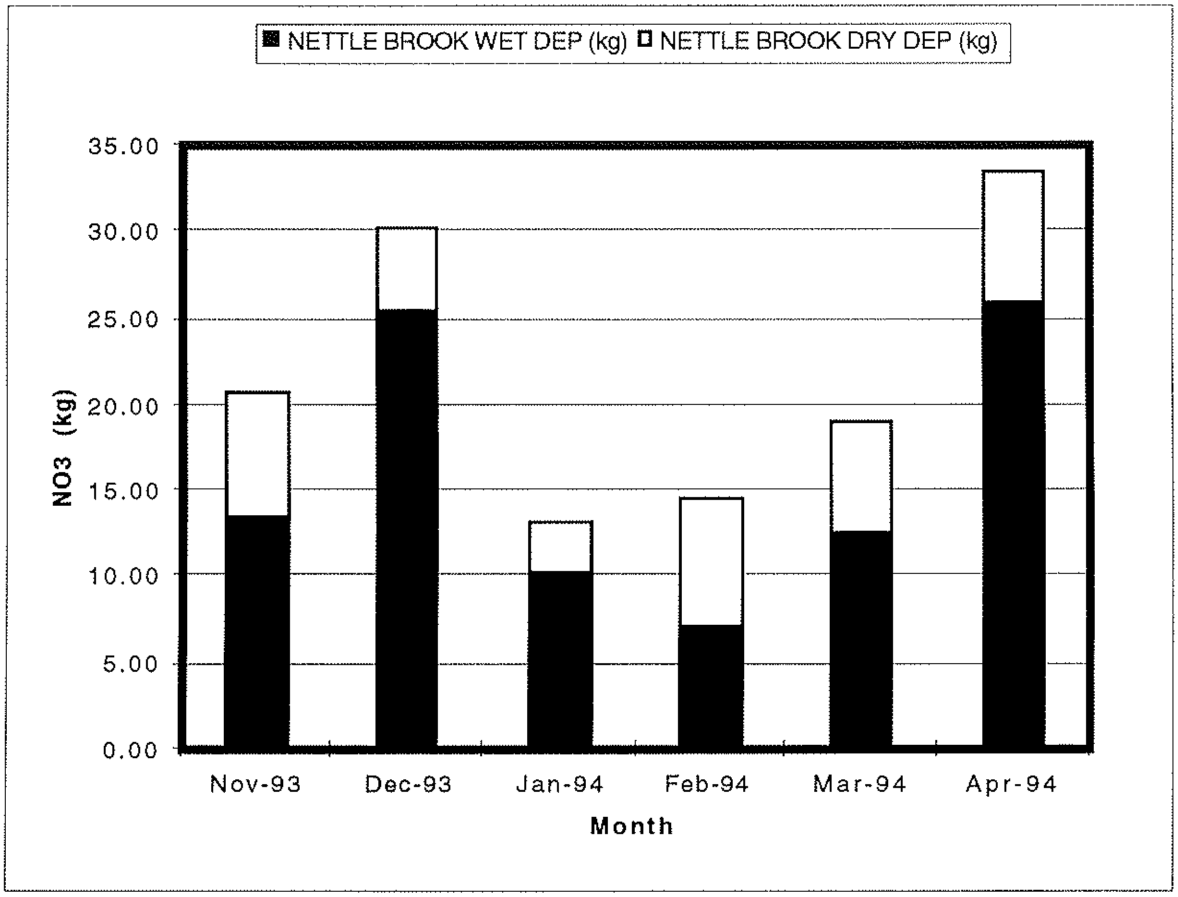

***Figure 2.*** Dry and Wet Nitrate Deposition into Nettle Brook Catchment. Wet deposition inputs dominate as a result of substantial overwinter precipitation inputs into the 11 ha catchment.

chromatograph and analysis of cations was accomplished on a Leeman 2.5 Plasma Spec inductively coupled plasma atomic emission spectrophotometer (ICP) in the Agricultural and Environmental Testing Laboratory at the University of Vermont.

Analysis of snowpack samples (one in each of three layers separated by two ice lenses) yielded $NO_3^-$ values (from snowpack top down) of 1.47, 0.74 and 3.62 mg/L. It is conjectured that the higher concentration layer (1.47 mg/L) overlaying a lower concentration layer (0.74 mg/L) is the result of relatively fresh precipitation on the surface not having had sufficient time for nitrate to leach downwards as did the older intermediate layer. Rasher *et al.* (1987) during research in the Adirondack region observed higher concentrations of chemical constituents in the upper layer of the snowpack and concluded that the depletion of chemical constituents in the lower strata of the snowpack was the result of melting and transport of solutes that occurred earlier in the winter season. Marsh and Pomeroy (1993) observed nitrate concentrations in the top layers of the snowpack that were one to two orders of magnitude larger than the bottom layers of the pack and concluded nitrate depletion, as a result of temperature-gradient metamorphism, was responsible for loss during the winter. It is suspected that the lower layer with the highest concentration observed in samples obtained at Nettle Brook (3.62 mg/L) was contaminated by forest floor litter/soil as a result of moisture from the unfrozen forest floor moving upwards by capillary action carrying soluble nitrate with it into the snowpack although nitrate redistributed from higher in the snowpack may also have contributed to the high concentration. The mean snowpack concentration (arithmetic average) of $NO_3^-$ was 1.94 mg/L. This concentration was exceeded in only 3 of 55 streamwater samples analyzed and those 3 were collected during peak snowmelt flows. Stottlemeyer and Troendle (1990) found snowpack nitrate concentrations typically greater than streamwater concentrations. Approximation of the snowpack load on March 21, 1994 was accomplished by multiplying the mean snowpack concentration by the estimated catchment snowpack water equivalent (SWE) of 24379 $m^3$. The SWE was estimated by multiplying the snowpack depth (0.853 m on March 21, 1994) by the average snowpack density observed at nearby Sleepers River (0.26; J. Shanley, personal communication,) by the catchment area (110,000 $m^3$). The calculated catchment $NO_3^-$ load was 47.3 kg, or 61 % of the overwinter (Dec 1 - Mar 21) deposition $NO_3^-$ input (77 kg). Results indicate a 29.7 kg (39%) loss of deposited nitrate from the snowpack. Rasher *et al.* (1987) found that partial melts in early January and mid-February contributed to the loss of snowpack constituents prior to spring melt. Solutes within a snowpack can migrate at temperatures below freezing. Stottlemeyer and Troendle (1992) reported that a loss of more than 50% of snowpack solute load was observed before significant melt occurred in late March or early April.

Soil pore-water was sampled in riparian soil 10 m upstream of the weir and 2 m from the stream in February, 1995. The rationale for locating the site 2 meters from the stream was based on the assumption that the riparian soil would have the greatest (if not the last) impact on soil water flowing towards the stream. Soil pore-water samples were taken at 4 depths, 2 above and 2 below the water table. The soil pore-water was extracted within 4 hours of obtaining samples using a syringe-pressure technique and apparatus developed by Ross and Bartlett (1990). Samples were stored at 4°C until analyzed for anions ($NO_3$, $SO_4$, Cl), cations (Ca, K, Mg, Na, Al, $NH_4$) and Si using the same methods as for snowpack samples.. Soil porewater sample analysis yielded $NO_3$-N values of 0.46 mg/L (0-13 cm; O and A horizon), 0.70 mg/L (13-16 cm; B horizon), <0.05 mg/L (16-33 cm; B and C horizon, saturated), and <0.05 mg/L (33-46 cm; C horizon, saturated).

## 2.4. Nitrate in Nettle Brook Streamwater

The Nettle Brook hydrograph for the water year, October 1, 1994 to September 30, 1994 is presented in *Figure 3*. Streamwater was sampled at the weir on an approximate monthly basis during the 1993-94 water year with the exception of twice daily during the spring snowmelt period and samples were analyzed as described above.

Sulfate, nitrate and chloride concentrations observed in streamwater samples are presented in *Figure 4*. Preferential elution of ions during snowmelt may be indicated by an elevated concentration of an ion before elevated concentrations of other ions during the early stages of snowmelt. No evidence of preferential elution of sulfate or chloride is observed during the melt period. The highest nitrate concentration during spring snowmelt was observed early in the spring melt period (April 6, 1994) while the highest sulfate and chloride concentrations occurred prior to spring snowmelt on March 2 and March 21 respectively.

Brimblecombe *et al.* (1987) note that, in the field, the effects of preferential elution would not be easy to observe during the initial loss of solute rich meltwater. Tranter *et al.*

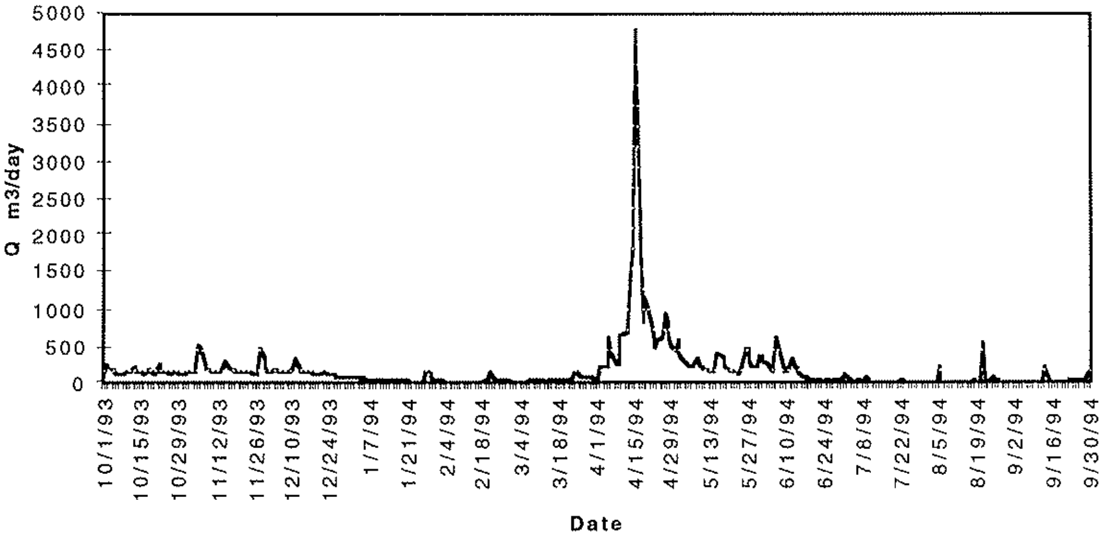

***Figure 3.*** Nettle Brook Hydrograph. Daily flow is averaged from rates recorded every 5 minutes. The spring snowmelt event (April 4 - 23) was responsible for substantially greater flow rates than the balance of the October 1, 1993 - September 30, 1994 water year.

(1987) found that preferential elution of ions was not reflected in the composition of streamwater in the Cairngorm Mountains of Scotland. In melting snowpacks, preferential elution of ions in meltwater can be masked by snowpack scale or catchment-scale hydrology (Davies *et al.*, 1987). Some of the effects that may be responsible for diminishing the streamwater response to preferential elution occurring within the snowpack are (Tranter *et al.*, 1987):

a) snowmelt is likely to break through the snowpack at different times at different places. The initial high concentration meltwaters would then mix with other less concentrated waters during transport to the stream.

b) the heterogeneous distribution of ion concentrations within the snowpack result in different solute concentrations to meltwater at different locations within the catchment.

c) the rapid differential ionic buffering of snowmelt ion concentrations in the soil during transport to the stream.

Results of analysis of streamwater samples for nitrate as $NO_3$-N and stream flow rate during spring snowmelt are presented in *Figure 5.* On April 16, during peak flow,

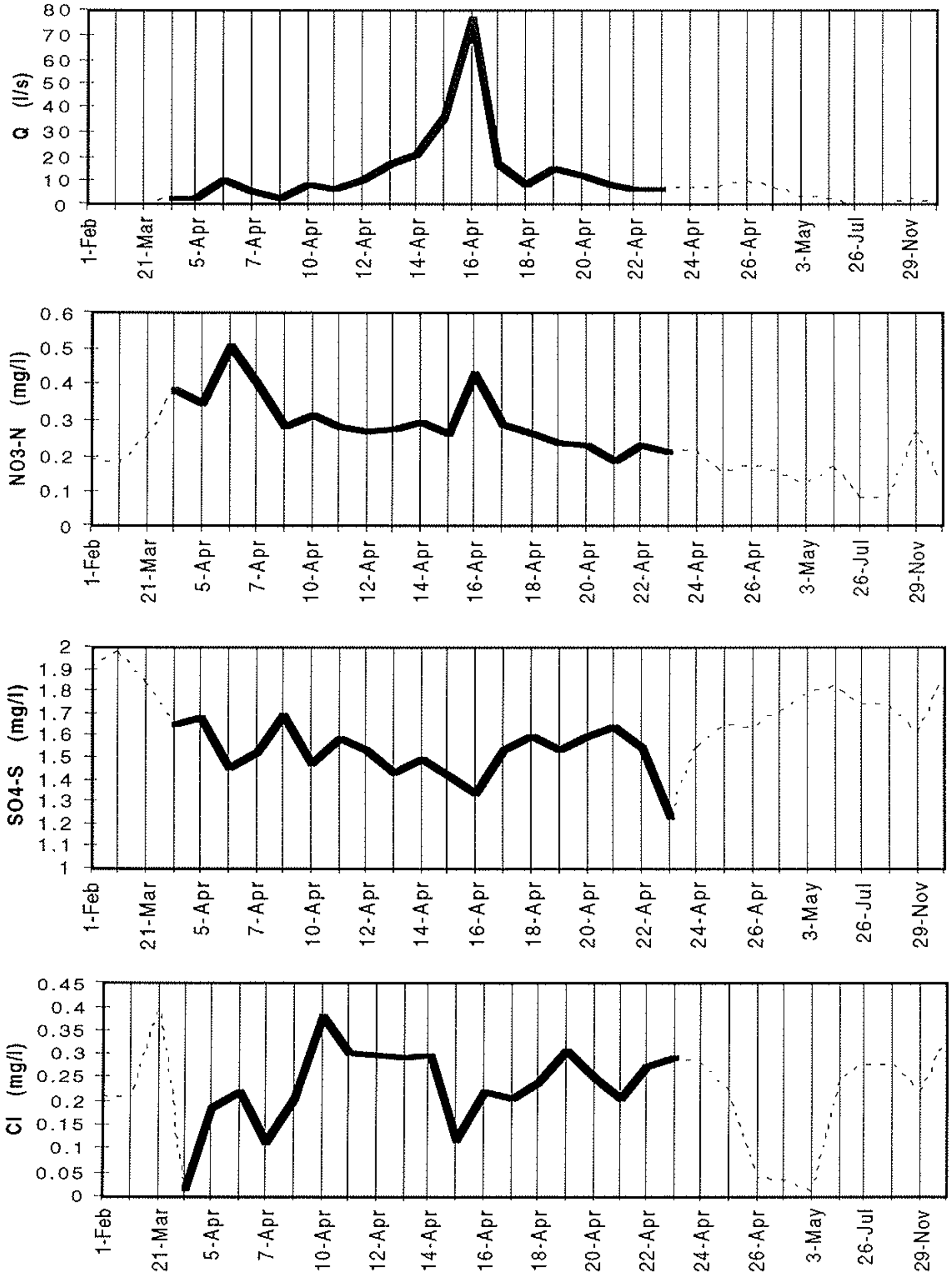

***Figure 4.*** Nettle Brook Nitrate, Sulfate and Chloride Concentrations. The heavier line indicates the spring snowmelt period, April 4, 1994 through April 23, 1994. Nitrate peaks early during the melt period while sulfate and chloride peaks occur at other times of the year.

streamwater samples yielded a $NO_3$-N average concentration of 0.43 mg/L (averaged from 0.509 mg/L and 0.350 mg/L). The highest daily concentration of streamwater nitrate, 0.508 mg/L (averaged from 0.534 mg/L and 0.481 mg/L), was recorded on April 6 at a substantially lower flow rate. Streamwater nitrate concentration typically increases with increasing flow rates during melt events. The highest nitrate concentration observed on April 6, 1994, was initially 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. However, as will be discussed in section 2.6, describing the simulation model developed during this study, this elevated $NO_3^-$ concentration may also be, at least in part, a result of processes occurring within the catchment soils.

## 2.5. Nitrate Mass Balance at Nettle Brook

Total estimated atmospheric inputs of $NO_3^-$ (dry and wet deposition) to the Nettle Brook catchment during the dormant period (October, 1993 through April, 1994) were 157 kg. Estimated streamflow $NO_3^-$ output for the same time period was 63 kg, indicating that the net retention and/or denitrification loss within the catchment was 94 kg or 60% of the input. Total estimated atmospheric inputs of $NO_3^-$ to the Nettle Brook catchment during the growing period (May, 1994 through September, 1994) were 140 kg. Estimated streamflow $NO_3^-$ output for the same time period was 27 kg indicating a net retention and/or denitrification loss within the catchment of 113 kg or 81% of the input. The higher retention during the growing period is probably due to biologic uptake (Gundersen and Baskin, 1994; Johnes and Burt, 1993; Mellilo, 1981).

Total estimated atmospheric inputs of $NO_3^-$ to the Nettle Brook catchment for the water year (October 1, 1993 through September 30, 1994) were 298 kg. Streamflow $NO_3^-$ output for the same time period was 89 kg indicating a net retention and/or denitrification loss within the catchment to be 209 kg or 70% of the input.

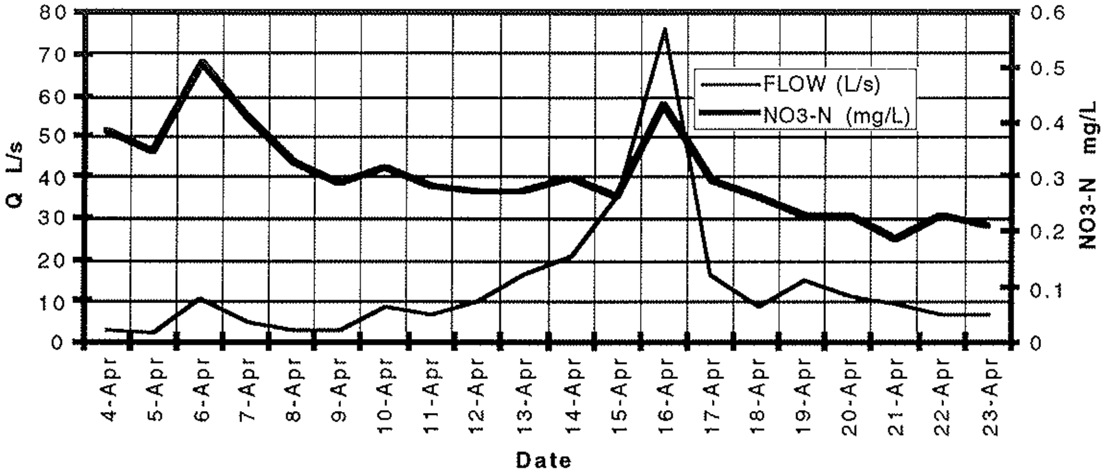

***Figure 5.*** Nettle Brook Nitrate. Nitrate is an ion that typically increases in concentration with increased flow, however the highest concentration during the snowmelt event (April 6) occurred at a substantially lower flow rate than the peak flow (April 16). This could be construed to be evidence of chemical fractionation occurring within the snowpack and sending an ionic pulse to the stream.

Nitrate retention within the watershed is in agreement with the findings of other researchers (Schuman and Burwell, 1974). A nitrate budget calculated for the research catchment at Birkenes, Norway, found that the catchment acts as a net sink for $NO_3^-$ (Christophersen *et al.*, 1982). Most temperate forest ecosystems have a significant capacity to assimilate and retain $NO_3^-$ (Aber, 1992). However Stevens *et al.* (1993), in research conducted at a forest catchment in Beddgelert, North Wales, report an net export of inorganic N which, they concluded, was mainly a result of nitrification rates in the soil being higher than the uptake rate.

The 20 days of spring snowmelt is estimated to account for over 33% of the nitrate export while April 16 alone accounts for 10% of the nitrate export observed. The major nitrate export observed during the Spring snowmelt event (and the largest observed during the year) occurred during the 1994 spring snowmelt event at peak flow on April 16 (*Figure 6* ). Most streamwater nitrate samples were obtained at times of the year other than spring snowmelt during non-event streamflow and, therefore, it is likely that the nitrate export estimate for the year is somewhat underestimated. Regardless, the data indicate that a

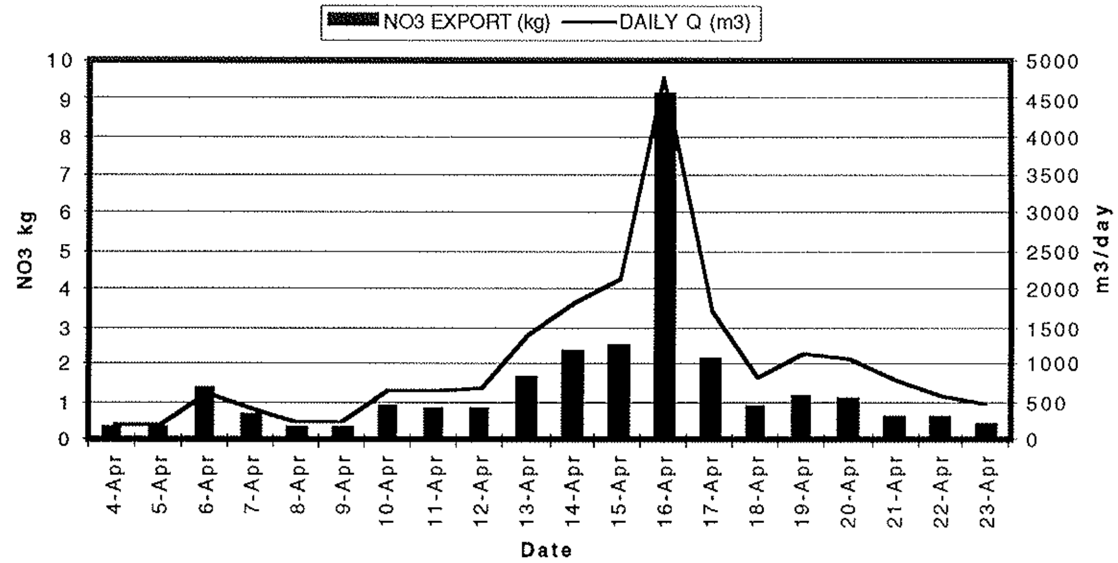

*Figure 6.* Nitrate Export in Nettle Brook Streamwater. The 20-day snowmelt period is estimated to account for 33% of the total annual nitrate export and April 16 to account for 10% of the total annual nitrate export from the catchment.

major nitrate flux occurred during the spring snowmelt period, a finding that is in agreement with the findings of other researchers in northern Vermont (Dunne and Leopold, 1978).

## 2.6. Modeling of Nettle Brook Snowmelt Nitrate

### 2.6.1 Model Types, Format and STELLA Software

A model is a greatly simplified representation of reality and in many instances may be considered in the nature of an hypothesis when dealing with a complex natural system. This is because, in many cases, there is a considerable degree of uncertainty as to which details are important, and even more uncertainty with respect to the values to be assigned to the details chosen (Addiscott, 1993).

There are many considerations and choices to be made prior to the actual development of a model. The initial step in model development should be an assessment of intended application and model objective(s) as well as the realities of data availability and monetary or time constraints. Once this assessment is completed, a model format may be chosen. Model formats may be generally classed as 1) *empirical* or statistically-based (stochastic), 2) *conceptual*, 3) *deterministic* or *process-based*, and 4) *hybrid*.

*Empirical* models include those that establish a statistical correspondence between input and output or those that use simple coefficients to quantify outputs. Watershed research has been significantly enhanced by empirical models but empirical models are limited in that they should be applied only to conditions similar to those in which they were developed (Stone *et al.*, 1990). Such models are, for some applications, capable of adequate prediction, but because of their lack of a physical basis, may not be appropriate when seeking to extrapolate beyond the range of historical data upon which they are based (Johnes and Burt, 1993).

*Conceptual* models occupy an intermediate position between empirical models and deterministic or process-based models. They are commonly formulated on the basis of a simple arrangement of a small number of components, each of which is a simplified representation of one part of the system being modeled. Pursuant to the current interest in the effects of acid precipitation and the buffering capacity of catchments there has been increased interest in the relationships between storm runoff and solute leaching. Conceptual models have been developed to describe solute leaching from small catchments using two or three reservoirs to model runoff components. Such models are usually mathematically simple and requirements for input data are usually modest, making them suitable for management purposes (Johnes and Burt, 1993).

*Deterministic* or *process-based* models are the most complex of the mathematical models. The physically-based parameters of the process models provide a larger measure of confidence in their validity and in their spatial and temporal transferability (Leavesley *et* *al.*, 1988). Another motivation for development of process-based models is that countries in other geographical regions have had difficulties amassing the extensive data base necessary to successfully apply empirical models. It is predicted that, with the development of powerful and readily available personal computers, empirical or statistic-based models will be replaced with technology based on fundamental hydrologic processes (Foster and Lane, 1986). *Hybrid* models combine elements of at least two of the model formats discussed above.

Another general descriptor applied to models of natural systems is *lumped.* Lumping is a procedure employed to calculate "effective or average values" of a particular parameter over an entire area thereby eliminating spatial non-uniformity and excessive model complexity. Lumped models may be based on either process or spatial aggregation or on both (Cosby *et al.*, 1985). A primary advantage of a lumped model is computational efficiency (Higgins and Burney, 1982). The use of "lumped parameters" is more accurate in small catchments than in large catchments because generally the heterogeneity of large catchments tends to be greater (Jenkins *et al.*, 1994). Gregory *et al.* (1986) found that the use of a lumped conceptual hydrochemical model could be used successfully for a small catchment (0.37 km2) but that the use of a distributed model was necessary for a larger basin (3.5 km2) in predicting the effect of snowmelt on streamwater quality.

The major advantage of simple methods is that they provide a rapid means of identifying critical areas with minimal effort and data requirements. The processes involved in the transport of chemicals from a watershed are very complex thus a theoretical model that represents simultaneously all of the processes involved may not be found useful as a practical tool because of the amount of information needed for simulation inputs. 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-empirical hybrid 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 and therefore the use of a purely empirical model, 2) complex deterministic models usually have large computing and data requirements, 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 models which may provide a basis for more sophisticated process-oriented model development. It was found, during the construction of what was initially intended to be a purely conceptual model, that it was necessary to develop empirical equations to simulate processes occurring within the solum, hence the conceptual-empirical hybrid model format was adopted.

### 2.6.2. SCATS

The model developed in this study has been termed SCATS (Small CAtchment Transport in Snowmelt). Nitrate was left out of the SCATS acronym (which otherwise may have been SCANS, Small CAtchment Nitrate in Snowmelt) with the intent that the method developed here may be used for ions other than nitrate by researchers at Nettle Brook.

Using definitions describing models of natural systems presented by Woolhiser and Brakensiek (1982), SCATS is categorized as a *formal mathematical model* with the following attributes. The model may be considered 1) an *integrated watershed model* in that it consists of linked component modules with flow following a logical order, 2) *dynamic* in that variables vary with time, 3) *conceptual* in that the physical laws are so complicated or numerous that it is more appropriate to simplify model behavior, 4) *deterministic* (used in a different sense than when classifying general model types) in that model variables are free from random variation, 5) to use *a "black box approach"* in that the system developed transforms input into output because the physical laws governing the system are too numerous and are not understood well enough to be employed, and 6) *lumped* because input, output or other parameters do not take into consideration spatial variability within the watershed.

SCATS is basically concerned with the movement of water through the watershed and the quantity of nitrate carried by that water, and therefore catchment hydrology is an important element. Using classifications of hydrology models presented by Larson et al. (1982), SCATS may be characterized as 1) an *event* model, focusing on spring snowmelt, 2)a *partial model* in that all flows are not rigorously accounted for (i.e. subsurface flows, and groundwater flows into and out of the catchment), 3) a *measured parameter model* in that inputs can be determined either by measurement or estimation satisfactorily from catchment characteristics, and 4) a *special purpose model* in that the model applies specifically to nitrate transport in a small upland watershed.

#### 2.6.2.1. STELLA Structure

The software chosen to run SCATS is STELLA, an object oriented program (OOP) that has greatly reduced human effort in modeling. Object-based software design may become the methodology of choice in the future (Woodfield, 1988). The STELLA II program has demonstrated it's 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 . Comprehensive and sophisticated models using STELLA have been developed. An example is the SSARR-DS developed by Cassell and Pangburn (1990). The existing SSARR (Streamflow Synthesis And River Regulation) model was modified using STELLA to enhance SSARR's ability to account for cold weather effects while facilitating data input and providing interactive features. 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.

After choosing the appropriate modeling program or software, model development can proceed in the following sequence; 1) *modeling strategy*, 2) *model conceptualization*,

3) *model structure*, 4) *model calibration*, 5) *model testing and verification*, 6) *model development dynamics*, and 7) *display and communication of model results*. (James and Burges, 1982). The *modeling strategy* of SCATS is to simulate water and nitrate movement through the watershed in a logical sequence while integrating water accounting calculations and sample analysis data for a spring snowmelt event. *Model conceptualization* determines the processes and degree of detail to be used in making model results reflect watershed characteristics which for SCATS is basic as possible while still providing a reasonable correlation between simulated and observed output. *Model structure* was developed according to the hypothetical movement of water and nitrate from the snowpack into the soil and subsequently to the stream. The degree of *model calibration* and *model testing and verification* for SCATS was determined by how well model simulation matched the observed data. *Model development dynamics* are explained in careful documentation within the STELLA program (Appendix C) which includes a clear presentation of model strategy, concepts, structure, and recommendations for application of SCATS to other ions and watersheds. The *display and communication of model results* (built into the STELLA software) allows an understanding of model structure, function and utility to other than highly specialized scientists thereby greatly increasing the utility of SCATS for use by other groups.

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

Within the modules are an appropriate combination of the four basic building blocks of the STELLA program; *stocks*, *flows*, *converters* and *connectors*. *Stocks* represent accumulations of material which, for this model, will be water and nitrate. *Flows* (fluxes) fill and drain the stocks. *Converters* change input into output and can define constants, calculate algebraic relationships, and store logic statements, functions or graphs.

*Connectors* provide the appropriate links (information/control) between model building blocks (Richmond and Peterson, 1992).

### 2.6.2.1.1. Snowpack Module

The SCATS STELLA snowpack module structural diagram is presented in *Figure 7*. The snowpack module consists of two stocks, a snowpack water equivalent stock (SWE m3) and a snowpack $NO_3^-$ stock (SP NO3 kg). The initial value for the SWE stock was set at 22000 m3, estimated from the sum of the initial SWE (Table 1: melt day # 0; SWE; 21578 m3) and the snow that increased the SWE value during the simulation period (Table 1: melt day # 5; SWE; 422 m3).

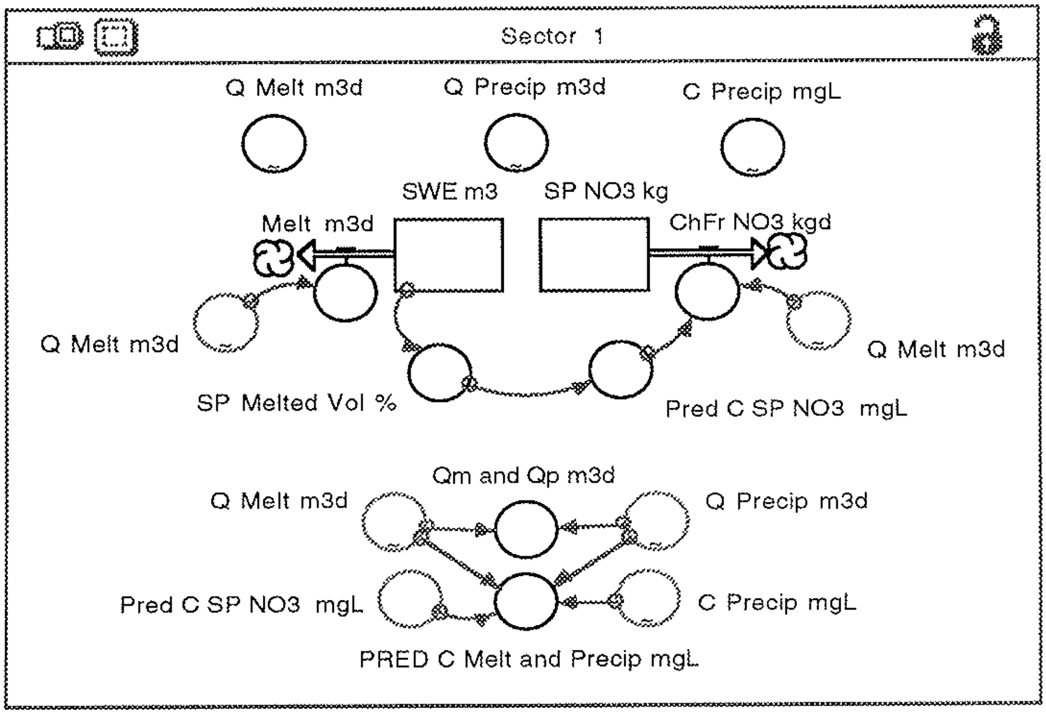

***Figure 7.*** SCATS Snowpack Module STELLA Diagram. The primary function of Sector 1 is to simulate the chemical fractionation of nitrate in the snowpack and to mix meltwater with precipitation containing dry and wet deposition.

The initial value for the snowpack nitrate stock was the product of the mean of snowpack sample concentrations obtained prior to snowmelt on March 21 and the initial SWE stock (1.94 mg/L $NO_3^-$ · 22000 $m^3$ = 42 kg $NO_3^-$) added to 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 (8 kg $NO_3^-$). An initial simulation run indicated that 2.93 kg nitrate remained in the snowpack nitrate stock after total snowpack ablation (SWE stock = 0). Simple mass balance considerations suggest that this amount may have been leached from the snowpack during the two weeks that occurred between snowpack sampling on March 21 and the commencement of the spring snowmelt event on April 4. The initial value of the snowpack nitrate stock was therefore set at 47 kg for all future runs.

**Table 1.** Nettle Brook Water Balance Calculations. Water balance values calculated on a spreadsheet were used as inputs into the SCATS snowpack module. The negative Q melt value on melt day 5 (-422 m3) is due to a SWE increase as a result of snowfall.

| Date (2330) | day # | SP (mm) | SWE (m3) | Q melt (m3) | Q stream (m3) | Q precip (m3) |
|---|---|---|---|---|---|---|
| 3-Apr | 0 | 613 | 21578 | 1795 | 220 | 1254 |
| 4-Apr | 1 | 595 | 20944 | 634 | 234 | 0 |
| 5-Apr | 2 | 585 | 20592 | 352 | 220 | 0 |
| 6-Apr | 3 | 576 | 20275 | 317 | 631 | 2156 |
| SNOW 7-Apr | 4 | 557 | 19606 | 669 | 409 | 2013 |
| 8-Apr | 5 | 569 | 20029 | -422 | 253 | 0 |
| 9-Apr | 6 | 568 | 19994 | 35 | 265 | 0 |
| 10-Apr | 7 | 549 | 19325 | 669 | 663 | 528 |
| 11-Apr | 8 | 508 | 17882 | 1443 | 662 | 0 |
| 12-Apr | 9 | 469 | 16509 | 1373 | 703 | 0 |
| 13-Apr | 10 | 413 | 14538 | 1971 | 1397 | 979 |
| 14-Apr | 11 | 351 | 12355 | 2182 | 1837 | 0 |
| 15-Apr | 12 | 292 | 10278 | 2077 | 2141 | 0 |
| 16-Apr | 13 | 0 | 0 | 10278 | 4801 | 2761 |
| 17-Apr | 14 | 0 | 0 | 0 | 1701 | 55 |
| 18-Apr | 15 | 0 | 0 | 0 | 834 | 33 |
| 19-Apr | 16 | 0 | 0 | 0 | 1164 | 55 |
| 20-Apr | 17 | 0 | 0 | 0 | 1097 | 110 |
| 21-Apr | 18 | 0 | 0 | 0 | 809 | 330 |
| 22-Apr | 19 | 0 | 0 | 0 | 593 | 33 |
| 23-Apr | 20 | 0 | 0 | 0 | 507 | 0 |

Meltwater leaves the snowpack (SWE m3) in the Q Melt m3d flow object. Q melt is calculated on a daily basis from the change in snowpack depth recorded at the weir (Table 1, Column 3). These values were input into the graphical time step object, Q Melt m3d. 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. Snowpack nitrate (kg/day) leaves the snowpack nitrate stock in the ChFr NO3 kgd flow object.

Perhaps the most simple 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):

$$C_I/C_M = 4.4699e^{-0.0466(\text{MELTWATER VOL \%})} \qquad (14).$$

Equation 14 is given in graphical form as a plot of concentration factor vs. percent volume melted in *Figure 8*. The concentration factor ($C_I/C_M$) in *Figure 8* is the ratio of the solute concentration in meltwater ($C_I$) to the original concentration in the snowpack ($C_M$). The mean concentration of $NO_3^-$ in the Nettle Brook snowpack prior to snowmelt was 1.94 mg/L $NO_3^-$. When this mean value is multiplied by the concentration factors in *Figure 9* (derived from *Figure 8* ), a plot shown in *Figure 10* results. This relationship of nitrate concentration (mg/L) vs. percent of snowpack melted (SP Melted Vol %) is described in equation 15 (*Figure 10*) and is embedded in the Pred C SP NO3 object:

$$\text{Pred C SP NO3} = 8.6703e^{-0.0466(\text{SP Melted Vol \%})} \qquad (15).$$

Equation 15 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 (*Figure 8)*). Equation 15 is used in all simulation runs in this work.

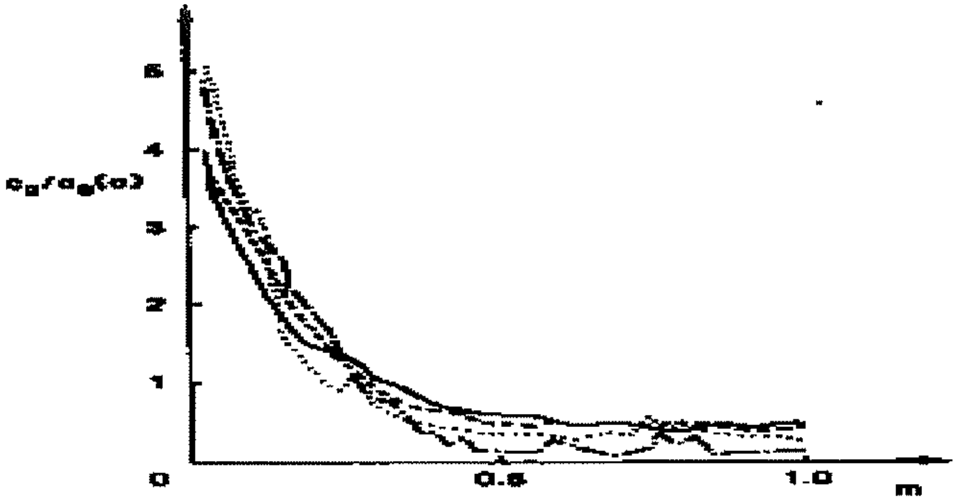

*Figure 8.* Data Plot by Johannessen and Hendriksen (1978). Selected data points for nitrate (dashed line) were acquired from this plot for use in deriving an equation describing chemical fractionation of nitrate in meltwater from a melting snowpack.

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. The 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 3 which was derived from a simple two-component mixing equation similar to that described by Pinder and Jones (1969):

$$C_{PRED} = ((Q_M \text{ x } C_M) + (Q_P \text{ x } C_P))/\ Q_T \qquad (16)$$

where

$Q_T$ = total flow

$C_{PRED}$ = predicted concentration of melt and precip

$Q_M$ = Q melt

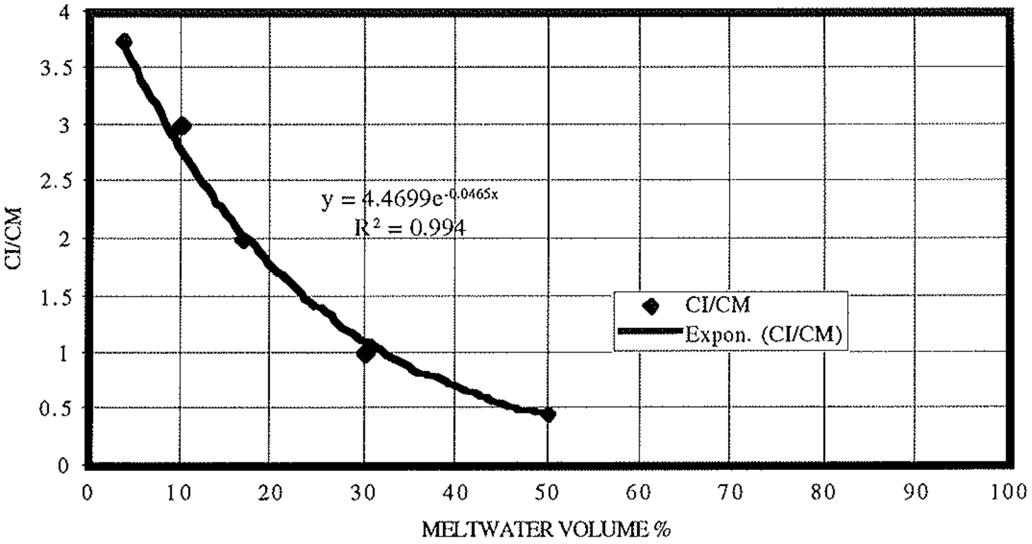

***Figure 9.*** Nitrate Fractionation Equation Based on Concentration Factor. This general equation was derived from data points on the graph in *Figure 8.*.

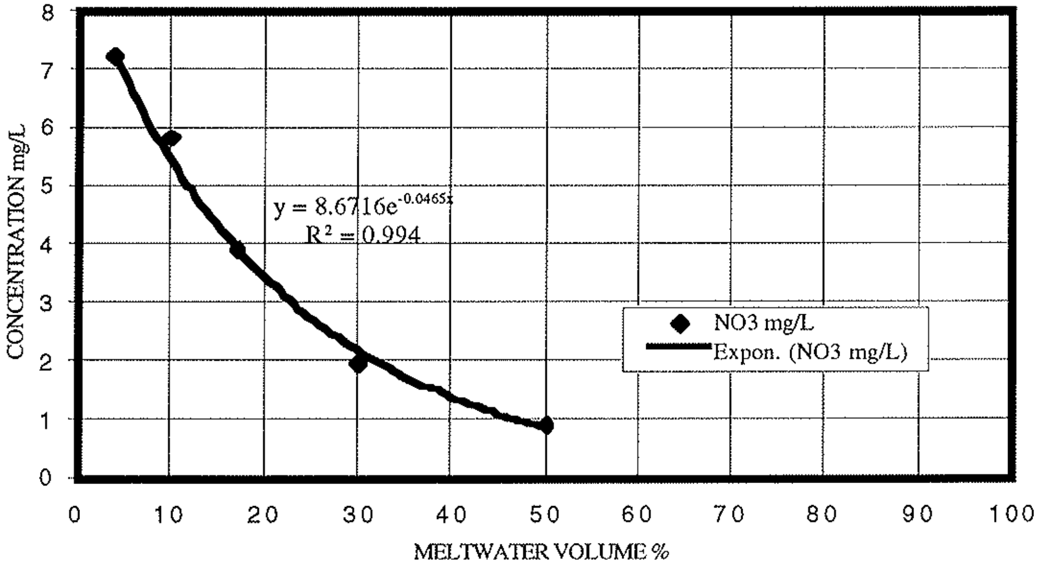

***Figure 10.*** Nitrate Fractionation Equation Based on Nettle Brook Snowpack. The equation was derived by multiplying the concentration factors (*Figure 9)* and the initial Nettle Brook snowpack concentration (1.94 mgl).

$Q_M$ = Q melt

$C_M$ = concentration of melt

$Q_P$ = Q precip

$C_P$ = concentration of precip (dry and 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.

#### 2.6.2.1.2. Solum Module

The SCATS STELLA solum module is presented in *Figure 11*. The method used in the solum module required that three stocks be used, one stock for solum water (SOLUM WATER m3) and two stocks for solum nitrate, mobile nitrate (MOBILE SOLUM NO3 kg) and relatively immobile nitrate (STORED SOLUM NO3 kg).

The mobile solum water stock was given an initial value estimated from Table 1 as Q melt + Q precip - Q stream on day 0 of the melt period. Water input into the solum module is by the snowpack module melt and precipitation output (Qm and Qp m3d). Output from the solum water stock to the stream is controlled by the amount of solum flow (Q M and S m3d) contributing to streamflow.

The initial value for the mobile solum nitrate stock (3.25 kg) 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 (1.15 mg/l). The dry/wet deposition and meltwater nitrate quantity (M and P NO3 kgd) 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 a result in mg/l. Nitrate output

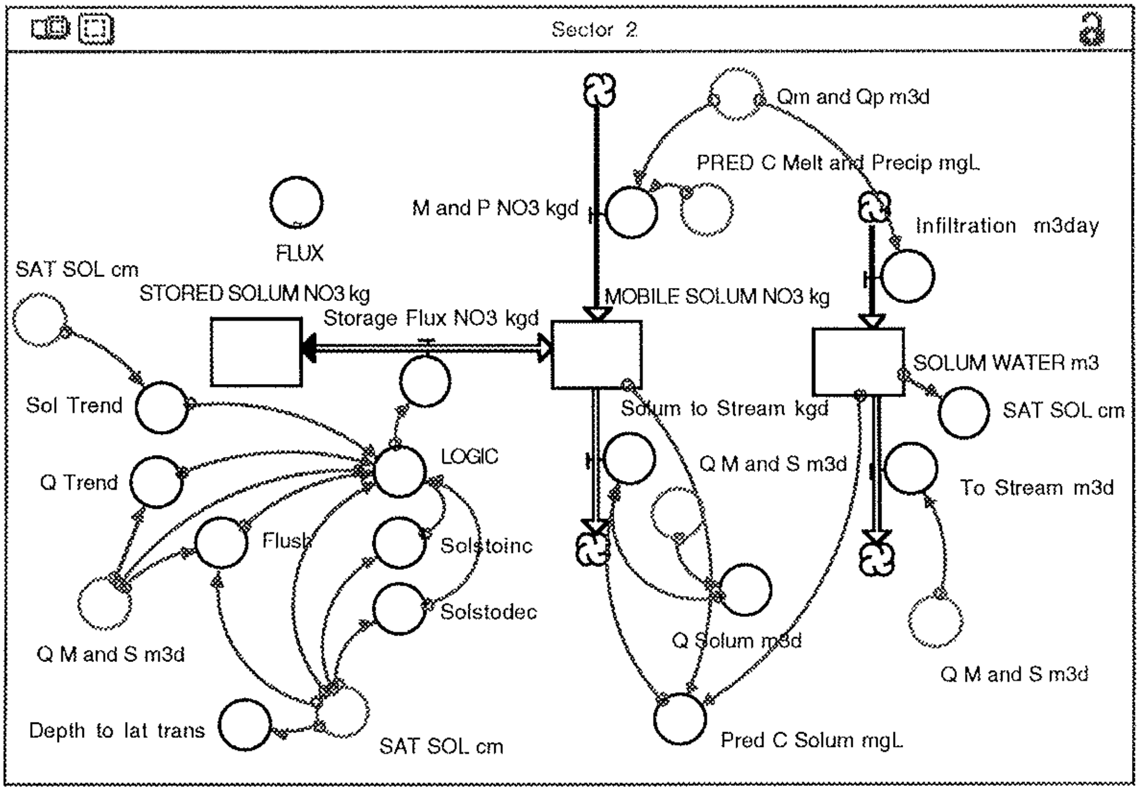

***Figure 11.*** SCATS Solum Module STELLA Diagram. The primary function of Sector 2 is to simulate the storage and release of nitrate in the solum and to mix snowpack meltwater with solum water.

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) and the simulated concentration of the mobile solum water contributing to the stream (Pred C Solum mg/L object). The immobile nitrate stock was given the initial value of nitrate that was calculated to have been lost from the snowpack prior to spring snowmelt (29.7 kg).

Equations based on flow through the solum (Q M and S m3d) and on solum water content (SAT SOL cm) were developed from the data (Appendices) to control nitrate flux between the nitrate stocks. The equation determining nitrate flux from the immobile nitrate stock (STORED SOLUM NO3 kg) to the mobile nitrate stock (MOBILE SOLUM NO3 kg) was input into the Flush object and was applied only when solum Q was increasing:

$$FLUSH = (-0.096(SATSOLcm) + 5.394)e^{0.001(QMandSm3d)} \qquad (17).$$

This equation simulates the flushing of nitrate (kg) from the immobile stock to the mobile nitrate stock as a function of 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). 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; Eq. 18) and the other applied when the solum water level is decreasing (Solstodec object; Eq. 19):

$$SOLSTOINC = 0.0029(SATSOLcm)^2 - 0.276(SATSOLcm) - 0.0007 \qquad (18)$$

and

$$SOLSTODEC = 0.0043(SATSOLcm)^2 - 0.276(SATSOLcm) - 0.0042 \qquad (19).$$

Equations 18 and 19 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). Application of 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 flow as the product of the predicted mobile solum concentration (PRED C Solum mgL object) and solum Q (Q M and S m3d object).

#### 2.6.2.1.3. Streamwater Module

The streamwater module for the SCATS model is presented in *Figure 12.* The hydrograph separation in the streamwater module was determined using silica as a naturally occurring conservative tracer. Si concentrations and Q vs. time at Nettle Brook are presented in *Figure 13.* Si is diluted with increasing discharge as a result of its conservative behavior in the catchment ecosystem. Using a representative concentration for low flow ($C_g$) and the observed low flow rate ($Q_g$), SCATS calculates a two-component mixing ratio developed from mass balance equations for groundwater and solum components as follows (Hendershot *et al.,* 1992):

$$Qt \times Ct = (Qg \times Cg) + (Qs \times Cs) \quad (20)$$

and

$$Qt = Qg + Qs \quad (21)$$

where

$Qt, Qg, Qs$ = discharge from stream, groundwater, and solum respectively

$Ct, Cg, Cs$ = silicon concentration of stream, groundwater, and solum respectively

Groundwater and solum contributions to total streamflow are calculated by

$$Qg = \text{ä}(Ct - Cs)/(Cg - Cs)\text{ä}Qt$$

(22)

and

$$Qs = Qt - Qg \quad (23)$$

The predicted Si concentrations (*Figure 14* ) are obtained from the following equation:

$$Ct,pred = (Qg \times Cg + Qs \times Cs)/Qt \quad (22)$$

where

Ct,pred = Predicted total conc of Si (mg/L)

Cg = Si conc of groundwater determined at low flow(mg/L)

Cs = Si conc of solum determined from conc at high flow (mg/L)

Qs = Predicted flow from solum (m3/day)

Qt = Observed streamflow (m3/day)

The hydrograph separation was derived by employing the following equation describing Qs which allowed the closest fit between observed Si and predicted Si concentrations at Nettle Brook (*Figure 14*):

$$Q_s = 0.34(Q_t - 21)^{1.13} \quad (25)$$

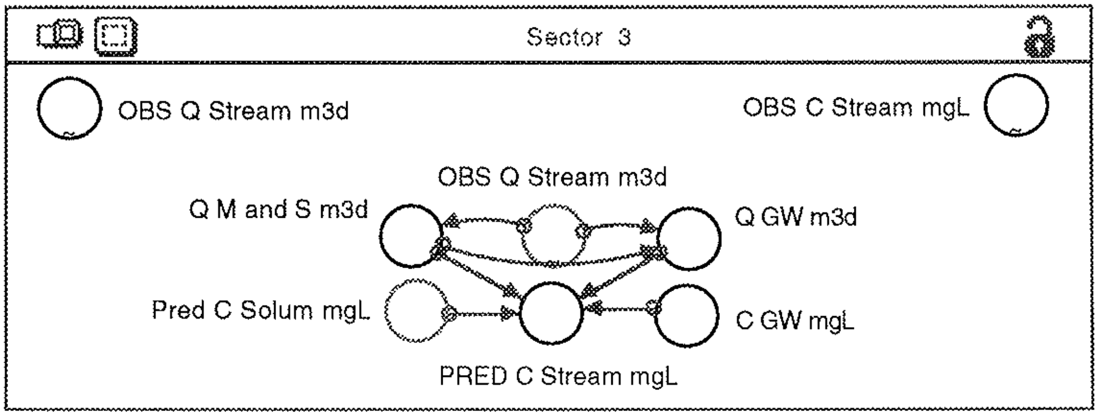

***Figure 12.*** SCATS Stream Module STELLA Diagram. The primary function of Sector 3 is to mix the varying solum water nitrate concentrations with a fixed groundwater nitrate concentration. The hydrograph separation was accomplished using Si as a naturally occurring conservative tracer.

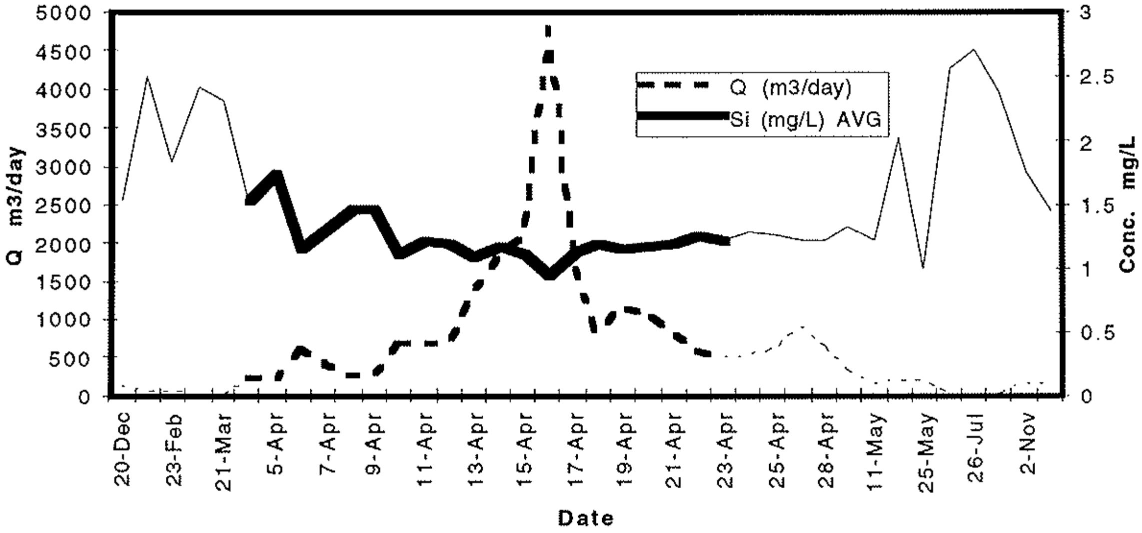

***Figure 13.*** Si Concentrations at Nettle Brook. This plot for 1993-1994 demonstrates the typical pattern of decreasing Si concentrations with increasing flow rates. Note that the darker line denotes the period simulated and that most data points on the plot are during the spring snowmelt period.

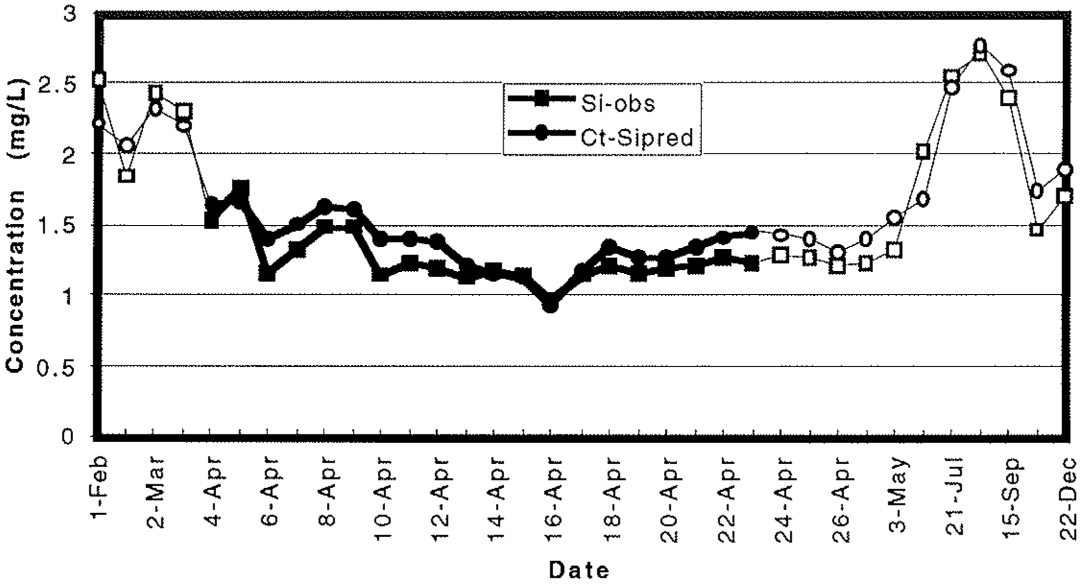

***Figure 14.*** Nettle Brook Observed and Predicted Si Concentrations. Ct-Sipred was predicted from equation 22. Qs (equation 23) describing the solum contribution to streamflow was derived by observing the graphical response and fit of observed to predicted Si concentrations while manipulating the variables in the equation. Note that the darker line denotes the period simulated and that most data points on the plot are during the spring snowmelt period.

The procedure used by Hendershot *et al,* (1992) was modified for this research in two ways. First, the Si concentration value for Cg was the streamwater Si concentration observed at base flow (21 m3/day), 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 Cs was the streamwater Si concentration observed at peak flow (4801 m3/day) during the spring melt event fromstreamwater sampling, rather than from soil pore-water samples obtained from the solum above the water table. *Figure 15* presents the hydrograph separation resulting from the use of equation 25 to give the best fit between observed and predicted streamwater Si concentrations describing the solum portion of streamflow in SCATS. The negative

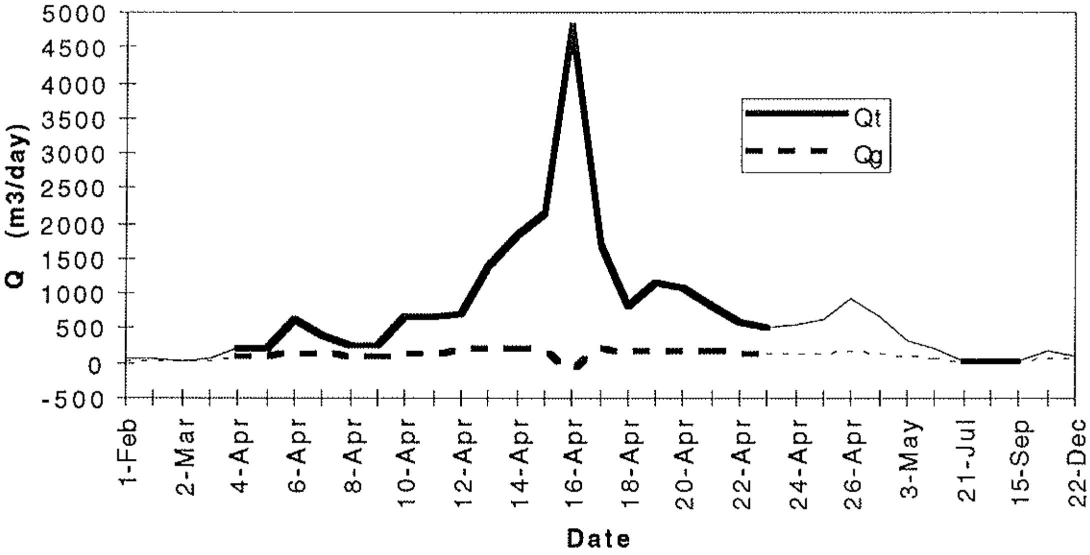

***Figure 15.*** Nettle Brook Hydrograph Separation. Groundwater dominates the hydrograph at all but the highest flow rates as is observed during the spring snowmelt event. Note that the darker line denotes the period simulated and that most data points on the plot are during the spring snowmelt period.

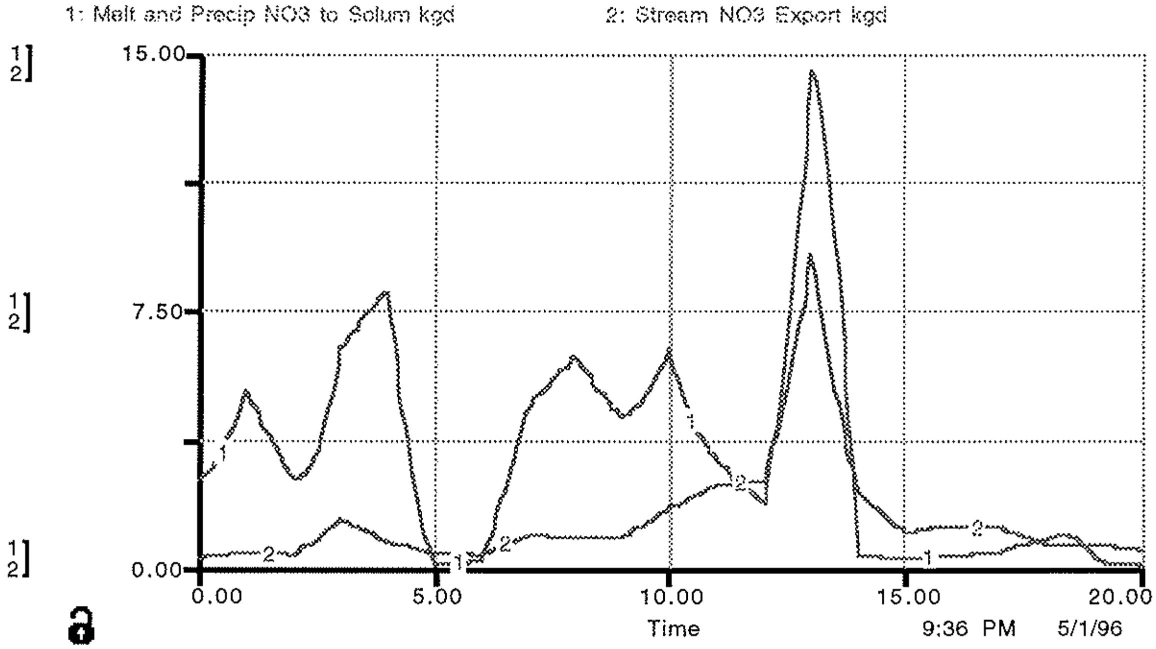

***Figure 16.*** Snowpack Nitrate vs. Streamwater Nitrate. In this STELLA plot curve 1 is simulated nitrate release from the snowpack and curve 2 is observed streamwater nitrate export from the catchment. Cold weather and snow decreased meltwater nitrate export on day 5-6 and total snowpack ablation occurred on day 13 of the 20-day simulation period. Nitrate input to the solum during periods when no melt occurred was the result of wet and dry deposition nitrate in rainfall.

groundwater contribution to streamflow at peak flow is a result of bank storage and is not uncommon during flood events (G. Pinder, personal communication).

### 2.6.2.2. SCATS Results

Simulated meltwater nitrate release from the snowpack using the equation derived from Johannessen and Hendriksen (1978) and the observed streamwater nitrate export determined from streamwater samples are plotted in *Figure 16* as curves 1 and 2 respectively. The curves differ in the temporal distribution of nitrate flux and in the quantity of nitrate flux. These observations suggest that meltwater nitrate does not move directly to the stream as a result of processes occurring within the solum that are capable of modifying nitrate flux from the snowpack and storing nitrate within the solum.

To examine processes occurring within the solum 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 it was assumed 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 solum nitrate was allowed to function in two phases, mobile (MOBILE SOLUM NO3 kg object) and relatively immobile (STORED SOLUM NO3 kg object) as suggested by Addiscott (1977).

The first run, plotted in *Figure 17,* 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 module and the hydrograph separation determined in the streamwater module. 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 18,* presents observed streamwater and simulated streamwater nitrate concentrations using the two-stock solum structure and the flux controlling equations described above (Eqs. 17-19). These equations are based on varying flow through the solum (Q M and S m3d) and solum water content (SAT SOL cm), shown in *Figure 19*. There is a significant improvement in the fit between observed and predicted streamwater nitrate concentrations using the two-stock approach (*Figures 17, 18*). This observation suggests that streamwater chemistry at Nettle Brook is significantly affected by processes occurring within the solum during spring snowmelt and that these processes operate in a manner that can be simulated by using two phases, mobile and immobile, to describe nitrate storage and release within the solum.

### 2.6.2.3. SCATS Discussion

#### 2.6.2.3.1. Snowmelt

Equation 12, derived from graphical data presented by Johannessen and

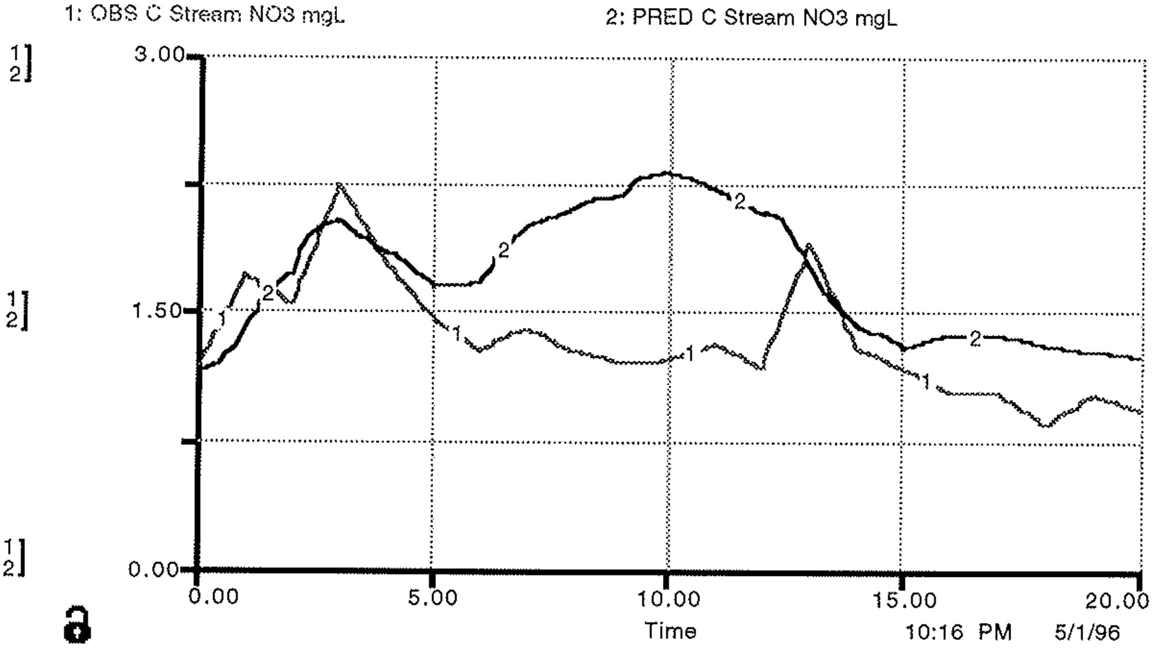

***Figure 17.*** First Run: One-Stock Solum. In this STELLA plot it is evident that when only one solum nitrate stock is used in the SCATS solum module that predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) do not fit observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) at Nettle Brook.

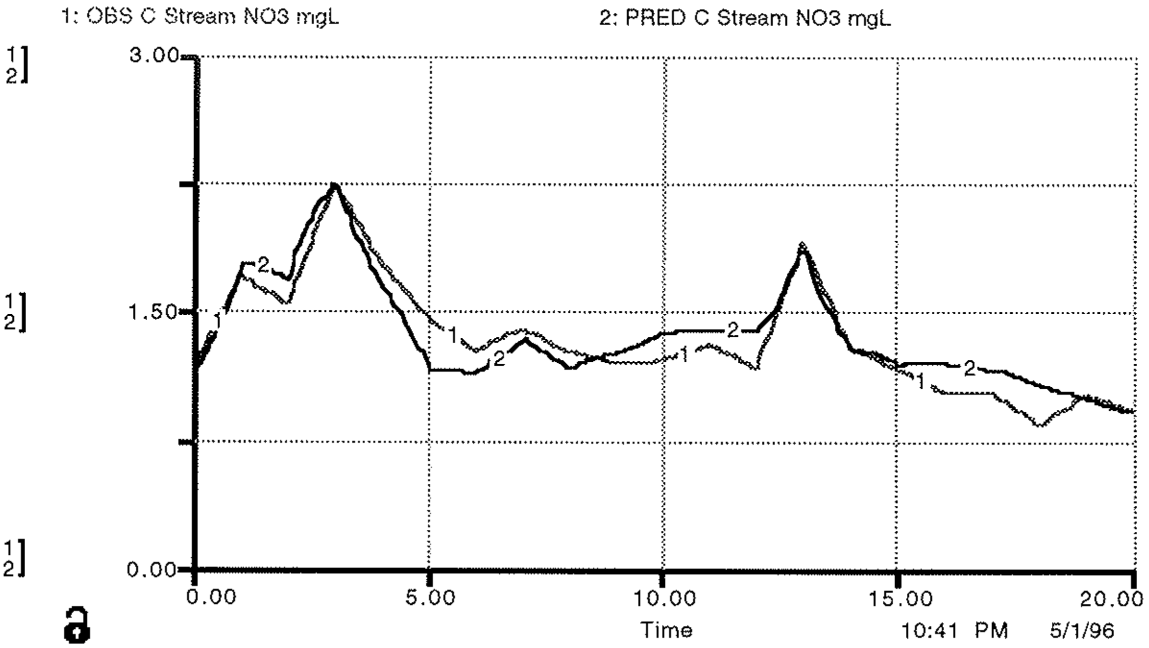

*Figure 18.* Second Run: Two-Stock Solum. In this STELLA plot a better fit is observed between predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) and observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) using the two-stock solum approach and equations 15-17 to control nitrate flux between the stocks.

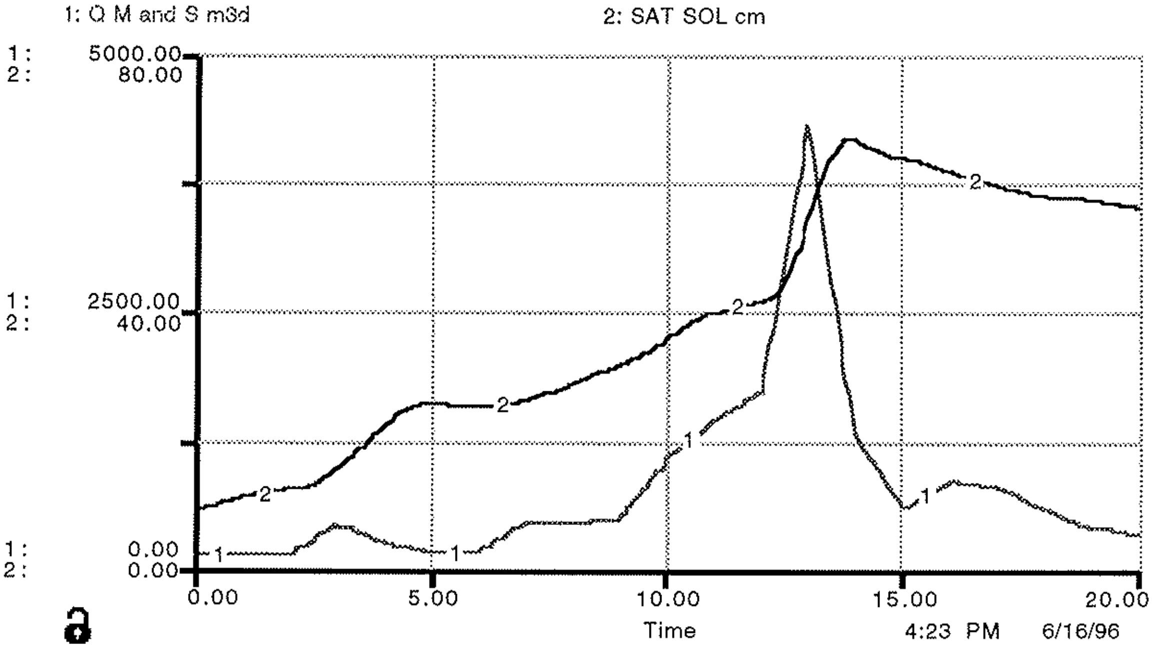

*Figure 19.* Solum Flow Rate and Stored Water Control Nitrate Flux Between Solum Stocks. In this STELLA plot curve 1 represents flow rate through the solum (Q M and S object) and provides input for equation 15. Curve 2 represents the estimated vertical height of water stored within the solum (SAT SOL cm object) and provides input for equations 15 - 17.

Hendriksen (1978) was used to simulate chemical fractionation of deposition nitrate within the snowpack. This method was chosen over more sophisticated methods because of its simplicity and the fact that meltwater samples were not collected at the site with which to calibrate the results using a more sophisticated approach.

The approach used for calculating Q Melt simulating snowpack runoff was the change in SWE calculated from change in snowpack depth from one time interval to the next. This method has been used successfully by Rasher et al. (1987) and proved adequate in SCATS. Meltwater is then mixed with precipitation in the SCATS model in the Qm and Qp m3d object. All precipitation was input to SCATS 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). The only snow that fell on the snowpack occurred on April 7-8 and was rapidly converted to water by rain and warm temperatures. It has been observed that rain commonly accompanies snowmelt in south-eastern Canada (Tranter, 1991) and in the nearby Adirondack Mountains (Peters and Driscoll, 1987).

Precipitation in SCATS contains both dry and wet deposition nitrate. 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 in SCATS during the daily time step is based on the concepts that higher concentration chemically fractionated solute is located on the outside of individual snow grains (Cragin *et al.*, 1993) and that meltwater and rain travel rapidly through the snowpack mixing with the chemically fractionated solute. Meltwater velocities in the snowpack 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. With 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 assumption of rapid mixing of precipitation and snowmelt in a ripe snowpack in active melt is in agreement with findings of Shanley *et al.* (1995) at the nearby Sleepers River Reaseach Watershed in Danville, Vermont.

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. In SCATS it is assumed that this input is accounted for by the fact that a snow sample from the contaminated lower layer of the snowpack was calculated into the mean snowpack concentration prior to spring snowmelt. During spring melt it is assumed that the downward flux of water renders further such contributions to snowpack nitrate relatively insignificant.

Other potential sources of nitrate inputs to the snowpack that were assumed relatively small and were therefore ignored for the purpose of maintaining the simplicity of this model include $NH_4^+$ inputs during melt, particulates from the forest canopy, and photochemical or biochemical reactions. Ammonia that was oxidized to nitrate in the snowpack prior to March 21 snowpack sampling is included in the initial snowpack nitrate load.

#### 2.6.2.3.2. Solum

SCATS is not a deterministic model, nor is it intended to be an empirical model. Although the solum is treated as a "black box", some conjecture as to the possible significance of the equations required to control the nitrate flux between the mobile and immobile solum stocks may serve as a useful academic exercise.

One may hypothesize that equation 17, based on the amount of water stored within the solum (cm) and the rate of flow of water through the solum (m3/day), simulates nitrate release from storage within the solum as catchment scale flushing of nitrate from the solum during a daily time step on a small catchment scale. Two natural phenomena that equation 17 may conceptually simulate are 1) differing nitrate release rates (nitrate movement from immobile to mobile water) as the chemical and physical properties of the soil strata change with changing lateral flowpaths (SATSOLcm portion of the equation) and 2) differing nitrate release from storage increasing as the flow of water through the solum increases (QMandSm3d portion of the equation). This movement may be considered to be a mechanical dispersion or advection dominated phenomenon.

Equations 18 and 19 may be hypothesized to represent movement of nitrate into storage (nitrate movement from mobile to immobile water) with this movement increasing as the solum water height increases. This movement may be considered to be a dispersion dominated phenomenon. A hysteresis effect was observed requiring the use of two equations, one for rising solum water and the other for decreasing solum water. More nitrate is stored or transferred from the mobile to the immobile nitrate stock as the water level rises than when the water level is decreasing. It seems reasonable that less transfer of nitrate would occur as water levels were decreasing because there would be less of a gradient between mobile and immobile nitrate concentrations as a result of nitrate transfer having taken place earlier during the rising water stage.

### 2.6.2.3.3. Stream

Inputs to stream channels occur as direct precipitation to the channel, overland flow, subsurface stormflow (solum water) and groundwater. Precipitation to the channel is 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 for inputs to streamwater in the SCATS stream module.

Quantification of storage change within the catchment as well as subsurface leakage, both of which may significantly affect water and nitrate mass balance calculations are 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 of these reservoirs would be helpful when calculating water and solute budgets. Flux into and out of these reservoirs may also be difficult to quantify. 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).

The use of naturally occurring tracers provides a useful approach for determining hydrograph separations. Silica (Si) is present in most 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 has been used successfully by a number of researchers (Pinder and Jones, 1969; Hooper, 1986; Maule and Stein, 1990; Hendershot *et al.*, 1992).

Soil pore-water samples obtained at Nettle Brook did not yield sufficiently distinct solum and groundwater Si concentrations (2.08 and 2.76 mg/L respectively) to separate the hydrograph into solum and groundwater components (Hendershot et al., 1992 used concentrations of 2.2 mgl and 3.9 mg/L, respectively). 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 mgl). For this study, the high flow concentration (0.96 mg/L) was used for the solum component, and the low flow concentration (2.72 mg/L) used for the groundwater component. 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 containing transported silica from groundwater to solum pore-water. Further, 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).

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, it has been found that 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 if not allowed adequate time. 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.

SCATS has functioned as an important research tool capable of simulating observed streamflow nitrate concentrations during a spring snowmelt event in this study at Nettle Brook (*Figure 18* ). It is believed that inputting actual snowmelt data, or refining the method used to predict chemical fractionation within the snowpack in the SCATS snowpack module, and confirming or refining the hydrograph separation in the SCATS stream module, may lead to development of useful empirical equations based on phenomena occurring within the solum as structured in the SCATS solum module (solum Q and stored water; *Figure 19* ). It is hoped that equations similar to equations 17, 18 and 19 would be capable of adequately describing catchment-scale transport of nitrate in the solum on a daily time-step basis during a spring snowmelt event at Nettle Brook.

# CHAPTER 3

# CONCLUSIONS AND RECOMMENDATIONS

## 3.1 Conclusions

This study examined the hypothesis that a spring snowmelt event may be responsible for major nitrate export from the Nettle Brook research catchment. The method employed was to conduct a field reconnaissance during which appropriate physical data were collected and to develop a simple conceptual computer model based on these data in an effort to gain insights into nitrate transport in snowmelt.

Specific research objectives were, 1) to estimate depositional inputs of nitrate to the Nettle Brook snowpack, 2) to estimate Nettle Brook streamflow nitrate outputs during a spring melt event, 3) to estimate overwinter nitrate mass balance within the Nettle Brook catchment, and 4) to gain insights into the transport of nitrate in snowmelt at Nettle Brook by developing a simple conceptual computer model.

Research results were:

1) Depositional input of $NO_3^-$ (dry and wet) into the Nettle Brook catchment snowpack is estimated to be 77 kg for the period of December, 1993 through March, 1994.

2) Output of $NO_3^-$ in Nettle Brook for the spring snowmelt period, April 4-23 is estimated to be 29 kg.

3) Output of $NO_3^-$ in Nettle Brook prior to spring snowmelt, December, 1993 through March, 1994, is estimated to be 5 kg, which when added to $NO_3^-$ output during the spring snowmelt event (29 kg) yields 34 kg $NO_3^-$. Inputs less outputs indicate a net $NO_3^-$ retention and/or loss to denitrification of 43 kg within the Nettle Brook catchment for the 1993-1994 winter period.

Depositional $NO_3^-$ inputs into the Nettle Brook catchment for 1994 calendar year were estimated to be 298 kg and $NO_3^-$ export in Nettle Brook was estimated to be 89 kg. $NO_3^-$ export during the spring melt event (29 kg) therefore accounted for 33% of the estimated annual export. This finding supports the hypothesis that major nitrate export occurred at Nettle Brook during the 1993-1994 spring snowmelt period.

4) An important insight gained from the model development and simulation runs was that the solum exerts a major influence on streamwater chemistry during spring snowmelt and that elevated streamwater nitrate concentration observed early in the spring melt event may not be due to chemical fractionation occurring within the snowpack, but rather the result of processes occurring within the solum. The finding that subsurface processes dominate streamwater chemistry in small upland catchments is in agreement with the findings of other researchers (Peters and Driscoll, 1987; 1989).

Another insight was gained by the observation that the two-stock solum module structure using mobile and immobile nitrate stocks for describing nitrate fluxes providing excellent simulations of the observed streamwater nitrate concentrations. This observation suggests that partitioning of nitrate into mobile and relatively immobile fractions may occur within the solum. This finding is in agreement with the findings of other researchers (Addiscott, 1977; White, 1985).

SCATS is a simple, non time-intensive, economical model that may be used with minimal field data to provide insights into nitrate transport in snowmelt and possibly serving as a starting point for more in-depth physical modeling. Perhaps the most obvious and simple method of model evaluation is to plot simulations against measurements and leave the reader to judge for himself (Whitmore, 1991). If SCATS is to be evaluated by this criteria, the excellent simulation results (*Figure* 18) indicate that the model is successful.

## 3.2 Recommendations

The attempt to explain streamwater nitrate chemistry by development of the SCATS model indicates that information is less than adequate or missing. A better understanding of ion flux and streamwater chemistry within the Nettle Brook catchment may be attained and future modeling efforts may benefit from increased and/or more accurate data. This data deficiency may be reduced by implementing the following recommendations:

a) This study was conducted without the benefit of snow courses and snowpack density measurements which would have increased the accuracy of water related flux in snowmelt. A better estimate of snowpack nitrate content (load) may be obtained by multiplying the mean nitrate content of representative cores from throughout the catchment by the ratio of the watershed area to the core area (Galvin and Cline, 1978).

b) The use of snowmelt lysimeters to quantify meltwater concentrations at the research site may provide a better understanding of processes occurring within the snowpack such as preferential elution and chemical fractionation and a better understanding of nitrate flux within the solum by providing actual meltwater nitrate inputs to the solum, thereby increasing the accuracy of the equations describing nitrate transport within the solum.

c) A soil survey and solum water chemistry study at the Nettle Brook catchment (perhaps nitrate leaching experiments) would be helpful in understanding the processes occurring within the solum which in this study is treated as a 'black box'.

d) Quantification of subsurface water movement within the Nettle Brook cathment would be helpful in estimating the extent of groundwater within the watershed and its contribution to streamflow and mass balance calculations. It would be helpful to estimate aquifer parameters such as thickness, spatial distribution, porosity and hydraulic conductivity. These parameters can generally be estimated from a combination of geophysical techniques such as seismic refraction, ground-penetrating radar, electromagnetic methods, and sampling of aquifer material during installation of wells. The potential problem of groundwater transfer between adjacent catchments requires that some water table measurements be made across catchment topographic divides (Jenkins et al., 1994). In order to study the process and mechanisms of groundwater discharge to a stream, a dense network of spatially and vertically distributed wells close to the stream should be installed.

e) The implementation of a more sophisticated sampling method to determine nitrate export from the Nettle Brook catchment. Studies of nitrate transport in the field require the measurement of water movement with dissolved solute (nitrate) and the total nitrate flux may be stated as:

$$\text{Total solute flux} = \sum (\text{flow x concentration})$$

No satisfactory continuously operating nitrate concentration probe is available, so that nitrate concentrations must be taken from the analysis of samples collected at various intervals in the field (Armstrong and Burt, 1993). The positive relationship between discharge and nitrate concentration may allow concentration to be adequately determined from discharge (Johnes and Burt, 1993). The implementation of a period-weighted method such as is described by Dann et al. (1986) is suggested.

f) Validation of the hydrograph separation for Nettle Brook with a method such as that used by Maule and Stein (1990) at Lac LaFlamme, Quebec. This method provides a more comprehensive approach to hydrograph separation of spring meltwater by using two environmental tracers, oxygen-18 and silica, to partition stream water into four components.

# CHAPTER 4

## RESEARCH PAPERS

4.1.

### Nitrate Transport in Snowmelt in the Green Mountains, Northern Vermont

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## ABSTRACT

Research of nitrate transport in snowmelt commenced October 1, 1993 and is ongoing at the Vermont Monitoring Cooperative (VMC) research watershed located on Mount Mansfield in the Green Mountains of northern Vermont. Wet and dry deposition data are collected 2 km from the research site. Streamflow on the research site is recorded at a weir installed by the United States Geological Survey (USGS). Streamwater samples were collected monthly, except twice daily during snowmelt and were analyzed for anions, NO3, SO4, Cl, and cations, Ca, K, Mg, Na, Al, NH4 and Si. Snowpack and soil samples were randomly collected and analyzed. Data suggest chemical fractionation occurred within the snowpack during snowmelt. Preferential elution was not evident. Nitrate export during snowmelt was found to be significant. Calculations suggest a loss of 57% of snowpack nitrate prior to spring snowmelt. Calculations based on total overwinter atmospheric nitrate inputs and observed streamflow outputs through the end of spring snowmelt indicate a net retention and/or loss of nitrate within the watershed of 66%. A streamflow hydrograph separation using Si was performed which is to be used in a model being developed to simulate nitrate transport in snowmelt at the Nettle Brook site.

Key words: nitrate, snowmelt, streamwater chemistry, hydrograph separation.

# INTRODUCTION

## Research Context and Objectives

The cycling of nutrients and the type and degree of ecosystem management in headwater forested watersheds is of growing concern to all. This is the result of the potential effects on terrestrial productivity and water quality downstream of these catchments (Lawrence and Wigington, 1988). The determination of the factors responsible for regulating streamwater ion (hence nutrient) concentrations in upland forested watersheds improves our understanding of these ecosystems. This understanding facilitates the making of informed management decisions, necessary for the preservation of our natural resources.

A number of organizations concerned with environmental change and natural resources in Vermont have created the Vermont Monitoring Cooperative (VMC) to measure conditions and changes in Vermont forested ecosystems. To accomplish this goal the VMC has implemented a long-term integrated multi-disciplinary monitoring program (Wilmot and Scherbatskoy, 1993). This holistic approach may provide insights into natural systems not obtainable by a highly focused view. It has been stated that if snow scientists do not take a holistic approach in their research studies they may misinterpret the processes driving the chemical changes within the snowpack (Jones, 1991). In keeping with this philosophy, research results from this study will be incorporated into a multi-disciplinary data base being compiled by the VMC.

This research focuses on the relationship between watershed hydrology and nitrate transport at Nettle Brook located at the VMC monitoring facility on Mount Mansfield. The spring snowmelt event is hypothesized to be responsible for major nitrate export at Nettle Brook. Specific research objectives are, 1) to determine depositional inputs of nitrate to the snowpack, 2) to determine streamflow nitrate outputs during the spring melt event, and 3) to determine nitrate mass balance within the research watershed.

## Nitrate in the Ecosystem

Nitrogen is a nutrient of major importance in the forest ecosystem but nitrogen compounds are also potential toxicants (Rosswall, 1981). Fahey *et al.* (1986) emphasized the need to understand the role of N storage and release from snowpacks, pointing to the fact that concentrations of antropogenic N in ambient air of high-elevation areas in the U.S. have increased as much as 30-fold in the last several decades.

In northern Vermont, it has been estimated that 25-35% of annual precipitation occurs as snowfall and is responsible for generating about one-half of the total annual runoff within a 30-day period during spring snowmelt (Dunne and Leopold, 1978). Most nitrogen contributing to forest growth or exported in streamflow exists in the inorganic forms as nitrate and ammonium. Nitrate is more mobile than ammonium primarily because it is not retained by soil cation exchange capacity (Thorne, 1985). Because of this high flux of water, the relatively high solubility of nitrate in water, and the relatively shallow hydrologic pathways dominating high flow events, spring snowmelt has the potential for significant export of nitrogen from the upland forest ecosystem.

## Nitrate in the Atmosphere

Nitrate and sulfate ions in precipitation are the major contributors to rain acidity in the Northeast United States (Altwicker, 1983). Much of the NO and NO2 which enters the atmosphere is ultimately removed as HNO3 (Huebert *et al.*, 1983). Nearly all of dry deposited nitrogen is in the form of HNO3 (Meyers *et al.,* 1990). HNO3 dissolves according to the equation:

$$(1)\ \mathrm{HNO3(g)} = \mathrm{H}^{+} + \mathrm{NO3}^{-},$$

thus providing the bulk of dry deposition nitrate.

HNO3 is removed from the atmosphere passively by gravitational sedimentation or actively by rainout or washout. Rainout includes all processes occurring within clouds. Washout refers to processes occurring below the clouds. Rain drops or snow flakes are nucleated in the atmosphere by micrometer size particles. These particles may originate from industrial emissions, sea spray, plants and wind-blown terrestrial dust. The primary scavenging mechanism for micrometer sized particles is inertial impaction (Cragin *et al.*, 1993). Raynor and Hayes (1983) found that nitrite and nitrate in snow average nearly five times the concentration found in rain as a result of more efficient scavenging by snow.

### Nitrate in the Snowpack

The nitrate that has accumulated in the snowpack as a result of deposition is subject to a number of processes which, during melt events, contributes to producing an ionic pulse. Among these processes are 1) *chemical fractionation*, 2) *preferential elution*, 3) *melt-freeze cycles*, and 4) *rain scavenging*. The initial 20-30% of meltwater may remove 40-80% of the solutes (Johannessen and Hendriksen, 1978; Cadle *et al.*, 1984; Bales *et al.*, 1989). Stottlemyer and Troendle (1992) found that maximum stream nitrate discharge occurred at the same time as the major snowmelt ionic pulse.

*Chemical fractionation* refers to the release of ions relative to release of water from the snowpack at variable rates over time. At the onset of major melt events, this phenomena has produced the highest concentrations of solute observed in snowmelt (Peters and Driscoll, 1989; Williams, 1993). *Preferential elution* refers to the release of some ions before others (some ions are enriched more than others at any given time). The elution sequence of major anions from melting snow has generally been found to be SO4 > NO3 > Cl (Brimblecombe *et al.*, 1987; Marsh and Pomeroy, 1993) but the sequence can vary. Davies *et al.* (1987) described the sequence as SO4 > Cl > NO3. Johannessen and Hendriksen (1978) found that Cl eluted prior to NO3 in a Norwegian snow but NO3 eluted out prior to Cl in a Scottish snow.

Cragin *et al.* (1993) conclude that chemical fractionation and preferential elution are the result of ion exclusion during snow grain metamorphosis rather than chromatographic effects. Ion and chemical exclusion processes during ice crystal growth has been cited as the underlying mechanism by a number of researchers (Marsh and Pomeroy, 1993; Bales 1991). Tranter *et al.* (1986) propose that condensation nuclei (Cl in sea salt aerosols) may be retained within the crystal while species scavenged during precipitation (SO4 and NO3) are eluted first. Whatever the process responsible, there seems to be considerable agreement that the snowpack is a multi-component system consisting of two components, a brine with a high concentration of solute at the boundary of ice grains, and a nearly pure ice containing low concentrations of chloride in the grain interior (Davies *et al,* 1987). The high initial concentrations found in meltwaters is thought to be the result of the leaching of these surficial brines by melt water an the onset of melting. The finding that preferential elution appears to be enhanced with time was construed to indicate that migration of ions into the brine continues with time (Brimblecombe *et al.*, 1987).

Redistribution of impurities within the snowpack may result from *melt-freeze cycles*. In a bench scale experiment, NO3 was found to have the highest concentration factor following melt-freeze cycles (Bales *et al.*, 1989). Williams and Melack (1991) found that a series of melt-freeze cycles which occurred after the initiation of snowpack runoff increased the concentration of solutes in the meltwater. Redistribution of impurities within the snowpack by *rainfall scavenging* may also result from water flux driven by rainfall events. Nitrate is transported to sites closer to the base of the snowpack where it has the potential for rapid transport out of the pack (Bales *et al.*, 1989).

Ion loss from the snowpack prior to spring melt may occur when soils remain unfrozen and infiltration from the snowpack base into the soil can take place. Stottlemyer and Troendle (1992) noted that solutes within a snowpack can migrate at temperatures 3-5°C below freezing possibly accounting for the loss of more than 50% of snowpack ions before significant spring melt occurred. Cadle *et al.* (1984), in comparing snowpack loading of ions and cumulative wet deposition, found no evidence of ion loss before the spring rain/thaw period.

## Nitrate in the Litter and Soil

Hooper (1986) hypothesized that two sources for streamwater nitrate during snowmelt exist: nitrate accumulated within the snowpack and nitrate accumulated in the soil during the winter months. Peters and Driscoll (1987;1989) found the major control on the chemical composition of stream waters to be a result of ground water and soil water contributions. Stottlemyer and Toczydlowski (1990) found that nitrate concentrations were higher in streamwater than snowmelt and that some nitrate input to the streamflow was likely the result of nitrification and mineralization in the soil.

Nitrate concentrations in meltwater are subject to change in or below the litter layer. Rascher *et al.* (1987) found forest floor processes resulted in a five-fold enrichment of H and NO3 over snowpack inputs. The increase in N in decaying litter has been demonstrated in forest and aquatic ecosystems and evidence suggests that decomposing heterotrophs are active during the winter months under a heavy snowpack. The amount of the increase was influenced by C:N and C:P ratios (Gosz *et al.*, 1973). Snowmelt may also be enriched as it passes through the litter layer if soluble impurities from atmospheric fallout (nitrate) accumulated on the litter/soil surface prior to the commencement of snowpack deposition (Colbeck, 1981). Microbial assimilation and denitrification may remove some nitrate from meltwaters percolating through the litter. Denitrification may occur if wetted litter develops anaerobic sites within the organic matrix, but snow meltwaters are well oxygenated and the existence of such sites is generally not favored (Jones, 1991).

Nitrate concentrations in meltwater may be further modified in the uppermost soil layers. Nitrification and decomposition of organic matter in unfrozen soils may be responsible for solute enrichment of meltwaters (Peters and Driscoll, 1989). Stottlemeyer and Toczydlowski (1990) found that meltwater picked up nitrate from soil surface organic and inorganic horizons as the water rapidly passed through macropores to the stream. The mineral N content of soils may also increase while soils are frozen. Nitrate and moisture may move upwards in the soil in the winter and then downwards in the spring (Malhi and Nyborg, 1986).

Nitrate concentrations may be further modified in meltwater in the deeper layers of soil. Elgood (1990) found that soil clearly accounted for most of the increase in groundwater N content during melt events and that most of the water contributing to the rise in water table was pre-event (new) water displaced from the unsaturated zone and capillary fringe area.

The spatial aspect of soil location and distribution also influences streamwater chemistry. Soils further from the stream impact the stream later in the melt event. Swistock *et al.* (1989) concluded that the importance of soil water to streamwater chemistry increases as storm size and/or antecedent moisture content increases the chance for younger soil water from higher elevations to contribute. Riparian soils may have the greatest influence on meltwater entering the stream (Hendershot *et al.,* 1992). Increased groundwater discharge during snowmelt is related to a rapid rise in hydraulic head along the stream perimeter which has been termed groundwater ridging. This phenomenon is thought to arise from an almost instantaneous conversion of the near-surface tension-saturated capillary fringe into phreatic water. Elgood (1990) found that an increase in NO3-N concentration usually occurs in association with, or immediately following, an increase in the near-stream saturated area during the initial stages of melt. Because of rapid equilibrium rates this water acquires the chemical signature of the riparian soil modifying streamwater chemical composition. It is clear that there are many factors to be considered when attempting to understand processes capable of affecting nitrate transport during snowmelt.

## METHODS AND STUDY AREA

### Site

The field work commenced on 1 October, 1993 and is ongoing. The research is conducted at a Vermont Monitoring Cooperative study site located on the southwest slope of Mount Mansfield in the Green Mountains of northern Vermont (44°30' N, 72°51' W). The drainage basin of the catchment has an estimated surface area of 0.11 km2 with a drainage system consisting of a small first-order stream, Nettle Brook. The catchment elevation extends from 445 m to 665 m above sea level. Mount Mansfield receives a mean annual total of 1140 mm precipitation of which between 25 and 35% is snow. The bedrock is predominately mica-albite-quartz schist. The soils are dominated by Peru extremely stony loam, Marlow extremely stony loam, Cabot extremely stony silt loam and Lyman-Marlow very rocky loam. The canopy vegetation is dominated by 70% hardwoods, primarily sugar maple, beech, yellow birch, and the remaining 30% are softwoods, primarily hemlock and red spruce (Wilmot and Scherbatskoy, 1993).

Streamflow is monitored by a United States Geological Survey (USGS) weir that was installed on 28 September, 1993 on Nettle Brook. Stage is recorded on a Campbell Scientific CR-10 at 5-minute intervals. Stream discharge was calculated by determining the stage above a 90° v-notch weir. Air, water, soil and snowpack temperatures as well as snowpack depth and reflected short wave radiation were also recorded at the site of the weir.

### Deposition Monitoring

Wet and dry deposition inputs and ambient meteorological data were measured at the nearby (2 km) VMC air quality monitoring station located at approximately the same elevation as the weir (425 m and 445m respectively). The wet deposition recorder is part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Dry deposition monitoring is by the Dry Deposition Inferential Measurement System

(DDIMS), part of the Environmental Protective Agencies National Dry Deposition Network (NDDN).

## Sampling

The snowpack in the watershed was sampled near the weir at three depths preceding snowmelt (March 21). Streamwater was sampled at the weir on an approximate monthly basis with the exception of twice daily during the main snowmelt period (April 4-28). Soil pore-water was sampled 10m upstream of the weir and 2m from the stream. Soil water samples were taken at 4 depths, 2 above and 2 below the water table. Locating the site 2 meters from the stream was based on the assumption that the riparian soil would have the greatest (if not the last) impact on soil water flowing towards the stream. The soil pore-water was extracted within 4 hours of obtaining samples using a syringe-pressure technique and apparatus developed by Ross and Bartlett (1990).

All water samples were collected in 0.5 liter plastic bottles (bottles were rinsed with deionized water for snowpack samples). Samples were stored at 4°C until analyzed for anions (NO3, SO4, Cl), cations (Ca, K, Mg, Na, Al, NH4) and Si. Analysis of anions was conducted on a Dionex 2010i ion chromatograph and analysis of cations was conducted on a Leeman ICP 2.5 inductively coupled plasma spectrophotometer in the Agricultural Testing Laboratory at the University of Vermont.

## Hydrograph Separation

In the past, water chemistry modeling has employed hydrograph separation focused on quantifying the components of streamflow into two fractions, water derived from precipitation (new water) and pre-event (old) water. Given the rapidity of many equilibrium reactions within the soil (minutes to hours), an alternative two-component partitioning based on rapid hydrochemical response may be more effective (Robson and Neal, 1990). Dissolved silica has been found by other researchers to act as a conservative tracer (Pinder and Jones, 1969; Hooper and Shoemaker, 1986). Hendershot *et al.* (1992), using an approach based on rapid hydrochemical response employed dissolved silica concentrations and concepts of mass balance to estimate the contributions of water flowing through the solum (soil above the C horizon) and subsoil (ground water). As all water samples collected in this study had been analyzed for Si, the method proposed by Hendershot *et al.* (1992) was chosen.

## RESULTS AND DISCUSSION

### Nitrate in Depositional Inputs

Wet and dry depositional inputs of nitrate into the catchment during the winter and spring of 1993-94 are presented in Figure 1. Dry deposition (Dec-Apr) accounted for 26% of the total NO3 deposition for the period. Dry deposition of nitrogen has been estimated to provide between 30 and 50% of the total annual input (wet and dry) for all sites in the eastern U. S (Meyers *et al.*, 1990). Meyers *et al.* (1990) note that an annual cycle is not evident in the time series of nitrogen deposition rates, although deposition rates appear higher during the spring period for nearly all sites in the monitoring network.

### Nitrate in the Snowpack and Soil

Analysis of snowpack samples (one in each of three layers separated by two ice lenses) collected prior to commencement of the spring snowmelt event (March 21) yielded values (from snowpack top down) of 0.332, 0.166 and 0.817 mg/L. It is conjectured that the relatively fresh precipitation on the surface did not have sufficient time for nitrate to leach downwards as did the older intermediate layer. It is suspected that the lower layer was contaminated by forest floor litter/soil or that moisture from the unfrozen forest floor moved upwards by capillary action carrying soluble nitrate into the snowpack. The

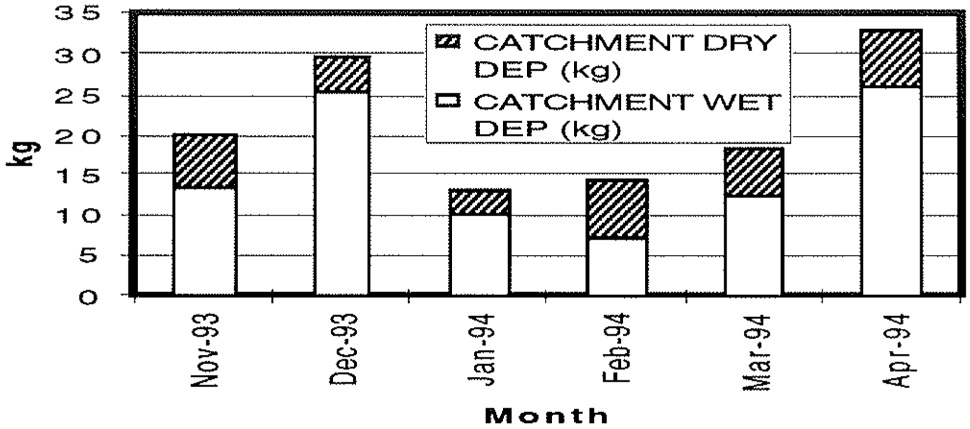

FIGURE 1. Nitrate deposition into the Nettle Brook catchment.

snowpack may exhibit considerable spatial and temporal heterogeneity (Marsh and Pomeroy, 1993). The mean snowpack concentration of NO3-N was 0.435 mg/L. This concentration was exceeded in only 3 of 55 streamwater samples analyzed and the 3 were collected during peak snowmelt flows. Stottlemeyer and Troendle (1990) found snowpack nitrate concentrations typically greater than streamwater concentrations.

Soil porewater sample analysis yielded NO3-N values of 0.46 mg/L (0-13 cm; O, A horizon), 0.70 mg/L (13-16 cm; B horizon), <0.05 mg/L (16-33 cm; B, C horizon, saturated), and <0.05 mg/L (33-46 cm; C horizon, saturated). Based on the method described by Hendershot *et al.* (1992), water in soils above the C horizon is classified as solum water and water in all materials from the C horizon and down is classified as groundwater. Mean Si and NO3-N concentrations of the solum pore-water were 2.08 and 0.58 mg/L respectively. Mean Si and NO3-N concentrations of the ground pore-water were 2.76 and < 0.05 mg/L respectively.

### Nitrate in Streamflow Outputs

Nitrate outputs at the Nettle Brook weir derived from the mean of sample

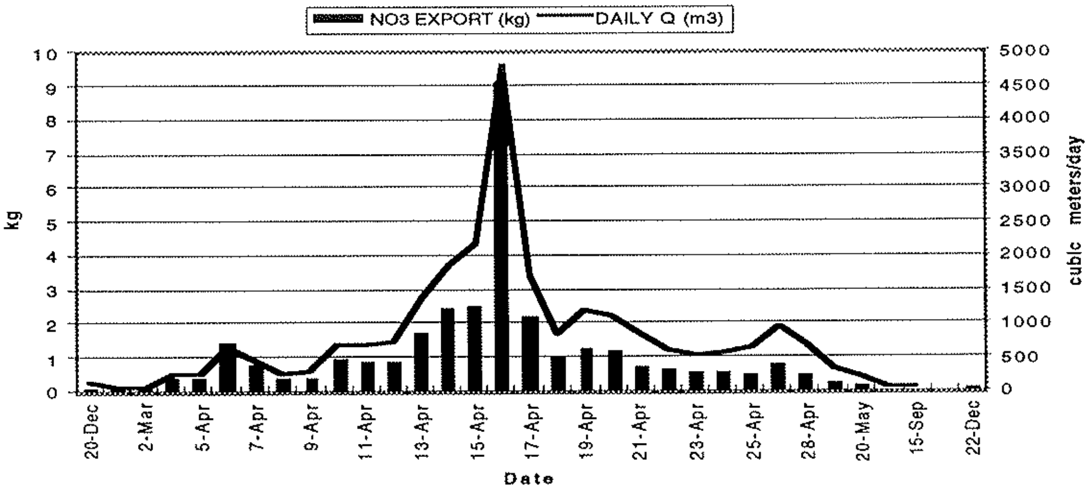

FIGURE 2. Nettle Brook nitrate export. Note that sample intervals are daily during Spring snowmelt and monthly during the rest of the year.

concentrations for that day (mg/L) multiplied by the volume of streamflow occurring during that day (L) are presented in Figure 2. The major nitrate export observed occurs during spring snowmelt at peak flow (April 16). If the mean of the daily nitrate export observed at other times of the year is multiplied by 341 (the balance of the year) the 24 days of spring snowmelt accounts for over 58% of the nitrate export while April 16 alone accounts for 17% of the nitrate export observed. It should be noted that some sampling during other times of the year occurred during non-event streamflow and therefore it is likely that the nitrate export estimate for the rest of the year is underestimated.

## Chemical Fractionation of Nitrate

Results of analysis of streamwater samples for nitrate as NO3-N and stream flow rate during Spring snowmelt is presented in Figure 3. On April 16 during peak flow streamwater samples yielded a NO3-N average concentration of 0.43 mg/L (averaged from 0.509 mg/L and 0.35 mg/L). The highest concentration of streamwater nitrate, 0.508 mg/L (averaged from 0.534 mg/L and 0.481 mg/L), was recorded on April 6 at the substantially

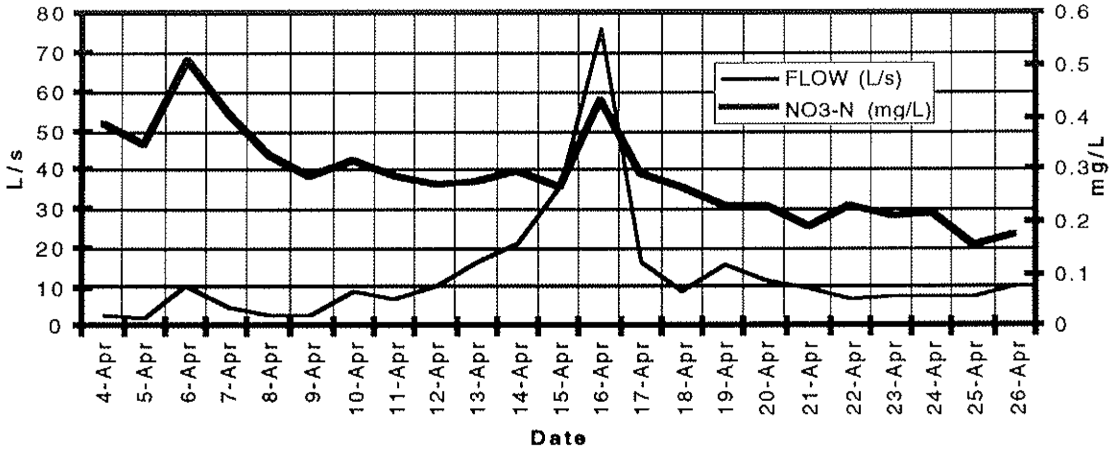

FIGURE 3. Probable chemical fractionation of nitrate at Nettle Brook. Notice that although nitrate concentration typically increases with increased flow, the peak nitrate concentration occurred on April 6, 1994 at a substantially lower flow rate than the peak flow rate observed on April 16, 1994.

lower flow rate. Nitrate is one of the ions that typically concentrate with increased flow rates. This nitrate concentration observed on April 6 may be evidence of chemical fractionation in the snowpack producing an ionic pulse in the stream.

### Preferential Elution of Ions

Sulfate, nitrate and chloride concentrations observed in streamwater samples are presented in Figure 4. The highest concentration of sulfate occurs prior to spring melt (March 21, 1994) and the highest nitrate concentration occurs during the earlier phase of the spring melt event (April 6, 1994). Cl concentrations remain relatively constant through the melt period. Evidence for preferential elution is often more difficult to discern than evidence for chemical fractionation. Brimblecombe *et al.* (1987) note that, in the field, the effects of preferential elution would not be easy to observe during the initial loss of solute rich meltwater. Bales *et al.* (1989) found no preferential elution of species unless initial distributions were different for each of four different experiments.

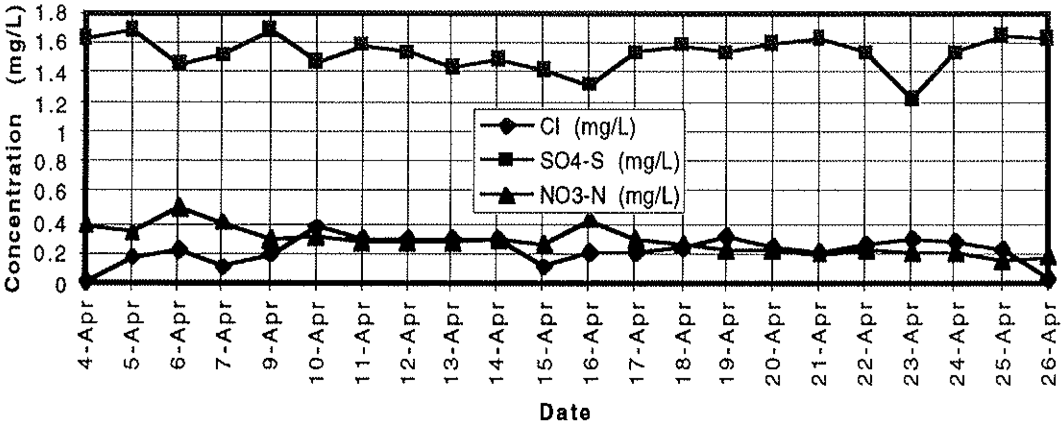

FIGURE 4. Anion concentrations at Nettle Brook during Spring snowmelt. No evidence of preferential elution of ions appears evident.

## Streamwater Chemistry

Observed streamwater concentrations are the result of the mixing of various components within the stream. Determining the relative contributions of soilwater and groundwater into the stream was accomplished by the method described by Hendershot *et al.* (1992). The hydrograph separation was derived from equation

$$(2)\ Q_s = 0.34(Q_t - 0.17)^{1.21}$$

where

$Q_s$ = flow from solum (L/s)

$Q_t$ = total flow (observed values - L/s).

Predicted concentrations are then obtained from equation

$$(3)\ C_{t,pred} = (Qg \times Cg + Qs \times Cs)/Qt$$

where

C t,pred = Predicted total conc of Si (mg/L)
Cg = Si conc of groundwater (mg/L)
Cs = Si conc of solum (soil) (mg/L)
Qg = flow from groundwater (L/s).

The value for Cg may be obtained from the Si concentration at baseflow (0.17 L/s) and Cs from the Si concentration observed from soil pore-water samples. A hydrograph plot of Qt and Qg was then constructed (Figure 5). The procedure outlined by Hendershot *et al,* (1992) was modified in two ways for this research. First, the Si concentration value for Cg was derived from soil samples below the water table rather than from stream samples at base flow (the values were in close agreement, 2.76 and 2.72 mg/L respectively). Second, equation (2) was derived from a sensitivity analysis involving simultaneous observation of predicted Si responses and hydrograph generation to modification of equation (2) constants. This was necessary to insure that a best fit for measured and predicted Si concentrations was obtained while keeping the groundwater contribution to the hydrograph following the trend of the total flow. Streamflow was calculated from the hydrograph separation to be 84% solum water (Qs) during peak flow and 100% groundwater (Qg) during low flow. These values are in agreement with findings by Hendershot *et al.* (1992) indicating high flow to be 50-95% solum water while low flow was mainly groundwater.

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, it has been found that Si concentrations are subject to change. 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 if not allowed adequate time. Pearce *et al.* (1986) note that the soil water store may not be completely

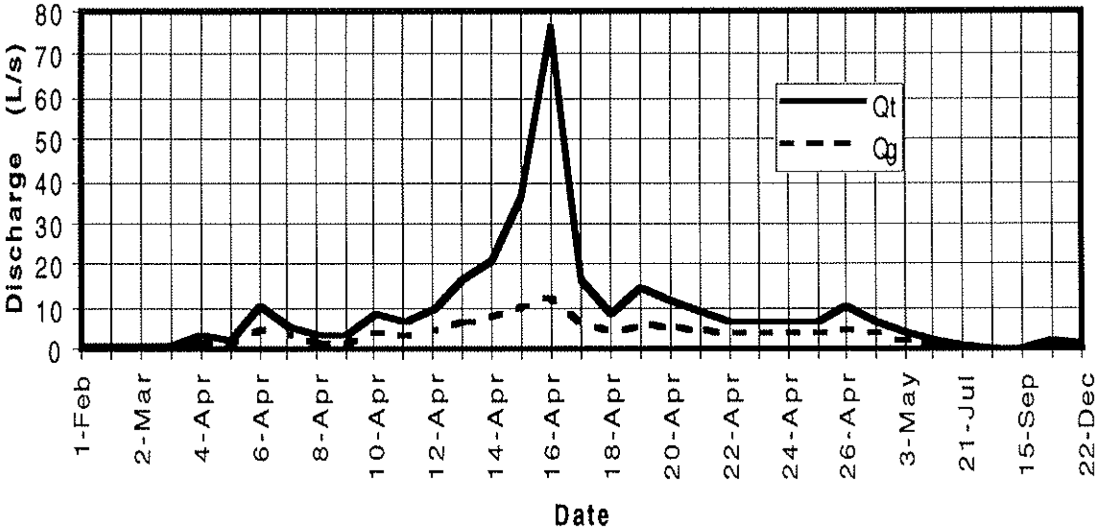

FIGURE 5. The hydrograph separation developed from the procedure described by Hendershot *et al.* (1992) using modifications described in the text showing the relative contributions of ground water (Qg) and solum water (Qs = Qt - Qg) to Nettle Brook streamflow.

mixed bringing into question the validity of a simple two-component mixing model. The hydrograph separation is therefore in question and will be compared with other techniques.

Figure 6 was obtained by inserting observed nitrate concentrations from soil samples obtained from above and below the water table into equation (3) and plotting the results along with the values derived from streamwater analysis. This figure is useful only to identify trends in nitrate concentrations. Nitrate concentrations in the solum and ground water contributions are subject to seasonal change and other fluxes, hence the input of two fixed concentrations to predict nitrate streamwater chemistry is not valid. The values predicted in Figure 6 underpredicts nitrate concentrations during the period of early snowmelt and overpredicts the latter period of snowmelt. This is a result, at least in part, of the ionic pulse provided by the melting snowpack at the onset of melt and the reduced snowpack concentrations following the pulse. Loss of nitrate is further enhanced at the end

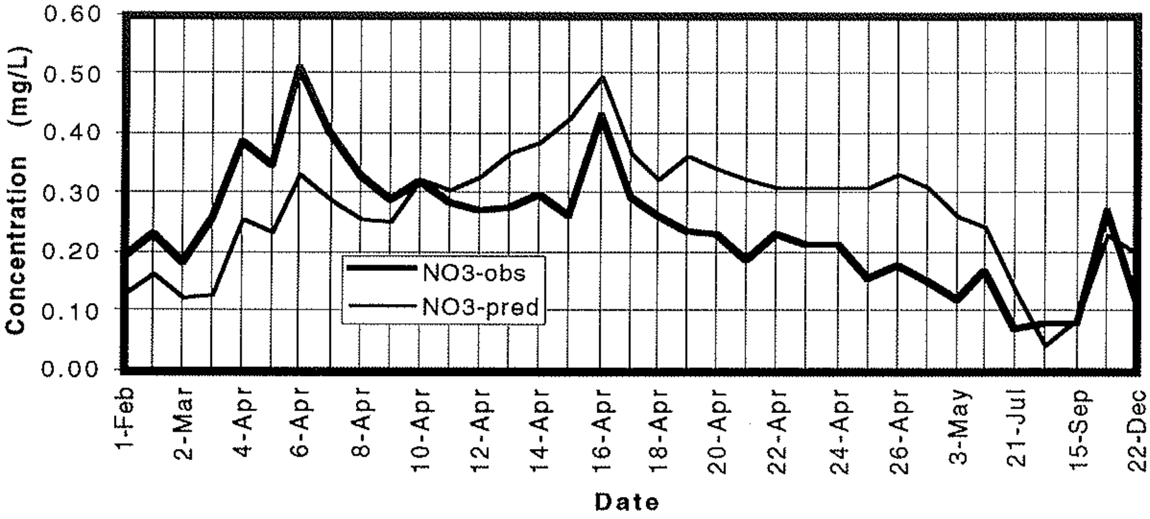

FIGURE 6. Predicted and observed nitrate concentrations based on the hydrograph separation discussed in the text and nitrate concentrations determined from soil sample analyses. Inputs for predicted nitrate were 0.58 mg/L (Cs) and 0.04 mg/L (Cg).

of spring melt as a result of increased biological activity as streamwater warms. Johnson *et al.* (1969) note that nitrogen is an element that is apparently in critical supply within forest ecosystems. The variation in biological demand is reflected in the changing concentrations of the element in stream water from season to season with concentrations reduced in the stream during the growing season.

## CONCLUSIONS

Nitrate inputs into the Nettle Brook catchment during the winter preceding snowmelt were estimated to be 76 kg. The estimated snowpack nitrate content prior to snowmelt (21 March) was 33 kg. This indicates a net loss of 43 kg or 57% of snowpack nitrate prior to spring snowmelt. Total nitrate atmospheric inputs through the end of spring snowmelt (96 kg) less streamflow outputs (33 kg) indicate a net retention and/or loss to denitrification within the watershed of 63 kg or 66%. However, as a result of the limitations of the experimental data (i.e. concentrations not recorded continuously) these results should be regarded as semiquantitative. The finding that snowmelt is responsible for major nitrate export from Nettle Brook is in agreement with the findings of other researchers in northern Vermont (Dunne and Leopold, 1978). The observed export of nitrate at Nettle Brook substantiates the hypothesis that major nitrate export occurred during spring snowmelt.

Chemical fractionation appeared evident in the analysis of streamwater samples (Figure 3), but no evidence of preferential elution was observed (Figure 4). Evidence for preferential elution would be best determined by collection of snowmelt leachate rather than analysis of streamwater chemistry as any observable trends may be attenuated by interactions of the eluted ions with soil components.

The hydrograph separation was performed as a first step in the development of a streamwater nitrate model and will be verified by use of other techniques. Pilgrim *et al.* (1979) has shown that the application of the mass balance approach using fixed concentrations for flow components may lead to invalid references regarding sources of flow. If the technique described in this paper is found to provide, upon verification, a reasonable estimate of the flow components, then the simplicity, economy and utility of this approach may provide a useful first step for field researchers in understanding streamwater chemistry.

Finally, it has been suggested that it should be possible to model movement of most major ions within the snowpack independently of each other (Bales, 1991). However, we are well aware that nutrient cycles are interconnected. The biogeochemical nitrogen cycle should not be viewed in isolation (Rosswall, 1981). The model being developed from data collected during this research may provide a template for other ions that can be modeled independently and it is hoped that, ultimately, relationships existing between the modeled ions within the research watershed may be examined and further insights gained into streamwater chemistry during Spring snowmelt.

## ACKNOWLEDGEMENTS

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## REFERENCES

Altwicker, E. R., 1983. Nitrate in Precipitation: How are the Observed Concentrations Explained? *Precipitation Scavenging, Dry Deposition and Resuspension,* vol 1, 283-291. Elsevier, New York.

Bales, R. C., 1991. Modeling In-Pack Chemical Transformations. *Seasonal Snowpacks: Processes of Compositional Change.* T. D. Davies, M. Tranter, and H. G. Jones (eds.). NATO Advanced Study Institute Series G, Vol. 28, Springer-Verlag, Berlin. 139-163.

Bales, R. C., R. E. Davis and D. A. Stanley, 1989. Ion Elution Through Shallow Homogeneous Snow. *Water Resources Research, 25.* 1869-1877.

Brimblecombe, P. M., S. Clegg, T.D. Davies, D. S. Shooter, and M. Tranter, 1987. Laboratory Observations of the Preferential Loss of Major Ions from Melting Snow and Laboratory Ice. *Water Research, 21.* 1279-1286.

Cadle, S. H., J. M. Dasch, and N. E. Grossnickle, 1984. Retention and Release of Chemical Species by a Northern Michigan Snowpack. *Water, Air and Soil Pollution, 22.* 303-319.

Colbeck, S. C., 1981. A Simulation of the Enrichment of Atmospheric Pollutants in Snow Cover Runoff. *Water Resources Research, 17.* 1383-1388.

Cragin, J. H., A. D. Hewitt, and S. C. Colbeck, 1993. Elution of Ions from Melting Snow: Chromatographic Versus Metamorphic Mechanisms. *Crrel Report 93-8.* U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Hanover, N. H.

Davies, T. D., P. Brimblecombe, M. Tranter, S. Tsiouris, C. E. Vincent, P. W. Abrahams, and I. L. Blackwood, 1987. The Removal of Soluble Ions from Melting Snowpacks. *Seasonal Snowcovers: Physics, Chemistry, Hydrology.* H. G. Jones and W. J, Orville-Thomas, eds. D. Reidel, Dordrecht. 337-392.

Dunne T., and L.B. Leopold, 1978. Water in Environmental Planning. W. H. Freeman and Company, New York, New York.

Elgood, R. J. 1990. The Effect of Mid-winter Snowmelt Events on Nitrate and Ammonium Concentration in the Unsaturated and Shallow Saturated Zones: A Case Study. M. A. Thesis. Wilfrid Laurier University, Ontario, Canada.

Fahey, D. W., G. Hubler, D. D. Parish, E. J. Williams, R. B. Norton, B. A. Ridley, H. B. Singh, S. C. Liu, and F. C. Fehsenfeld (1986). Reactive Nitrogen Species in the Troposphere. *Journal of Geophysical Research 91.* 9781-9793.

Gosz, J. R., G. E. Likens, and F. H. Bormann, 1973. Nutrient Content of Litter Fall on the Hubbard Brook Experimental Forest, New Hampshire. *Ecological Monographs, 43.* 173-191.

Hendershot, W. H., S. Savoie, and F. Courchesne, 1992. Simulation of Stream-Water Chemistry with Soil Solution and Groundwater Flow Contributions. *Journal of Hydrology, 136.* 237-252.

Hooper, R. P., 1986. The Chemical Response of an Acid-Sensitive Headwater Stream to Snowmelt and Storm Events: A Field Study and Simulation Model. Ph. D. Thesis, Cornell University, New York.

Hooper, R. P., and C. A. Shoemaker, 1986. A Comparison of Chemical and Isotopic Hydrograph Separation. *Water Resources Research, 22 (10).* 1444-1454.

Huebert, B. J., F. C Fehsenfeld, R. B. Norton, and D. Albritton, 1983. The Scavenging of Nitric Acid Vapor by Snow. *Precipitation Scavenging, Dry Deposition and Resuspension,* vol 1, 293-300. Elsevier, New York.

Johannessen, M., and A. Hendriksen, 1978. Chemistry of Snow Meltwater. Changes in Concentration During Melting. *Water Resources Research, 14.* 615-619.

Johnson, N. M., G. E. Likens, F. H. Bormann, D. W. Fisher, and R. S. Pierce, 1969. A Working Model for the Variation in Streamwater Chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resources Research 5 (6).* 1353-1363.

Jones, H. G., 1991. Snow Chemistry and Biological Activity: A Particular Perspective on Nutrient Cycling. *Seasonal Snowpacks: Processes of Compositional Change,* T. D. Davies, M. Trantor, and H. G. Jones (Eds.), NATO Advanced Study Institute Series G, Vol. 28, Springer-Verlag, Berlin. 173-228.

Lawrence, S.J., and P.J. Wigington, Jr., 1988. Oxidized Nitrogen in Precipitation, Throughfall, and Streamfall from a Forested Watershed in Oklahoma. *Water Resources Bulletin, 23.* 1069-1076.

Malhi, S. S., and M. Nyborg, 1986. Increase in Mineral N in Soils During Winter and Loss of Mineral N During Early Spring in North-Central Alberta. *Canadian Journal of Soil Science, 66.* 397-409.

Marsh, P., and J. W. Pomeroy, 1993. The Impact of Heterogeneous Flowpaths on Snowmelt Runoff Chemistry. *Proceedings of the Eastern Snow Conference, Fiftieth Annual Meeting June 8-10, 1993, Quebec City, Quebec* . 255-264.

Maule, C. P., and J. Stein, 1990. Hydrologic Flow Path Definition and Partitioning of Spring Meltwater. *Water Resources Research, 26 (12).* 2959-2970.

Meyers, T. P., B. B. Hicks, R. P. Hosker Jr., J. D. Womack, and Lynne C. Satterfield, 1990. Dry Deposition Inferential Measurement Techniques III; Seasonal and Annual Deposition Rates of Sulfur and Nitrate. NOAA/ERL/Air Resources Laboratory. Oak Ridge, TN.

Pearce, A. J., M. K. Steward, and M. G. Sklash, 1986. Storm Runoff Generation in Humid Headwater Catchments: 1. Where Does the Water Come From? *Water Resources Research, 22 (8).* 1263-1272.

Peters, N. E., and C. T. Driscoll, 1989. Temporal Variations in Solute Concentrations of Meltwater and Forest Floor Leachate at a Forested Site in the Adirondacks, New York. *Proceedings of the Eastern Snow Conference, Forty-Sixth Annual Meeting June 8-9, 1989, Quebec City, Quebec* . 45-56.

Peters, N. E., and C. T. Driscoll, 1987. Sources of Acidity During Snowmelt at a Forested Site in the West-Central Adirondack Mountains, New York. *Proceedings of the Vancouver Symposium, Publication No. 167.* 99-108.

Pilgrim, D.H., D. D, Huff, and T. D. Steele, 1979. Use of Specific Conductance and Contact Time Relations for Separating Flow Components in Storm Runoff. *Water Resources Research, 15 (2).* 329-339.

Pinder, G. F., and J. F. Jones, 1969. Determination of the Ground-Water Component of Peak Discharge from the Chemistry of Total Runoff. *Water Resources Research, 5 (2).* 438-445.

Rasher, C. M., C. T. Driscoll, and N. E. Peters, 1987. Concentration and Flux of Solutes from Snow and Forest Floor During Snowmelt in the West-Central Adirondack Region of New York. *Biogeochemistry, 3.* 209-224.

Raynor, G. S., and J. V. Hayes, 1983. Differential Rain and Snow Scavenging Efficiency Implied by Ionic Concentration Differences in Winter Precipitation. *Precipitation Scavenging, Dry Deposition and Resuspension,* vol 1, 249-261. Elsevier, New York.

Robson, A., and C. Neal, 1990. Hydrograph Separation Using Chemical Techniques: An Application to Catchments in Mid-Wales. *Journal of Hydrology, 116.* 345-363.

Ross, D. S., and R. J. Bartlett (1990). Effects of Extraction Methods and Sample Storage on Properties of Solutions Obtained from Forested Spodosols. *Journal of Environmental Quality 19* (1). 108-113.

Rosswall, T., 1981. The Biogeochemical Nitrogen Cycle. *Some Perspectives of the Major Biogeochemical Cycles.* Likens, G. E., (ed.) SCOPE 17, John Wiley & Sons, New York. 25-49.

Stottlemyer, R., and C.A. Troendle, 1992. Nutrient Concentration Patterns in Streams Draining Alpine and Subalpine Catchments, Fraser Experimental Forest, Colorado. *Journal of Hydrology, 140* . 179-208.

Stottlemeyer, R., and D. Toczcydlowski, 1990. Pattern of Solute Movement from Snow Into an Upper Michigan Stream. *Canadian Journal of Fisheries and Aquatic Sciences, 47 (2).* 290-300.

Swistock, B. R., D. R. DeWalle, and W. E. Sharpe, 1989. Sources of Acidic Stormflow in an Appalachian Headwater Stream. *Water Resources Research, 25 (10).* 2139-2147.

Thorne, J.F., 1985. Nitrogen Cycling in a Base Poor and a Relatively Base Rich Northern Hardwood Forest Ecosystem. University Microforms International, Ann Arbor, Mich.

Tranter, M., P. Brimblecombe, T. D. Davies, C. E. Vincent, P. W. Abrahams, and I. Blackwood, 1986. The Composition of Snowfall, Snowpack, and Meltwater in the Scottish Highlands - Evidence For Preferential Elution. *Atmospheric Environment, 20.* 517-525.

Williams, M. W., 1993. Snowpack Storage and Release of Nitrogen in the Emerald Lake Watershed, Sierra Nevada. *Proceedings of the Eastern Snow Conference, Fiftieth Annual Meeting June 8-10, 1993, Quebec City, Quebec* . 239-245.

Williams, M. W., and J. M. Melack, 1991. Solute Chemistry and Runoff in an Alpine Basin, Sierra Nevada. *Water Resources Research, 27 (7).* 1575-1588.

Wilmot S. H., and T. D. Scherbatskoy (1993). VMC Annual Report for 1992. VMC Ann. Rep. No.2. Vt. Dept. Forests, Parks and Recreation. Waterbury, Vt. 138pp.

4.2.

# 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.* (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

$\theta$ = 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

### 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.

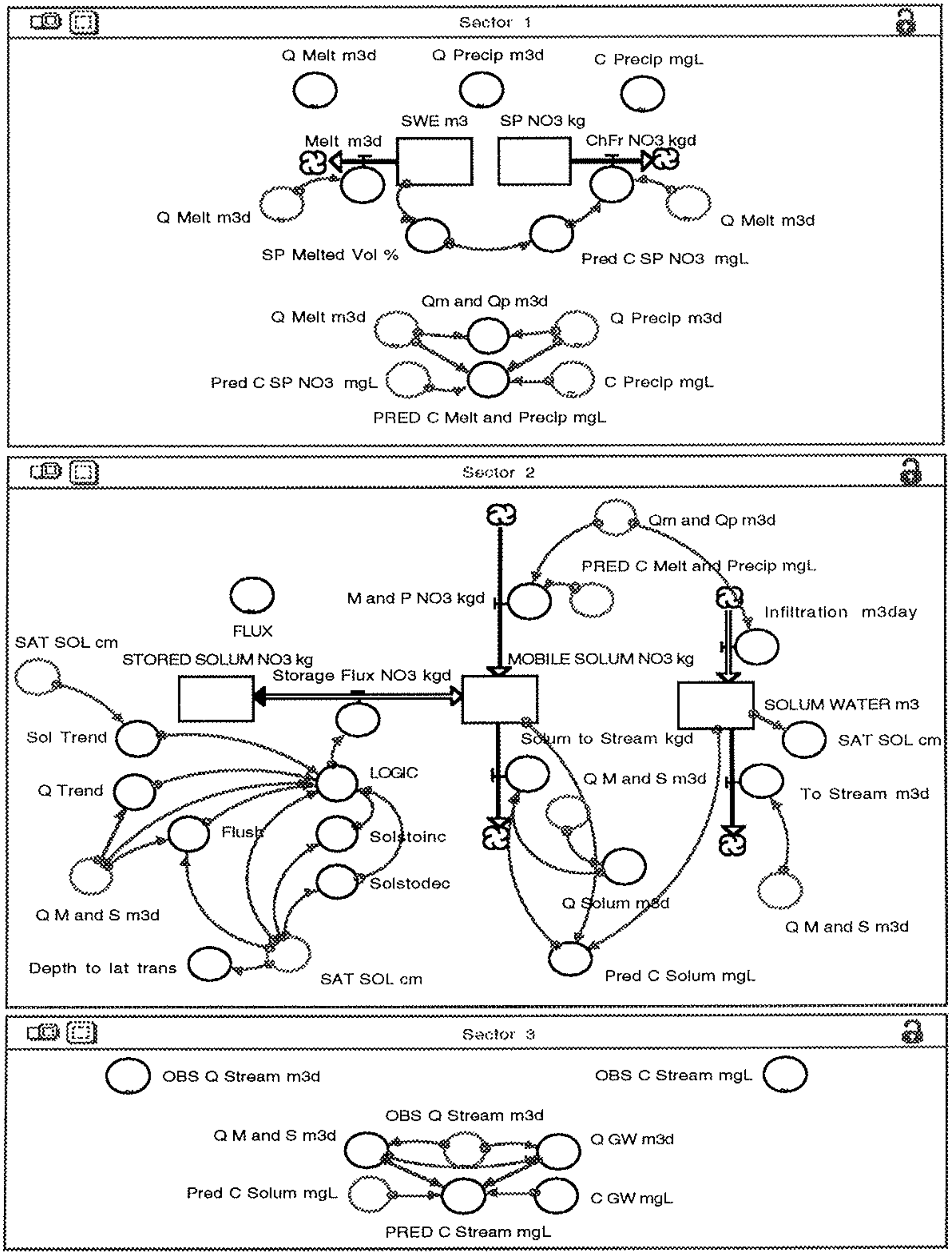


***Figure 1.*** SCATS structural diagram in STELLA format. Sector 1 simulates meltwater nitrate concentrations from the snowpack. Sector 2 simulates the influence of the solum on meltwater nitrate concentrations. Sector 3 mixes variable solum water nitrate concentrations with a fixed groundwater nitrate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

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 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 $NO_3^-$ 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:

$$y\ (\mathrm{NO_3^-}\ CF) = 4.4699e^{-0.0466x(\%\ \text{snowpack vol. melted})} \quad (4)$$

The concentration factor *(CF)* is the ratio of the solute concentration in meltwater to the original concentration in the snowpack. The mean concentration of $NO_3^-$ in the Nettle Brook snowpack prior to snowmelt was 1.94 mg/l $NO_3^-$. 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:

$$y\ (\mathrm{NO_3^-}\ \mathrm{mg/L}) = 8.6703e^{-0.0466x(\%\ \text{snowpack vol. melted})} \quad (5)$$

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):

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

where

$Q_T$ = total flow
$C_{PRED}$ = predicted $NO_3^-$ concentration of melt and precipitation
$Q_M$ = Q melt
$C_M$ = $NO_3^-$ concentration of melt
$Q_P$ = Q precipitation
$C_P$ = $NO_3^-$ 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:

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

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),

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

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

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

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

$Q_s$ = 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 ($N0_3^-$) 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 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

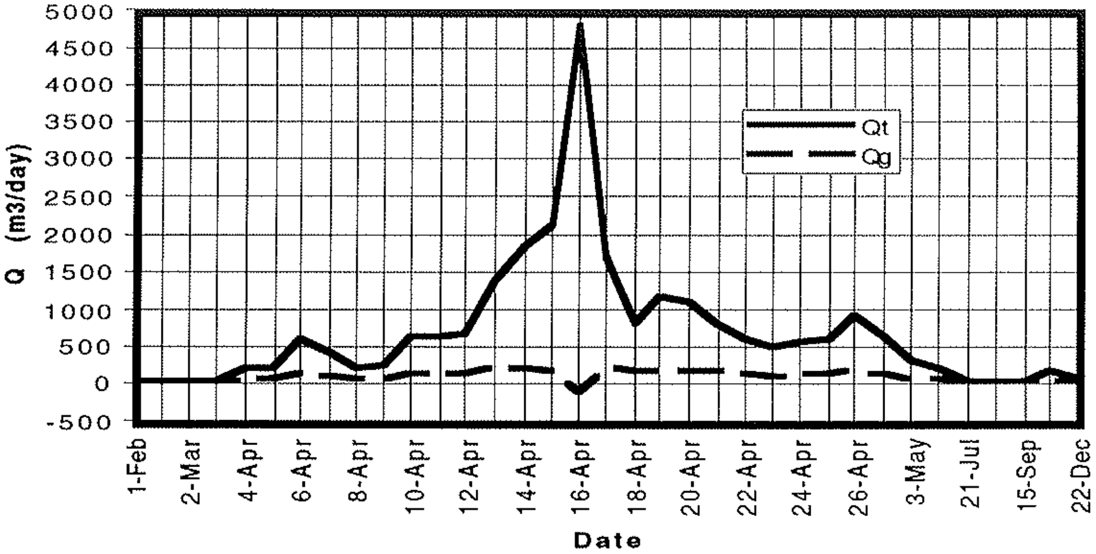


*Figure 2.* Nettle Brook Hydrograph Separation. Groundwater dominates the hydrograph at all but the highest flow rates as is observed during the Spring snowmelt event. Note that data points are primarily during the Spring snowmelt event.

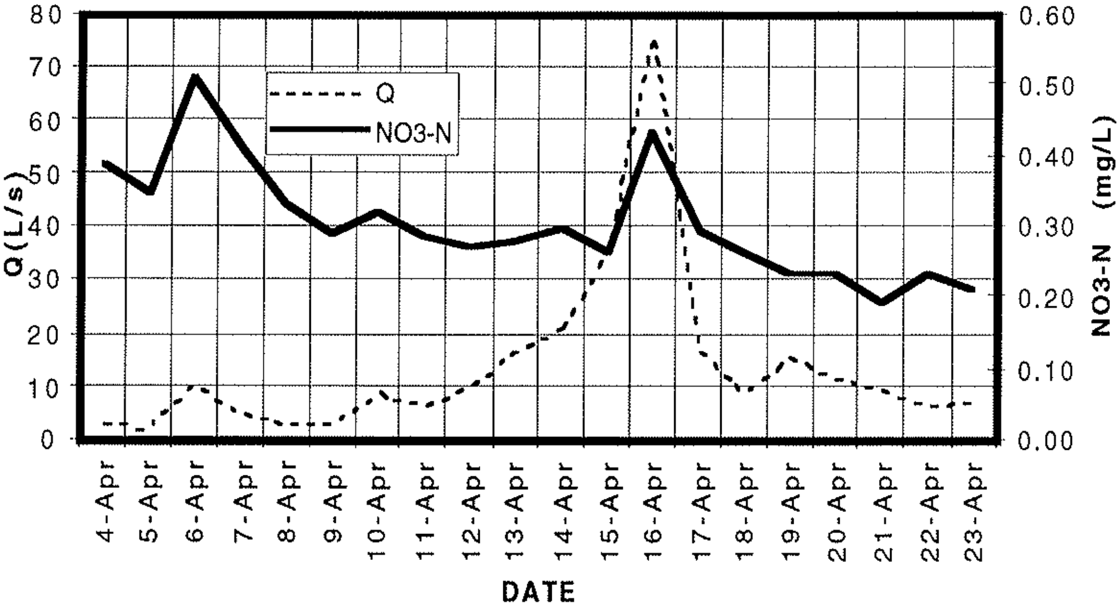


*Figure 3.* Nettle Brook nitrate during the 1994 Spring melt event.

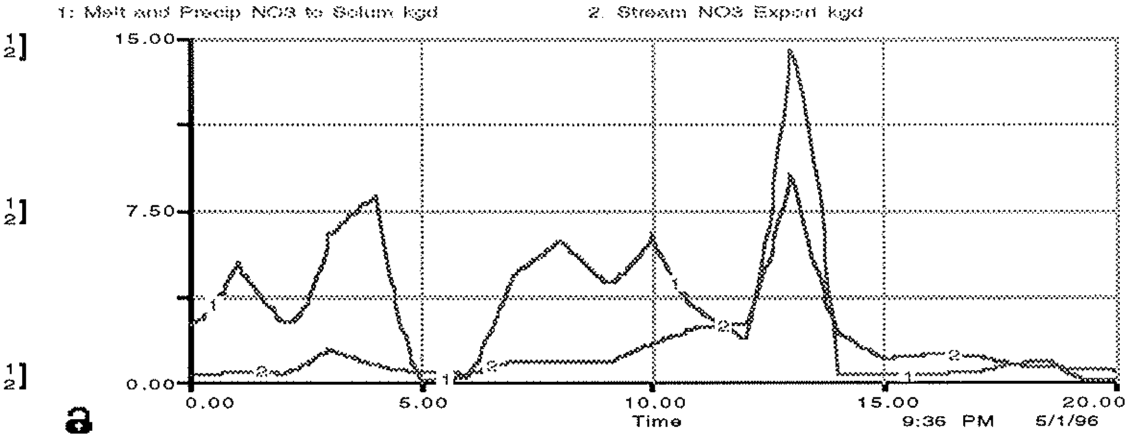


*Figure 4.* Nitrate release from the snowpack (curve 1) is greater than observed streamwater nitrate export (curve 2) through most of the simulation period suggesting overall retention of nitrate within the solum. Cold weather and snow decreased meltwater nitrate export on day 5-6 and total snowpack ablation occurred on day 13.

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 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).*

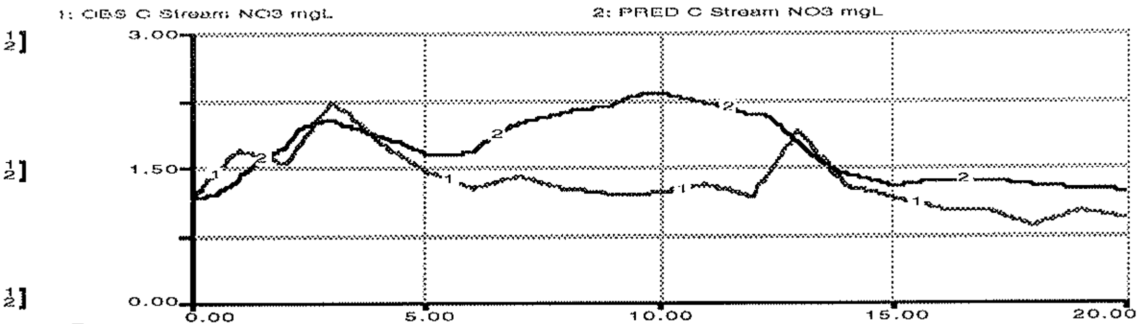


***Figure 5.*** First Run: One-Stock Solum. It is evident that when only one solum nitrate stock is used in the SCATS solum module that predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) do not fit observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) at Nettle Brook.

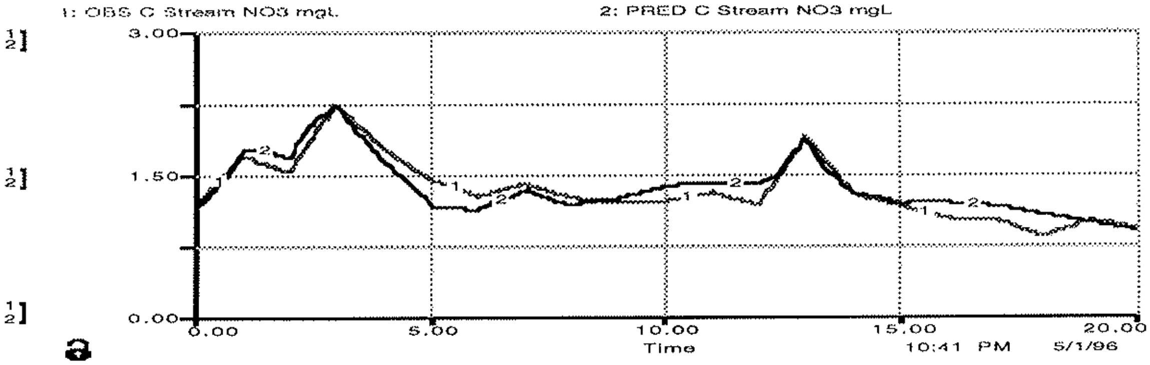


***Figure 6.*** Second Run: Two-Stock Solum. A considerably better fit was obtained between observed streamwater nitrate concentrations (OBS C Stream NO3 mgL object; curve 1) and predicted streamwater nitrate concentrations (PRED C Stream NO3 mgL object; curve 2) using the two-stock solum approach and equations 7 - 9 to control nitrate flux between the stocks.

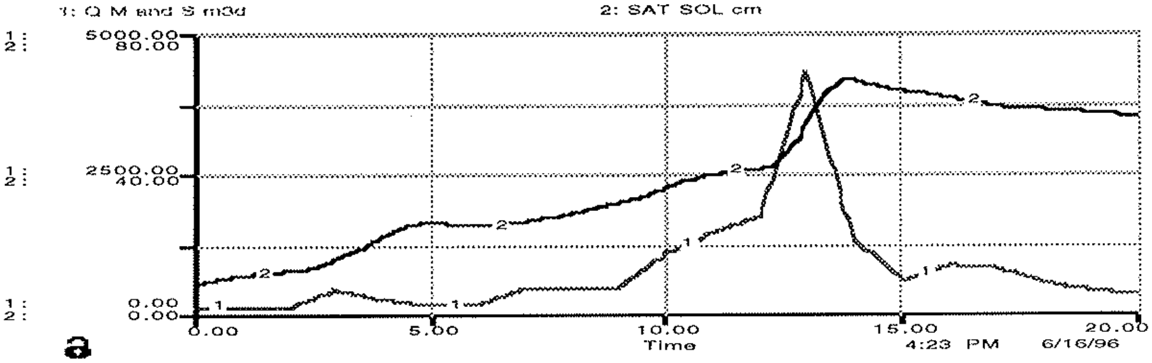


***Figure 7.*** Flow Rate (Curve 1) and Stored Water (Curve 2) Control Nitrate Flux Between Solum Stocks. Curve 1 represents flow through the solum (Q M and S object) and provides input for equation 7. Curve 2 represents the vertical height of water stored within the solum (SAT SOL cm object) and provides input for equations 7 - 9.

# 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 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.

## REFERENCES

Addiscott, T. M. 1977. 'A simple computer model for leaching in structured soils'. *Journal of Soil Science,* **28**. 554-563.

Addiscott, T. M. and R. J. Wagenet 1985. 'Concepts of solute leaching in soils: a review of modeling approaches'. *Journal of Soil Science* , **36**. 411-424.

Amerman, C. R., and J.W. Naney 1982. 'Subsurface flow and ground water systems'. in Haan, C. T., Johnson, H. P., and D. L. Brakensiek (Eds) 1982. *Hydrologic Modeling of Small Watersheds.* ASAE.

Burt, T. P., and S. T. Trudgill 1993. 'Nitrate in groundwater'. in Heathwaithe, A. L., Burt, T. P., and S. T. Trudgill (Eds) 1993. *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Cassell, E. A., and T. Pangburn 1990. 'Interactive modelling of cold regions watersheds with SSARR'. in Prowse, T. D. and C S. L. Ommanney, (Eds) 1990. *Northern Hydrology: Selected Perspectives. Proceedings of the Northern Hydrology Symposium*, 10-12 July. Saskatoon, Saskatchewan, Canada. 363-377.

Christopherson, N., Neal, C., Hooper, R. P., Vogt, R. D. and S. Andersen 1990. 'Modeling streamwater chemistry as a mixture of soilwater endmembers: a step towards second-generation acidification models'. *Journal of Hydrology*, **116**. 307-320.

Cragin, J. H., Hewitt, A. D., and S. C. Colbeck 1993. *Elution of Ions from Melting Snow: Chromatographic Versus Metamorphic Mechanisms.* CRREL Report 93-8. U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Hanover, N. H.

Daly, D. M. 1995. 'Nitrate transport in snowmelt in the Green Mountains of northern Vermont'. *Proceedings of the 52nd Annual Eastern Snow Conference.* 229-238.

Freeze, R.A., and J. A. Cherry 1979. *Groundwater.* Prentice-Hall Inc. New Jersey.

Gregory, J., Collins, D. N., and E. M. Morris 1986. 'Modelling the effect of snowmelt on stream water quality'. in Morris, E. M. (Ed) *Modeling Snowmelt-Induced Processes*, IAHS Publication 155. 311-324.

Hendershot, W. H., Savoie, S., and F. Courchesne 1992. 'Simulation of stream-water chemistry with soil solution and groundwater flow contributions'. *Journal of Hydrology*, **136**. 237-252.

Higgins, L.F., and J. R. Burney, J. 1982. 'Surface runoff, storage, and routing'. in Haan, C. T., Johnson, H. P., and D. L. Brakensiek (Eds) 1982. *Hydrologic Modeling of Small Watersheds.* ASAE.

Hooper, R. P. 1986. *The Chemical Response of an Acid-Sensitive Headwater Stream to Snowmelt and Storm Events: A Field Study and Simulation Model.* Ph. D. Thesis, Cornell University, New York.

Hooper, R. P., and C. A. Shoemaker, C. 1986. 'A comparison of chemical and isotopic hydrograph separation'. *Water Resources Research*, **22** (10). 1444-1454.

Hornbeck, J. W. 1986. 'Modelling the accumulation and effects of chemicals in snow'. in Morris, E. M. (Ed) *Modeling Snowmelt-Induced Processes*, IAHS Publication 155.

Jackson, T. J. 1982. 'Application and selection of hydrologic models'. in Haan, C. T., Johnson, H. P., and D. L. Brakensiek (Eds) 1982 *Hydrologic Modeling of Small Watersheds.* ASAE.

Johannessen, M., and A. Hendriksen 1978. 'Chemistry of snow meltwater: changes in concentration during melting'. *Water Resources Research*, **14**. 615-619.

Johnes, P. J., and T. P. Burt 1993. 'Nitrate in surface waters'. in Heathwaithe, A. L., Burt, T. P., and S. T. Trudgill (Eds) 1993. *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Johnson, P. L., and W. T. Swank 1973. 'Studies of cation budgets in the southern Appalachians on four experimental watersheds with contrasting vegetation'. *Ecology*, **54**. 70-80.

Johnson, N. M., Likens, G. E., Bormann, F. H., Fisher, D. W., and R. S. Pierce 1969. 'A working model for the variation in streamwater chemistry at the Hubbard Brook Experimental Forest, New Hampshire'. *Water Resources Research*, **5**. 1353-1363.

Male, D. H., and D. M. Gray 1981. *Handbook of Snow.* Pergamon Press, Toronto, Canada.

Maule, C. P., and J. Stein 1990. 'Hydrologic flow path definition and partitioning of spring meltwater'. *Water Resources Research,* **26** (12). 2959-2970.

Moldan, B. and J. Cerny, 1994. 'Small catchment research'. in Moldan, B. and J. Cerny (Eds) 1994. *Biogeochemistry of Small Catchments: A Tool for Environmental Research.* SCOPE. John Wiley & Sons Ltd.

Morris, E. M. and A. G. Thomas 1987. 'Transient acid surges in an upland stream'. *Water, Air, and Soil Pollution* , **34**. 429-438.

Pearce, A. J., Steward, M. K., and M. G. Sklash 1986. 'Storm runoff generation in humid headwater catchments: 1. where does the water come from?'. *Water Resources Research,* **22** (8). 1263-1272.

Peters, N. E., and C. T. Driscoll 1987. 'Sources of acidity during snowmelt at a forested site in the west-central Adirondack Mountains, New York'. *Proceedings of the Vancouver Symposium*, IAHS Publication No. 167. 99-108.

Peters, N. E., and C. T. Driscoll, C. 1989. 'Temporal variations in solute concentrations of meltwater and forest floor leachate at a forested site in the Adirondacks, New York'. *Proceedings of the Forty-Sixth Annual Eastern Snow Conference.* 45-56.

Pilgrim, D.H., Huff, D. D., and T. D. Steele, 1979. 'Use of specific conductance and contact time relations for separating flow components in storm runoff'. *Water Resources Research,* **15**. 329-339.

Pinder, G. F., and J. F. Jones 1969. 'Determination of the ground-water component of peak discharge from the chemistry of total runoff'. *Water Resources Research,* **5** (2). 438-445.

Rasher, C. M., Driscoll, C. T., and N. E. Peters 1987. 'Concentration and flux of solutes from snow and forest floor during snowmelt in the west-central Adirondack region of New York'. *Biogeochemistry,* **3**. 209-224.

Richmond, B., and S. Peterson, 1992. *STELLA II: Tutorial and Technical Documentation.* High Performance Systems. Hanover, New Hampshire.

Robson, A., and C. Neal 1990. 'Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales'. *Journal of Hydrology,* **116**. 345-363.

Rosswall, T. 1981. 'The biogeochemical nitrogen cycle'. in Likens, G. E. (Ed), *Some Perspectives of the Major Biogeochemical Cycles.* SCOPE 17, John Wiley & Sons, New York.

Tranter, M. 1991. 'Controls on the composition of snowmelt'. in Davies, T. D., Trantor, M., and H. G. Jones (Eds), *Seasonal Snowpacks: Processes of Compositional Change*, NATO Advanced Study Institute Series G, Vol. 28, Springer-Verlag, Berlin. 241-271.

Vitousek, P. M. 1977. 'The regulation of element concentrations in mountain streams in the northeastern United States'. *Ecological Monographs* **47**. 65-87.

White, R.E. 1985. 'A model for nitrate leaching in undisturbed structured clay soil during unsteady flow'. *Journal of Hydrology*, **79**. 37-51.

Woodfield, S. N. 1988. 'Object-based software development'. in Decoursey, D. G. (Ed) 1990. *Proceedings of the International Symposium on Water Quality Modeling of Agricultural Non-Point Sources, Parts 1 &* 2, USDA, Agricultural Research Service, ARS-81, June, 1990.

# COMPREHENSIVE BIBLIOGRAPHY

Aber, J. D. 1992. 'Nitrogen cycling and nitrogen saturation in temperate forest ecosystems'. *Tree*, 7 (7), 220-223

Addiscott, T. M. 1977. 'A simple computer model for leaching in structured soils'. *Journal of Soil Science,* 28, 554-563.

Addiscott, T. M., and Whitmore, A. P. 1987. 'Computer simulation of changes in soil mineral nitrogen and crop nitrogen during autumn, winter and spring'. *Journal of Agriculture Science*, 109, 141-157.

Addiscott, T. M. 1993. 'Simulation modelling and soil behaviour'. *Geoderma*, 60 (1-4), 15-40.

Addiscott, T. M., Heys, P. J. and Whitmore, A. P. 1986. 'Application of simple leaching models in heterogenous soils'. *Geoderma,* **38** (1-4), 185-194.

Addiscott, T. M. and Wagenet, R. J. 1985. 'Concepts of solute leaching in soils: a review of modelling approaches'. *Journal of Soil Science* , **36**, 411-424.

Altwicker, E. R. 1983. 'Nitrate in precipitation: how are the observed concentrations explained? *Precipitation Scavenging, Dry Deposition and Resuspension,* Vol 1, 283-291. Elsevier, New York.

Amerman, C. R., and Naney, J. W. 1982. 'Subsurface flow and ground water systems' in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

Armstrong, A. C. and Burt, T. P. 1993. 'Nitrate losses from agricultural land', in Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T. (Eds), *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Bales, R. C. 1991. 'Modeling in-pack chemical transformations' in Davies, T. D., Tranter, M., and Jones, H. G., (Eds), *Seasonal Snowpacks: Processes of Compositional Change.* NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

Bales, R. C., Davis, R. E., and Stanley, D. A. 1989. 'Ion elution through shallow homogeneous snow'. *Water Resources Research,* **25**. 1869-1877.

Bales, R. C., Davis, R. E., and Williams, M. W. 1993. 'Tracer release in melting snow: diurnal and seasonal patterns', *Hydrological Processes*, **7**, 389-401.

Barry, R., Prevost, M., Stein, J., and Plamondon, A. P. 1990. 'Simulation of snowmelt runoff pathways on the Lac La Flamme watershed', *Journal of Hydrology*, **113**, 103-121.

Bedient, P. B., and Huber, W. C. 1992. *Hydrology and Flood Plain Analysis.*, Addison-Wesley Publishing Company, New York.

Brimblecombe, P. M., Clegg, S., Davies, T. D., Shooter, D. S., and Tranter, M. 1987. 'Observations of the preferential loss of major ions from melting snow and laboratory ice', *Water Research,* **21**. 1279-1286.

Burt, T. P., and Trudgill, S. T. 1993. 'Nitrate in groundwater', in Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T., *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Cadle, S. H. 1991. 'Dry deposition to snowpacks', in Davies, T. D., Tranter, M., and Jones, H. G., (Eds), *Seasonal Snowpacks: Processes of Compositional Change.* NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

Cadle, S. H., Dasch, J. M., and Grossnickle, N. E. 1984. 'Retention and release of chemical species by a northern Michigan snowpack', *Water, Air and Soil Pollution,* **22**, 303-319.

Carmichael, G. R., Kitada, T., and Peters, L. K. 1983. 'The effects of in-cloud scavenging on the transport and gas phase reactions of SOx, NOx, HCx, HxOy, and O3 Compounds', *Precipitation Scavenging, Dry Deposition and Resuspension,* Vol 1, 293-300. Elsevier, New York.

Cassell, E. A., and Pangburn, T. 1990. 'Interactive modelling of cold regions watersheds with SSARR'. in Prowse, T. D. and Ommanney, C. S. L. (Eds), *Northern Hydrology: Selected Perspectives. Proceedings of the Northern Hydrology Symposium,* 10-12 July. Saskatoon, Saskatchewan, Canada.

Cerny, J., Billett, M. F., and Cresser, M. S. 1994. 'Element budgets', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Christopherson, N. C., Seip, H. M., and Wright, R. F. 1982. 'A model for streamwater chemistry at Birkenes, Norway', *Water Resources Research,* **18** (4). 977-996.

Christopherson, N., Neal, C., Hooper, R. P., Vogt, R. D. and Andersen, S. 1990. 'Modeling streamwater chemistry as a mixture of soilwater endmembers: a step towards second-generation acidification models', *Journal of Hydrology,* **116**. 307-320.

Colbeck, S. C. 1981. 'A simulation of the enrichment of atmospheric pollutants in snow cover runoff', *Water Resources Research,* **17**. 1383-1388.

Cosby, B. J., Hornberger, G. M., Galloway, J. N., and Wright, R. F. 1985. 'Modeling the effects of acid deposition: sssessment of a lumped parameter model of soil water and stream chemistry', *Water Resources Research,* **21** (1). 51-63.

Cragin, J. H., Hewitt, A. D., and Colbeck, S. C. 1993. 'Elution of ions from melting snow: chromatographic versus metamorphic mechanisms', *Crrel Report 93-8.* U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Hanover, N. H.

Cragin, J. H., and Hewitt, A. D. 1993. 'Aerosol scavenging by falling snow', *Proceedings of the Fiftieth Annual Eastern Snow Conference*, pp. 307-314.

Daly, D. M. 1995. 'Nitrate transport in snowmelt in the Green Mountains of northern Vermont', *Proceedings of the Fifty-Second Annual Eastern Snow Conference*, pp. 229-238.

Dann, M. S., Lynch, J, A., and Corbett, E. S. 1986. 'Comparison of methods for estimating sulfate export from a forested watershed', *Journal of Environmental Quality,* **15** (2). 140-145.

Davidson, C. I. 1989. 'Mechanisms of wet and dry deposition of atmospheric contaminants to snow surfaces', in Oeschger, H., and Langway, Jr., C. C. (Eds),*The Environmental Record in Glaciers and Ice Sheets.* John Wiley & Sons, New York.

Davies, T. D., Brimblecombe, P., Tranter, M., Tsiouris, S., Vincent, C. E., Abrahams, P. W., and Blackwood, I. L. 1987. 'The removal of soluble ions from melting snowpacks', in Jones, H. G., and Orville-Thomas, E. J. (Eds), *Seasonal Snowcovers: Physics, Chemistry, Hydrology* , D. Reidel, Dordrecht.

Davis, R. E. 1991. 'Links between snowpack physics and snowpack chemistry', in Davies, T. D., Tranter, M., and Jones, H. G., (Eds), *Seasonal Snowpacks: Processes of Compositional Change.* NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

De Leval, J., and Remacle, J. 1976. 'The influence of environmental factors on nitrification', in Nriagu, J.O (Ed), *Environmental Biochemistry.* Ann Arbor Science, Michigan.

Doner, H. E., and McLaren, A. D. 1976. 'Soil nitrogen transformations: a modeling study', in Nriagu, J.O (Ed), *Environmental Biochemistry.* Ann Arbor Science, Michigan.

Dowdell, R. J. 1976. 'The fate of nitrogen in soil: losses by denitrification and leaching', in Nriagu, J.O (Ed), *Environmental Biochemistry.* Ann Arbor Science, Michigan.

Dozier, J., Gjessing, Y. T., Johannes, A. J., and Morris, E. M. 1991. 'Chemical processes in snow - where should we go?', in Davies, T. D., Tranter, M., and Jones, H. G., (Eds), *Seasonal Snowpacks: Processes of Compositional Change.* NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

Dunne T., and Leopold, L. B. 1978. *Water in Environmental Planning.* W.H. Freeman and Company., New York.

Edmonds, R. L., Thomas, T. B., and Rhodes, J. J. 1991. 'Canopy and soil modification of precipitation chemistry in a temperate rain forest', *Soil Science Society of America Journal.,* **55**. 1685-1693.

Elgood, R. J. 1990. 'The effect of mid-winter snowmelt events on nitrate and ammonium concentration in the unsaturated and shallow saturated zones: a case study', M. A. Thesis, Wilfrid Laurier University, Ontario, Canada.

Fahey, D. W., Hubler, G., Parish, D. D., Williams, E. J., Norton, R. B., Ridley, B. A., Singh, H. B., Liu, S. C., and Fehsenfeld, F. C. 1986. 'Reactive nitrogen species in the troposphere', *Journal of Geophysical Research,* **91**. 9781-9793.

Foster, N.W., Nicolson, J. A., and Hazlett, P. W. 1989. 'Temporal variation in nitrate and nutrient cations in drainage waters from a deciduous forest', *Journal of Environmental Quality,* **18**. 238-244.

Fox, J. D. 1976. 'A forest hydrology model of vegetation-streamflow relations', Ph. D. Thesis, Univ. Laval., Quebec, Canada.

Freeze, R.A., and Cherry, J. A. 1979. *Groundwater*. Prentice-Hall Inc., New Jersey.

Frere, M. H., Seely, E. H., and Leonard, R. A. 1982. 'Modeling the quality of water from agricultural land', in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

Galvin, P. J., and Cline, J. A. 1978. 'Measurement of anions in the snow cover of the Adirondack Mountains. *Atmospheric Environment*, **12**. 1163-1167.

Gosz, J. R., Likens, G. E., and Bormann, F. H. 1973. 'Nutrient content of litterfFall on the Hubbard Brook Experimental Forest, New Hampshire', *Ecological Monographs,* **43**. 173-191.

Gregory, J., Collins, D. N., and Morris, E. M. 1986. 'Modelling the effect of snowmelt on stream water quality', in Morris, E. M. (Ed) *Modeling Snowmelt-Induced Processes*, IAHS Publication 155.

Gundersen, P., and Bashkin, V. N. 1994. 'Nitrogen cycling', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T. 1993. 'Overview: the nitrate issue', in Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T. (Eds), *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Hendershot, W. H., Savoie, S., and Courchesne, F. 1992. 'Simulation of stream-water chemistry with soil solution and groundwater flow contributions'. *Journal of Hydrology*, **136**. 237-252.

Higgins, L.F., and Burney, J. R. 1982. 'Surface runoff, storage, and routing', in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

Hooper, R. P. 1986. 'The chemical response of an acid-sensitive headwater stream to snowmelt and storm events: a field study and simulation model', Ph. D. Thesis, Cornell University, New York.

Hooper, R. P., and Shoemaker, C. A. 1986. 'A comparison of chemical and isotopic hydrograph separation', *Water Resources Research*, **22** (10). 1444-1454.

Hooper, R. P., Christopherson, N., and Peters, N. E. 1990. 'Modelling streamwater chemistry as a mixture of soilwater end-members - an application to the Panola Mountain catchment, Georgia, U. S. A.', *Journal of Hydrology*, **116**. 321-343.

Hornbeck, J. W. 1986. 'Modelling the accumulation and effects of chemicals in snow', in Morris, E. M. (Ed) *Modeling Snowmelt-Induced Processes*, IAHS Publication 155.

Huebert, B. J., Fehsenfeld, F. C., Norton, R. B., and Albritton, D. 1983. 'The scavenging of nitric acid vapor by snow', *Precipitation Scavenging, Dry Deposition and Resuspension,* Vol 1, 293-300. Elsevier, New York.

Huntington, T. G., Hooper, R. P., and Aulenbach, B. T. 1994. 'Hydrologic processes controlling sulfate mobility in a small forested watershed', *Water Resources Research*, **30**.(2). 283-295.

Jackson, T. J. 1982. 'Application and selection of hydrologic models', in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

James, LAD., and Burges, S. J. 1982. 'Selection, calibration, and testing of hydrologic models', in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

Jenkins, A., Peters, N. E., and Rodhe, A. 1994. 'Hydrology', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Johannessen, M., and Hendriksen, A. 1978. 'Chemistry of snow meltwater: changes in concentration during melting', *Water Resources Research*, **14**. 615-619.

Johnes, P. J., and Burt, T. P. 1993. 'Nitrate in surface waters', in Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T. (Eds), *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Johnson, N. M., Likens, G. E., Bormann, F. H., Fisher, D. W., and Pierce, R. S. 1969. 'A working model for the variation in streamwater chemistry at the Hubbard Brook Experimental Forest, New Hampshire', *Water Resources Research,* **5**. 1353-1363.

Johnson, P. L., and Swank, W. T. 1973. 'Studies of cation budgets in the southern Appalachians on four experimental watersheds with contrasting vegetation', *Ecology,* **54**. 70-80.

Jones, H. G. 1987. 'Chemical dynamics of snowcover and snowmelt in a boreal forest', in Jones, H. G., and Orville-Thomas, E. J. (Eds), *Seasonal Snowcovers: Physics, Chemistry, Hydrology* , D. Reidel, Dordrecht.

Jones, H. G. 1991. 'Snow chemistry and biological activity: a particular perspective on nutrient cycling', in Davies, T. D., Tranter, M., and Jones, H. G., (Eds), *Seasonal Snowpacks: Processes of Compositional Change.* NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

Jones, H. G., and Tranter, M. 1989. 'Interactions between meltwater and organic-rich particulate material in boreal forest snowpacks: evidence for both physico-chemical and microbiological Influences', in Miles E., (Ed),*Water-Rock Interaction..* Balkema, Rotterdam.

Jones, H. G., Davies, T. D., Pomeroy, J. W., Marsh, P., and Tranter, M. 1993. 'Snow-atmosphere interactions in Arctic snowpacks: net fluxes of $NO_3$ , $SO_4$ and influence of solar radiation', *Proceedings of the Fiftieth Annual Eastern Snow Conference*, pp. 255-264.

Kuusisto, E. 1986. 'The mass balance of snowcover in the accumulation and ablation periods', *Cold Regions Hydrology Symposium*, American Water Resources Association, Fairbanks, Alaska.

Larson, C. L., Onstad, C. A., Richardson, H. H. and Brooks, K. N. 1982. 'Some particular watershed models', in Haan, C.T., Johnson, H.P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

Lawrence, S. J., and Wigington, Jr., P. J. 1988. 'Oxidized nitrogen in precipitation, throughfall, and streamfall from a forested watershed in Oklahoma', *Water Resources Bulletin,* **23**. 1069-1076.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S. and Johnson, N. M. 1995. *Biogeochemistry of a Forested Ecosystem..* Springer-Verlag, New York.

Male, D. H., and Gray, D. M. 1981. *Handbook of Snow.* Pergamon Press, Toronto, Canada.

Malhi, S. S., and Nyborg, M. 1986. 'Increase in mineral N in soils during winter and loss of mineral N during early spring in north-central Alberta. *Canadian Journal of Soil Science,* **66**. 397-409.

Marsh, P., and Pomeroy, J. W. 1993. 'The impact of heterogeneous flowpaths on snowmelt runoff chemistry', *Proceedings of the Fiftieth Annual Eastern Snow Conference*, pp. 255-264.

Maule, C. P., and Stein, J. 1990. 'Hydrologic flow path definition and partitioning of spring meltwater', *Water Resources Research,* **26**. 2959-2970.

Melillo, J. M. 1981. 'Nitrogen cycling in deciduous forests', in Clark, F.E., and Rosswall, T. (Eds), *Terrestrial Nitrogen Cycles: Processes, Ecosystem Strategies and Management Impacts.* Ecol. Bull. (Stockholm).

Meyers, T. P., B. B. Hicks, R. P. Hosker Jr., J. D. Womack, and Lynne C. Satterfield, 1990. *Dry Deposition Inferential Measurement Techniques III; Seasonal and Annual Deposition Rates of Sulfur and Nitrate.* NOAA/ERL/Air Resources Laboratory. Oak Ridge, TN.

Moldan, B., and Cerny, J. 1994. 'Small catchment research', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Morris, E. M. and Thomas, A. G. 1985. 'Preferential discharge of pollutants during snowmelt in Scotland', *Journal of Glaciology*, Vol **31** (108). 190-193.

Morris, E. M. and Thomas, A. G. 1987. 'Transient acid surges in an upland stream', *Water, Air, and Soil Pollution* , **34**. 429-438.

Mulder, J., and Cresser, M. S. 1994. 'Soil and soil solution chemistry', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Mulder, J., Christophersen, N., Haughs, M., Vogt, R. D., Andersen, S., and Andersen, D. O. 1990. 'Water flow paths and hydrochemical controls in the Birkenes catchment as inferred from a rainstorm high in seasalts', *Water Resources Research* , **26** (4), 611-622.

Murdoch, P. S., and Stoddard, J. L. 1992. 'The role of nitrate in the acidification of streams in the Catskill Mountains of New York', *Water Resources Research,* **28** (10). 2707-2720.

Neubauer, J., and Heumann, K. G. 1988. 'Nitrate trace determinations in snow and firn core samples of ice shelves at the Weddel Sea, Antarctica', *Atmospheric Environment* , **22**. 537-545.

Newbould, P. 1981. 'Terrestrial nitrogen cycles: problems, present knowledge, and research trends', in Clark, F.E., and Rosswall, T. (Eds), *Terrestrial Nitrogen Cycles: Processes, Ecosystem Strategies and Management Impacts.* Ecol. Bull. (Stockholm).

Paul, E. A. 1977. 'Nitrogen cycling in terrestrial ecosystems', in Nriagu, J.O (Ed), *Environmental Biochemistry.* Ann Arbor Science, Michigan.

Paul, E. A., and Victoria, R. L. 1977. 'Nitrogen transfers between the soil and atmosphere', in Nriagu, J.O (Ed), *Environmental Biochemistry.* Ann Arbor Science, Michigan.

Pearce, A. J., Steward, M. K., and Sklash, M. G. 1986. 'Storm runoff generation in humid headwater catchments: 1. where does the water come from?', *Water Resources Research,* **22**. 1263-1272.

Peters, N. E., and Driscoll, C. T. 1987. 'Sources of acidity during snowmelt at a forested site in the west-central Adirondack Mountains, New York. *Proceedings of the Vancouver Symposium,* Publication No. 167. 99-108.

Peters, N. E., and Driscoll, C. T. 1989. 'Temporal variations in solute concentrations of meltwater and forest floor leachate at a forested site in the Adirondacks, New York', *Proceedings of the Forty-Sixth Annual Eastern Snow Conference,* pp45-56.

Peters, N. E., and Leavesley, G. E. 1993. 'Hydrogeochemistry of snowmelt at Rabbit Ears Pass, Rocky Mountains, Colorado', *Proceedings of the Fiftieth Annual Eastern Snow Conference.* pp. 339-346.

Peters, N. E., and P. S. Murdoch, 1985. 'Hydrogeologic comparison of an acid-lake basin with a neutral-lake basin in the west-central Adirondack Mountains, New York. *Water, Air and Soil Pollution*, **26**. 387-402.

Peters, N. E. 1994. 'Hydrologic processes', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Pilgrim, D.H., Huff, D. D., and Steele, T. D. 1979. 'Use of specific conductance and contact time relations for separating flow components in storm runoff', *Water Resources Research,* **15**. 329-339.

Pinder, G. F., and Jones, J. F. 1969. 'Determination of the ground-water component of peak discharge from the chemistry of total runoff', *Water Resources Research,* **5**. 438-445.

Rasher, C. M., Driscoll, C. T., and Peters, N. E. 1987. 'Concentration and flux of solutes from snow and forest floor during snowmelt in the west-central Adirondack region of New York', *Biogeochemistry,* **3**. 209-224.

Raynor, G. S., and Hayes, J. V. 1983. 'Differential rain and snow scavenging efficiency implied by ionic concentration differences in winter precipitation', *Precipitation Scavenging, Dry Deposition and Resuspension,* Vol 1, 249-261. Elsevier, New York.

Reynolds, B., Emmett, B. A., and Woods, C. 1992. *Variations in Streamwater Nitrate Concentrations and Nitrogen Budgets over 10 Years in a Headwater Catchment in Mid-Wales.* Elsevier Science Publishers, B. V.

Rhodes, J. J., Skau, C. M., and Greenlee, D. L. 1986. 'The role of snowcover on diurnal nitrate concentration patterns in streamflow from a forested watershed in the Sierra Nevada, Nevada, U.S.A.', *Cold Regions Hydrology Symposium*, American Water Resources Association, Fairbanks, Alaska.

Richmond, B., and Peterson, S. 1992. *STELLA II: Tutorial and Technical Documentation.* High Performance Systems, Hanover, New Hampshire.

Robson, A., and Neal, C. 1990. 'Hydrograph separation using chemical techniques: an application to catchments in Mid-Wales', *Journal of Hydrology,* **116**. 345-363.

Rosich, R. S., and Cullen, P. 1982. 'Interactions of phosphorus, nitrogen and carbon at the sediment-water interface', in Freney, J. R., and Galbally I. E. (Eds), *Cycling of Carbon, Nitrogen, Sulfur and Phosphorus in Terrestrial and Aquatic Ecosystems..* Springer-Verlag, New York.

Ross, D. S., and Bartlett, R. J. (1990). 'Effects of extraction methods and sample storage on properties of solutions obtained from forested spodosols', *Journal of Environmental Quality* , **19**. 108-113.

Ross, H.B. and Lindberg, S. E. 1994. 'Atmospheric chemical input to small catchments', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Rosswall, T. 1981. 'The biogeochemical nitrogen cycle'. in Likens, G. E. (Ed), *Some Perspectives of the Major Biogeochemical Cycles.* SCOPE 17, John Wiley & Sons, New York.

Schofield, C.L., Galloway, J.N. and Hendry, G. R. 1985. 'Surface water chemistry in the ILWAS basins', *Water, Soil, and Water Pollution* , **26**. 403-423.

Schuman, G. E., and Burwell, R. E. 1974. 'Precipitation nitrogen contribution relative to surface runoff discharges', *Journal of Environmental Quality*, **3** . 366-368.

Semkin, R. J., Jeffries, D. S., and Clair, T. A. 1994. 'Hydrochemical methods and relationships for study of stream output from small catchments', in Molden, B., and Cerny, J. (Eds), *Biogeochemistry of Small Catchments: A Tool for Environmental Research,* SCOPE. John Wiley and Sons, New York.

Shanley, J. B., Kendall, C., Albert, M. R., and Hardy, J. P. 1995. 'Chemical and isotopic evolution of a layered eastern U.S. snowpack and its relation to stream-water composition', *Biogeochemistry of Seasonally Snow-Covered Catchments.* Proceedings of a Boulder Symposium, July. 1995. IAHS Publication no. 228, 1995.

Shanley, J. B. and Peters, N. E. 1993. 'Variations in aqueous sulfate concentrations at Panola Mountain, Georgia', *Journal of Hydrology*, **146**. 361-382.

Stein, J., Jones, H. G., Roberge, J., and Sochaskna, W. 1986. 'The prediction of both runoff quality and quantity by the use of an integrated snowmelt model', *Modeling Snowmelt-Induced Processes.* International Association of Hydrologic Sciences, Oxfordshire, U. K.

Stevens, P.A., Williams, T. G., and Norris, D. A. 1993. 'Dissolved inorganic nitrogen budget for a forested catchment at Beddgelert, North Wales', *Environmental Pollution*, **80**. 1-8.

Stottlemeyer, R., and Toczcydlowski, D. 1990. 'Pattern of solute movement from snow into an upper Michigan stream', *Canadian Journal of Fisheries and Aquatic Sciences,* **47**. 290-300.

Stottlemyer, R., and Troendle, C. A. 1992. 'Nutrient concentration patterns in streams draining alpine and subalpine catchments, Fraser Experimental Forest, Colorado'. *Journal of Hydrology*, **140**. 179-208.

Swistock, B. R., DeWalle, D. R., and Sharpe, W. E. 1989. 'Sources of acidic stormflow in an Appalachian headwater stream', *Water Resources Research,* **25**. 2139-2147.

Thorne, J. F., 1985. *Nitrogen Cycling in a Base Poor and a Relatively Base Rich Northern Hardwood Forest Ecosystem.* University Microforms International, Ann Arbor, Mich.

Tranter, M. 1991. 'Controls on the composition of snowmelt', in Davies, T. D., Trantor, M., and Jones, H. G. (Eds), *Seasonal Snowpacks: Processes of Compositional Change*, NATO Advanced Study Institute Series G, Vol. 28. Springer-Verlag, Berlin.

Tranter, M., Brimblecombe, P., Davies, T. D., Vincent, C. E., Abrahams, P. W., and Blackwood, I. 1986. 'The composition of snowfall, snowpack, and meltwater in the Scottish Highlands - evidence for preferential elution', *Atmospheric Environment,* **20**. 517-525.

Tranter, M., Abrahams, P. W., Blackwood, I., Davies, T. D., Brimblecombe, P., Thompson, I. P., and Vincent, C. E. 1987. 'Changes in streamwater chemistry during snowmelt', in Jones, H. G., and Orville-Thomas, E. J. (Eds), *Seasonal Snowcovers: Physics, Chemistry, Hydrology* . D. Reidel, Dordrecht.

Vinten, A. J., and Smith, K. A. 1993. 'Nitrogen cycling in agricultural soils', in Heathwaithe, A. L., Burt, T. P., and Trudgill, S. T. (Eds), *Nitrate: Processes, Patterns and Management.* John Wiley & Sons Ltd.

Visocky, A. P. 1969. 'Estimating the ground-water contribution to storm runoff by the electrical conductance method', *Groundwater,* **8**. 5-10.

Vitousek, P. M. 1977. 'The regulation of element concentrations in mountain streams in the northeastern United States', *Ecological Monographs,* **47**. 65-87.

Walling, D. E., and Foster, I. D. L. 1975. 'Variations in the natural chemical concentration of river water during flood flows, and the lag effect: some further comments', *Journal of Hydrology*, **26**. 237-244.

White, R. E. 1985. 'A model for nitrate leaching in undisturbed structured clay soil during unsteady flow', *Journal of Hydrology*, **79**. 37-51.

Whitmore, A. P. 1991. 'A method of assessing the goodness of computer simulation of soil processes', *Journal of Soil Science* , **42**. 289-299.

Williams, M. W. 1993. 'Snowpack storage and release of nitrogen in the Emerald Lake Watershed, Sierra Nevada', *Proceedings of the Fiftieth Annual Eastern Snow Conference*. pp. 239-245.

Williams, M. W., and Melack, J. M. 1991. 'Solute chemistry and runoff in an alpine basin, Sierra Nevada', *Water Resources Research,* **27**. 1575-1588.

Wilmot S. H., and Scherbatskoy, T. D. 1993. *VMC Annual Report for 1992*. VMC Ann. Rep. No.2. Vt. Dept. Forests, Parks and Recreation. Waterbury, Vt.

Woodfield, S. N. 1988. 'Object-based software development', in Decoursey, D. G. (Ed), *Proceedings of the International Symposium on Water Quality Modeling of Agricultural Non-Point Sources, Parts 1 & 2*, USDA, Agricultural Research Service, ARS-81, June, 1990.

Woolhiser, D.A., and Brakensiek, D. L. 1982. 'Hydrologic modeling of small watersheds', in Haan, C. T., Johnson, H. P., and Brakensiek, D. L. (Eds), *Hydrologic Modeling of Small Watersheds.* ASAE.

World Meteorological Organization, 1986. 'Results of an intercomparison of models of snowmelt runoff', in Morris, E. M. (Ed), *Modeling Snowmelt-Induced Processes*, IAHS Publication 155.

# APPENDICES

# APPENDIX A: ANALYSIS OF STREAM, SNOW AND SOIL WATER SAMPLES.

| DATE | Sample# | Q (l/s) | AM/PM | pH | NO3-N(mg/L) | Cl- (mg/L) | SO4-S(mg/L) | PO4-P (mg/L) | Ca (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| **20-Dec-93** | NB53 | 1.4 | PM | 6.31 | 0.070 | 0.200 | 1.79 | <0.1 | 2.50 |
| **1-Feb-94** | NB1 | 0.5 | PM | 6.49 | 0.190 | 0.214 | 1.901 | <0.1 | 3.64 |
| **23-Feb-94** | NB52 | 7.2 | AM | 6.24 | 0.230 | 0.240 | 1.75 | ND | 3.02 |
| **2-Mar-94** | NB38 | 0.4 | AM | 6.48 | 0.188 | 0.201 | 1.974 | ND | 3.60 |
| **2-Mar-94** | SP39 | 0.4 | AM | 5.77 | 0.173 | 0.589 | 0.137 | ND | 0.13 |
| **21-Mar-94** | NB45 | 0.5 | PM | 6.47 | 0.259 | 0.405 | 1.839 | ND | 3.68 |
| **21-Mar-94** | SP35 | 0.5 | PM | 4.79 | 0.332 | 0.151 | 0.07 | ND | 0.11 |
| **21-Mar-94** | SP36 | 0.5 | PM | 4.99 | 0.166 | 0.254 | 0.166 | ND | 0.26 |
| **21-Mar-94** | SP37 | 0.5 | PM | 4.31 | 0.817 | 0.239 | 0.631 | ND | 0.11 |
| **4-Apr-94** | NB40 | 2.9 | PM | 6.28 | 0.387 | 0.014 | 1.643 | ND | 3.02 |
| **5-Apr-94** | NB2 | 2.0 | AM | 6.09 | 0.354 | 0.229 | 1.664 | ND | 3.14 |
| **5-Apr-94** | NB3 | 2.0 | PM | 6.23 | 0.339 | 0.137 | 1.694 | ND | 3.37 |
| **6-Apr-94** | NB4 | 10.2 | AM | 5.96 | 0.534 | 1.410 | 1.447 | ND | 2.93 |
| **6-Apr-94** | NB5 | 10.2 | PM | 5.98 | 0.481 | 0.201 | 1.451 | ND | 2.73 |
| **7-Apr-94** | NB6 | 5.1 | AM | 6.05 | 0.405 | 0.110 | 1.521 | ND | 2.79 |
| **8-Apr-94** | NB48 | 2.9 | AM | 6.12 | 0.330 | 0.327 | 1.537 | ND | 2.69 |
| **8-Apr-94** | NB8 | 2.9 | PM | 6.14 | 0.330 | 0.368 | 1.683 | ND | 2.74 |
| **9-Apr-94** | NB7 | 2.8 | AM | 6.11 | 0.296 | 0.392 | 1.701 | ND | 2.81 |
| **9-Apr-94** | NB41 | 2.8 | PM | 6.10 | 0.277 | 0.015 | 1.685 | ND | 2.70 |
| **10-Apr-94** | NB9 | 8.6 | AM | 5.91 | 0.304 | 0.304 | 1.502 | ND | 2.47 |
| **10-Apr-94** | NB43 | 8.6 | PM | 5.87 | 0.330 | 0.447 | 1.433 | ND | 2.39 |
| **11-Apr-94** | NB10 | 6.5 | AM | 5.88 | 0.288 | 0.300 | 1.607 | ND | 2.39 |
| **11-Apr-94** | NB12 | 6.5 | PM | 5.80 | 0.280 | 0.304 | 1.565 | ND | 2.39 |
| **12-Apr-94** | NB13 | 9.9 | AM | 5.98 | 0.275 | 0.300 | 1.624 | ND | 2.51 |
| **12-Apr-94** | NB14 | 9.9 | PM | 5.92 | 0.266 | 0.291 | 1.446 | ND | 2.24 |
| **13-Apr-94** | NB15 | 16.6 | AM | 5.84 | 0.254 | 0.291 | 1.514 | ND | 2.26 |
| **13-Apr-94** | NB16 | 16.6 | PM | 5.60 | 0.294 | 0.291 | 1.351 | ND | 2.24 |
| **14-Apr-94** | NB17 | 20.6 | AM | 5.65 | 0.311 | 0.291 | 1.479 | ND | 2.23 |
| **14-Apr-94** | NB18 | 20.6 | PM | 5.65 | 0.278 | 0.300 | 1.451 | ND | 2.28 |
| **15-Apr-94** | NB19 | 35.7 | AM | 5.69 | 0.258 | 0.241 | 1.521 | ND | 2.24 |
| **15-Apr-94** | NB42 | 35.7 | PM | 5.50 | 0.269 | 0.000 | 1.312 | ND | 2.02 |
| **16-Apr-94** | NB20 | 76.2 | AM | 5.41 | 0.509 | 0.228 | 1.259 | ND | 2.49 |
| **16-Apr-94** | NB21 | 76.2 | PM | 5.30 | 0.350 | 0.209 | 1.4 | ND | 1.91 |
| **17-Apr-94** | NB22 | 16.6 | AM | 5.33 | 0.302 | 0.234 | 1.54 | ND | 2.08 |
| **17-Apr-94** | NB23 | 16.6 | PM | 5.66 | 0.280 | 0.178 | 1.53 | ND | 2.10 |
| **18-Apr-94** | NB24 | 8.6 | AM | 6.01 | 0.249 | 0.212 | 1.58 | ND | 2.18 |
| **18-Apr-94** | NB25 | 8.6 | PM | 6.04 | 0.273 | 0.263 | 1.605 | ND | 2.17 |
| **19-Apr-94** | NB26 | 15.3 | AM | 6.25 | 0.223 | 0.212 | 1.59 | ND | 2.14 |
| **19-Apr-94** | NB27 | 15.3 | PM | 6.08 | 0.237 | 0.407 | 1.476 | ND | 2.14 |
| **20-Apr-94** | NB28 | 11.3 | AM | 5.69 | 0.230 | 0.246 | 1.599 | ND | 2.19 |
| **21-Apr-94** | NB29 | 9.1 | PM | 5.70 | 0.189 | 0.205 | 1.635 | ND | 2.23 |
| **22-Apr-94** | NB44 | 6.8 | PM | 5.52 | 0.229 | 0.269 | 1.544 | ND | 2.19 |
| **23-Apr-94** | NB46 | 6.9 | PM | 5.81 | 0.211 | 0.289 | 1.221 | ND | 2.14 |
| **24-Apr-94** | NB47 | 7.0 | AM | 6.00 | 0.214 | 0.283 | 1.539 | ND | 2.20 |
| **25-Apr-94** | NB30 | 7.1 | PM | 5.75 | 0.153 | 0.222 | 1.649 | ND | 2.30 |
| **26-Apr-94** | NB31 | 10.2 | PM | 5.74 | 0.174 | 0.039 | 1.638 | ND | 2.17 |
| **28-Apr-94** | NB32 | 7.1 | PM | 5.52 | 0.152 | 0.035 | 1.71 | ND | 2.30 |
| **3-May-94** | NB33 | 3.4 | PM | 5.85 | 0.122 | 0.000 | 1.79 | ND | 2.39 |
| **11-May-94** | NB34 | 2.0 | PM | 6.09 | ND | 0.003 | 1.851 | ND | 2.56 |
| **20-May-94** | NB49 | 2.4 | AM | 6.36 | 0.168 | 0.246 | 1.816 | ND | 3.04 |
| **25-May-94** | NB50 | 2.4 | PM | 6.13 | ND | 0.352 | 1.662 | ND | 2.54 |
| **21-Jul-94** | NB54 | 0.5 | PM | 6.51 | 0.070 | 0.230 | 1.58 | <0.1 | 3.69 |
| **26-Jul-94** | NB51 | 0.2 | PM | 6.63 | 0.080 | 0.270 | 1.78 | <0.1 | 4.00 |
| **15-Sep-94** | NB56 | 0.3 | AM | 6.75 | 0.080 | 0.280 | 1.73 | <0.1 | 3.61 |
| **2-Nov-94** | NB57 | 2.0 | AM | 6.40 | 0.000 | 0.520 | 1.73 | <0.1 | 3.00 |
| **29-Nov-94** | NB58 | 2.0 | AM | 6.36 | 0.270 | 0.220 | 1.61 | <0.1 | 2.49 |
| **22-Dec-94** | NB59 | ND | ND | ND | 0.120 | 0.330 | 1.86 | <0.1 | 2.69 |
| **27-Jan-95** | NB60 | ND | ND | ND | 0.160 | 0.310 | 1.74 | <0.1 | 2.46 |
| **12-Feb-95** | SP61 | ND | PM | ND | 0.410 | 0.500 | 0.1 | <0.1 | 0.35 |
| **12-Feb-95** | S62 | ND | PM | ND | 0.460 | 5.700 | 2.66 | <0.1 | 7.50 |
| **12-Feb-95** | S63 | ND | PM | ND | 0.700 | 2.290 | 1.95 | <0.1 | 4.03 |
| **12-Feb-95** | S64 | ND | PM | ND | <0.05 | 2.220 | 1.44 | <0.1 | 3.78 |
| **12-Feb-95** | S65 | ND | PM | ND | <0.05 | 2.350 | 2.12 | <0.1 | 4.23 |
| | | | | | | | | | |
| **KEY:** | | | | | | | | | |
| NB = Nettle Brook | | | | | | | | | |
| SP = Snowpack | | | | | | | | | |
| S = Soil | | | | | | | | | |
| ND = No data | | | | | | | | | |

| **APPENDIX** | | | | | | |
|---|---|---|---|---|---|---|
| **DATE** | **K (mg/L)** | **Mg (mg/L)** | **Na (mg/L)** | **Al (mg/L)** | **Si (mg/L)** | **NH4-N (mg/L)** |
| **20-Dec-93** | 0.02 | 0.31 | 0.54 | 0.07 | 1.53 | <0.05 |
| **1-Feb-94** | 0.26 | 0.54 | 0.54 | 0.07 | 2.51 | <0.05 |
| **23-Feb-94** | 0.05 | 0.41 | 0.64 | 0.07 | 1.84 | <0.05 |
| **2-Mar-94** | 0.27 | 0.54 | 0.55 | 0.06 | 2.42 | <0.05 |
| **2-Mar-94** | 0.20 | 0.07 | 0.37 | 0.03 | 0.03 | 0.3 |
| **21-Mar-94** | 0.24 | 0.53 | 0.49 | 0.04 | 2.31 | <0.05 |
| **21-Mar-94** | 0.00 | 0.00 | 0.06 | 0.00 | 0.00 | 0.12 |
| **21-Mar-94** | 0.12 | 0.05 | 1.33 | 0.06 | 0.03 | 0.15 |
| **21-Mar-94** | 0.07 | 0.05 | 0.08 | 0.02 | 0.02 | 0.36 |
| **4-Apr-94** | 0.17 | 0.43 | 0.30 | 0.05 | 1.53 | <0.05 |
| **5-Apr-94** | O.26 | 0.44 | 0.45 | 0.11 | 1.68 | <0.05 |
| **5-Apr-94** | 0.27 | 0.48 | 0.50 | 0.09 | 1.82 | <0.05 |
| **6-Apr-94** | 1.34 | 0.40 | 0.43 | 0.08 | 1.19 | <0.05 |
| **6-Apr-94** | 0.33 | 0.37 | 0.38 | 0.06 | 1.13 | <0.05 |
| **7-Apr-94** | 0.24 | 0.39 | 0.33 | 0.05 | 1.32 | <0.05 |
| **8-Apr-94** | 0.24 | 0.40 | 0.37 | 0.09 | 1.47 | <0.05 |
| **8-Apr-94** | 0.28 | 0.37 | 0.32 | 0.06 | 1.50 | <0.05 |
| **9-Apr-94** | 0.22 | 0.37 | 0.33 | 0.08 | 1.49 | <0.05 |
| **9-Apr-94** | 0.26 | 0.38 | 0.29 | 0.03 | 1.48 | <0.05 |
| **10-Apr-94** | 0.23 | 0.34 | 0.35 | 0.09 | 1.13 | <0.05 |
| **10-Apr-94** | 0.24 | 0.32 | 0.29 | 0.06 | 1.14 | <0.05 |
| **11-Apr-94** | 0.21 | 0.32 | 0.39 | 0.08 | 1.26 | <0.05 |
| **11-Apr-94** | 0.22 | 0.31 | 0.32 | 0.04 | 1.22 | <0.05 |
| **12-Apr-94** | 0.22 | 0.36 | 0.33 | 0.04 | 1.28 | <0.05 |
| **12-Apr-94** | 0.17 | 0.30 | 0.28 | 0.01 | 1.13 | <0.05 |
| **13-Apr-94** | 0.21 | 0.32 | 0.30 | 0.08 | 1.20 | <0.05; |
| **13-Apr-94** | 0.22 | 0.29 | 0.29 | 0.06 | 1.04 | <0.05 |
| **14-Apr-94** | 0.23 | 0.31 | 0.26 | 0.06 | 1.18 | <0.05 |
| **14-Apr-94** | 0.23 | 0.34 | 0.28 | 0.13 | 1.20 | <0.05 |
| **15-Apr-94** | 0.20 | 0.34 | 0.34 | 0.10 | 1.27 | <0.05 |
| **15-Apr-94** | 0.28 | 0.28 | 0.21 | 0.11 | 1.00 | <0.05 |
| **16-Apr-94** | 0.30 | 0.33 | 0.28 | 0.14 | 0.92 | 0.08 |
| **16-Apr-94** | 0.28 | 0.34 | 0.23 | 0.15 | 1.00 | 7.4 |
| **17-Apr-94** | 0.28 | 0.33 | 0.27 | 0.12 | 1.16 | 0.09 |
| **17-Apr-94** | 0.21 | 0.33 | 0.26 | 0.09 | 1.13 | <0.05 |
| **18-Apr-94** | 0.24 | 0.32 | 0.28 | 0.10 | 1.19 | 4.1 |
| **18-Apr-94** | 0.26 | 0.32 | 0.34 | 0.09 | 1.24 | 6.4 |
| **19-Apr-94** | 0.25 | 0.31 | 0.35 | 0.11 | 1.22 | 0.33 |
| **19-Apr-94** | 0.31 | 0.32 | 0.48 | 0.10 | 1.11 | 9.2 |
| **20-Apr-94** | 0.25 | 0.32 | 0.30 | 0.06 | 1.19 | 8.9 |
| **21-Apr-94** | 0.29 | 0.34 | 0.33 | 0.08 | 1.22 | 5.8 |
| **22-Apr-94** | 0.21 | 0.32 | 0.26 | 0.10 | 1.27 | <0.05 |
| **23-Apr-94** | 0.22 | 0.32 | 0.30 | 0.09 | 1.23 | <0.05 |
| **24-Apr-94** | 0.19 | 0.35 | 0.33 | 0.11 | 1.28 | 0.11 |
| **25-Apr-94** | 0.24 | 0.31 | 0.27 | 0.10 | 1.27 | 8.8 |
| **26-Apr-94** | 0.23 | 0.31 | 0.30 | 0.10 | 1.21 | 8.5 |
| **28-Apr-94** | 0.21 | 0.32 | 0.34 | 0.12 | 1.23 | 7.5 |
| **3-May-94** | 0.24 | 0.33 | 0.38 | 0.06 | 1.32 | 0.06 |
| **11-May-94** | 0.26 | 0.35 | 0.47 | 0.09 | 1.24 | 0.06 |
| **20-May-94** | 0.09 | 0.43 | 0.45 | 0.05 | 2.02 | <0.05 |
| **25-May-94** | 0.16 | 0.35 | 0.84 | 0.10 | 1.01 | <0.05 |
| **21-Jul-94** | 0.30 | 0.48 | 0.81 | 0.05 | 2.56 | <0.05 |
| **26-Jul-94** | 0.60 | 0.56 | 0.80 | 0.07 | 2.72 | <0.05 |
| **15-Sep-94** | 0.50 | 0.49 | 0.35 | 0.02 | 2.39 | <0.05 |
| **2-Nov-94** | 0.50 | 0.41 | 0.40 | 0.05 | 1.74 | <0.05 |
| **29-Nov-94** | 0.60 | 0.36 | 0.42 | 0.03 | 1.47 | <0.05 |
| **22-Dec-94** | 0.20 | 0.34 | 0.22 | 0.05 | 1.70 | <0.05 |
| **27-Jan-95** | 0.20 | 0.34 | 0.52 | 0.05 | 1.47 | <0.05 |
| **12-Feb-95** | 0.00 | 0.08 | 0.46 | 0.03 | 0.00 | 0.19 |
| **12-Feb-95** | 1.40 | 0.70 | 1.90 | 0.51 | 2.13 | 1.47 |
| **12-Feb-95** | 0.30 | 0.46 | 1.16 | 0.30 | 2.03 | 0.66 |
| **12-Feb-95** | 0.60 | 0.51 | 1.13 | 1.43 | 2.97 | 1.44 |
| **12-Feb-95** | 0.70 | 0.62 | 1.12 | 0.90 | 2.54 | 1.33 |
| | | | | | | |
| **KEY:** | | | | | | |
| NB = Nettle Brook | | | | | | |
| SP = Snowpack | | | | | | |
| S = Soil | | | | | | |
| ND = No data | | | | | | |

from D.D. Hess

**APPENDIX B1: PMRC DRY DEPOSITION INPUTS (2km from Nettle Brook catchment)**

| Proctor Maple Res -- MET DATA | | HNO3 | NO3 | HNO3+NO3 | Period | month | month | month | daily |
|---|---|---|---|---|---|---|---|---|---|
| Start (EST) | End (EST) | mg/m2/period | | | | mg/m2 | kg/ha | kg/cat | kg/cat |
| ------------------------- | ------------------------- | ------------------------------ | | | | | | | |
| 9/28/93, 1045 | 10/5/93, 1030 | 15.17 | 0.09 | 15.26 | | | | | |
| 10/5/93, 1045 | 10/12/93, 1015 | 28.57 | 0.08 | 28.66 | | | | | |
| 10/12/93, 1030 | 10/19/93, 1145 | 25.63 | 0.06 | 25.68 | | | | | |
| 10/19/93, 1200 | 11/2/93, 1200 | 6.93 | 0.08 | 7.01 | Oct '93 | 71.21 | 0.71 | 7.83 | 0.26 |
| 11/2/93, 1215 | 11/9/93, 1145 | 16.56 | 0.05 | 16.61 | | | | | |
| 11/9/93, 1200 | 11/16/93, 1230 | 17.65 | 0.06 | 17.72 | | | | | |
| 11/16/93, 1245 | 11/23/93, 1200 | 16.50 | 0.06 | 16.56 | | | | | |
| 11/23/93, 1215 | 11/30/93, 1315 | 9.62 | 0.16 | 9.78 | Nov '93 | 61.65 | 0.62 | 6.78 | 0.23 |
| 11/30/93, 1330 | 12/7/93, 1430 | 11.84 | 0.12 | 11.96 | | | | | |
| 12/7/93, 1445 | 12/14/93, 1345 | 14.90 | 0.18 | 15.08 | | | | | |
| 12/14/93, 1400 | 12/28/93, 1645 | 10.95 | 0.07 | 11.02 | Dec' 93 | 39.93 | 0.40 | 4.39 | 0.15 |
| 12/28/93, 1700 | 1/11/94, 1415 | 8.81 | 0.08 | 8.89 | | | | | |
| 1/11/94, 1430 | 1/25/94, 1400 | 9.17 | 0.05 | 9.21 | | | | | |
| 1/25/94, 1415 | 2/1/94, 1500 | 6.46 | 0.26 | 6.72 | Jan '94 | 22.96 | 0.23 | 2.53 | 0.08 |
| 2/1/94, 1515 | 2/8/94, 1200 | 25.57 | 0.28 | 25.85 | | | | | |
| 2/8/94, 1215 | 2/15/94, 1500 | 7.59 | 0.10 | 7.69 | | | | | |
| 2/15/94, 1515 | 2/22/94, 1430 | 27.53 | 0.36 | 27.88 | | | | | |
| 2/22/94, 1445 | 3/1/94, 1230 | 5.13 | 0.14 | 5.27 | Feb '94 | 66.69 | 0.67 | 7.34 | 0.24 |
| 3/1/94, 1245 | 3/8/94, 1430 | 15.43 | 0.08 | 15.51 | | | | | |
| 3/8/94, 1445 | 3/15/94, 1430 | 23.43 | 0.04 | 23.47 | | | | | |
| 3/15/94, 1445 | 3/22/94, 1445 | 8.84 | 0.07 | 8.91 | | | | | |
| 3/22/94, 1500 | 4/5/94, 1315 | 11.62 | 0.09 | 11.71 | Mar '94 | 55.38 | 0.55 | 6.09 | 0.20 |
| 4/5/94, 1315 | 4/12/94, 1400 | 18.81 | 0.08 | 18.89 | | | | | |
| 4/12/94, 1415 | 4/19/94, 1400 | 18.35 | 0.04 | 18.39 | | | | | |
| 4/19/94, 1415 | 4/26/94, 1315 | 12.57 | 0.18 | 12.75 | | | | | |
| 4/26/94, 1330 | 5/3/94, 1315 | 16.29 | 0.18 | 16.47 | Apr '94 | 63.64 | 0.64 | 7.00 | 0.23 |
| 5/3/94, 1330 | 5/10/94, 1400 | 17.12 | 0.16 | 17.28 | | | | | |
| 5/10/94, 1415 | 5/17/94, 1315 | 18.01 | 0.06 | 18.06 | | | | | |
| 5/17/94, 1330 | 5/24/94, 1445 | 20.02 | 0.31 | 20.33 | | | | | |
| 5/24/94, 1500 | 5/31/94, 1215 | 22.15 | 0.10 | 22.25 | May '94 | 85.00 | 0.85 | 9.35 | 0.31 |
| 5/31/94, 1230 | 6/7/94, 1400 | 28.51 | 0.09 | 28.59 | | | | | |
| 6/7/94, 1415 | 6/14/94, 1215 | 30.34 | 0.11 | 30.45 | | | | | |
| 6/15/93, 930 | 6/22/93, 900 | 17.05 | 0.01 | 17.06 | | | | | |
| 6/22/93, 915 | 6/29/93, 900 | 23.28 | 0.12 | 23.41 | June '94 | 101.93 | 1.02 | 11.21 | 0.37 |
| 6/29/93, 915 | 7/6/93, 900 | 17.20 | 0.09 | 17.30 | | | | | |
| 7/6/93, 915 | 7/13/93, 945 | 17.66 | 0.15 | 17.81 | | | | | |
| 7/13/93, 1000 | 7/20/93, 930 | 12.18 | 0.05 | 12.23 | | | | | |
| 7/20/93, 945 | 7/27/93, 915 | 11.53 | 0.06 | 11.59 | | | | | |
| 7/27/93, 930 | 8/3/93, 1045 | 16.15 | 0.06 | 16.21 | July '94 | 65.74 | 0.66 | 7.23 | 0.24 |
| 8/3/93, 1100 | 8/10/93, 930 | 14.42 | 0.06 | 14.48 | | | | | |
| 8/10/93, 945 | 8/17/93, 1030 | 22.70 | 0.06 | 22.76 | | | | | |
| 8/17/93, 1045 | 8/24/93, 1345 | 15.44 | 0.04 | 15.48 | | | | | |
| 8/24/93, 1400 | 8/31/93, 1400 | 20.74 | 0.11 | 20.86 | Aug '94 | 80.54 | 0.81 | 8.86 | 0.30 |
| 8/31/93, 1415 | 9/7/93, 930 | 17.55 | 0.04 | 17.59 | | | | | |
| 9/7/93, 945 | 9/14/93, 930 | 26.66 | 0.07 | 26.73 | | | | | |
| 9/14/93, 945 | 9/21/93, 1045 | 19.02 | 0.11 | 19.13 | | | | | |
| 9/21/93, 1115 | 9/28/93, 1030 | 18.60 | 0.05 | 18.65 | Sept '94 | 82.10 | 0.82 | 9.03 | 0.30 |
| | | | | | | | | | |
| | | | | | Water Yr Sum | = | 7.97 | 87.65 | |
| | | | | | Dec-Mar Sum | = | 1.85 | 20.35 | |
| | | | | | Dec-Apr Sum | = | 2.49 | 27.35 | |

## APPENDIX B2: PMRC WET DEPOSITION INPUTS

| code | Per. | Year | NO3 (mg/L) | Ppt | Days | Dates | Dates | NO3 (kg/ha) | NO3 (kg/cat) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | |
| VT99 | oct | 1993 | 1.41 | 13.11 | 35 | 930928 | 931102 | 1.85 | 20.33 |
| VT99 | nov | 1993 | 1.87 | 6.6 | 28 | 931102 | 931130 | 1.23 | 13.58 |
| VT99 | dec | 1993 | 3.52 | 6.6 | 35 | 931130 | 940104 | 2.32 | 25.56 |
| VT99 | jan | 1994 | 1.27 | 7.39 | 28 | 940104 | 940201 | 0.94 | 10.32 |
| VT99 | feb | 1994 | 1.83 | 3.58 | 28 | 940201 | 940301 | 0.66 | 7.21 |
| VT99 | mar | 1994 | 1.21 | 9.4 | 29 | 940301 | 940330 | 1.14 | 12.51 |
| VT99 | apr | 1994 | 1.88 | 12.55 | 34 | 940330 | 940503 | 2.36 | 25.95 |
| VT99 | may | 1994 | 1.49 | 9.78 | 28 | 940503 | 940531 | 1.46 | 16.03 |
| VT99 | jun | 1994 | 2.09 | 12.09 | 28 | 940531 | 940628 | 2.53 | 27.79 |
| VT99 | jul | 1994 | 1.52 | 11.2 | 35 | 940628 | 940802 | 1.70 | 18.73 |
| VT99 | aug | 1994 | 1.06 | 18.57 | 28 | 940802 | 940830 | 1.97 | 21.65 |
| VT99 | sep | 1994 | 1.13 | 9.65 | 35 | 940830 | 941004 | 1.09 | 11.99 |
| | | | | | | | | | |
| | | | | | | TOTALS | Water Yr | 19.24 | 211.66 |
| | | | | | | | nov-apr | 8.65 | 95.13 |
| | | | | | | | dec-apr | 7.41 | 81.55 |
| | | | | | | | dec-mar | 5.05 | 55.60 |

## APPENDIX C1: SCATS MODEL DOCUMENTATION.

### SECTOR 1 (SNOWPACK MODULE)

*STOCK:*
**SP_NO3_kg**(t) = SP_NO3_kg(t - dt) + (- ChFr_NO3_kgd) * dt
INIT SP_NO3_kg = 47.07
DOCUMENT: This stock contains the estimated snowpack N03 content prior to spring melt. An initial value was obtained from snowpack sampling (3 samples distributed vertically through the snowpack) prior to the Spring snowmelt event (21 Mar '94). The mean concentration of samples (1.941 mg/L) is multiplied by the estimated SWE prior to the first day of melt (3 Apr '94 - 21578 m3 - 21,578,000 L) and the result converted to kg (42 kg). Estimated wet and dry deposition for the 13 days elapsed between SP sampling and commencement of the spring melt is approximately 8 kg. Initial input is therefore set at 50 kg. After one run it was found that 2.93 kg remained in the snowpack at total ablation. Options were to modify Johannessens equation or reduce the estimated initial amount. The initial amount was reduced based on the logic that it is likely that some nitrate was leached from the snowpack between 21 March and 3 April. It would have been preferable to have obtained snowpack samples on the day that Spring Melt commenced. INITIAL VALUE WAS SET AT 47.07

*OUTFLOW:*
**ChFr_NO3_kgd** = (Q_Melt_m3d * Pred_C_SP_NO3__mgL) / 1000
DOCUMENT: This flow predicts NO3 loss from the snowpack (kgs) by multiplying SWE melted (m3) by the predicted concentration of the melt (mg/L) and converting to kgs.

*STOCK:*
**SWE_m3**(t) = SWE_m3(t - dt) + (- Melt_m3d) * dt
INIT SWE_m3 = 22000
DOCUMENT: The initial value in this stock is estimated for the 11 hectare catchment on the date prior to the first day of the final melt period. The snowpack water equivalent (SWE) is calculated by multiplying the snowpack depth recorded at the weir by 0.32 (March 5, Sleepers River data) and multiplying by 110000 m2 (catchment area) to yield 21578 m3. 422 m3 were added to account for snowfall that occurred on April7-8. 22000 is therefore the initial value. SEE EXCEL SP TABLE 1 IN SUPPORTING DOCUMENTATION.

*OUTFLOW:*
**Melt_m3d** = Q_Melt_m3d
DOCUMENT: See documentation for Q Melt m3d.

*CONVERTERS:*
**PRED_C_Melt_and_Precip_mgL** = ((((Q_Melt_m3d*1000)*Pred_C_SP_NO3__mgL)+((Q_Precip_m3d*1000)*C_Precip_mgL))+.00001)/(((Q_Melt_m3d+Q_Precip_m3d)*1000)+.001)
DOCUMENT: This converter predicts leachate concentration as a result of the mixing of snowpack meltwater and precipitation. Relatively small values have been added to the numerator and denominator of the equation Cpred = ((Qmelt * Cmelt) + (Qprecip * Cprecip)) / (Qmelt + Qprecip) to prevent 0 from occurring in either the numerator or the

denominator and resulting in an error message (?) for the entire time series of calculations. These small values are insignificant relative to the magnitude of the calculations.
**Pred_C_SP_NO3__mgL** = IF (SP_Melted_Vol_% < 50) THEN (8.6703 * EXP(-0.0465*SP_Melted_Vol_%)) ELSE (0.89)
DOCUMENT: The equation derived from data presented by Johannessen et al. (1978), C NO3 (mgL) = 7.3709 * exp (-0.0466 * SP Vol Melted %), represents chemical fractionation concentrations occurring within a snowpack.

**Qm_and_Qp_m3d** = Q_Melt_m3d + Q_Precip_m3d
DOCUMENT: Prior to total snowpack ablation, flow to the solum is the result of snowpack meltwater and precipitation. Flow to the solum is the result of precipitation after total ablation.

**SP_Melted_Vol_%** = ((1-(SWE_m3/22000))*100)
DOCUMENT: Percent volume of snowpack melted is calculated by dividing current SWE values by the premelt estimated SWE ( 22000 m3), subtracting the result from unity (1) and multiplying by 100.

**C_Precip_mgL** = GRAPH(TIME)
(0.00, 2.02), (1.00, 0.00), (2.00, 0.00), (3.00, 1.96), (4.00, 1.97), (5.00, 0.00), (6.00, 0.00), (7.00, 2.22), (8.00, 0.00), (9.00, 0.00), (10.0, 2.06), (11.0, 0.00), (12.0, 0.00), (13.0, 1.95), (14.0, 5.15), (15.0, 7.33), (16.0, 5.15), (17.0, 3.52), (18.0, 2.43), (19.0, 7.33), (20.0, 0.00)
DOCUMENT: The average wet deposition NO3 concentration value for the month of April was 1.88 mg/L (NADP) and the daily average dry deposition rate was 0.18 kg/d (PMRC). It assumed that dry deposition is mobilized with wet deposition and therefore accumulated dry deposition quantities(kg/day) were added to precipitation quantities (kg/day) and adjusted values for the resulting wet deposition concentrations are calculated for precipitation events (mg/L)) during the spring melt period. SEE SP TABLE 2.

**Q_Melt_m3d** = GRAPH(TIME)
(0.00, 0.00), (1.00, 634), (2.00, 352), (3.00, 317), (4.00, 669), (5.00, 0.00), (6.00, 35.0), (7.00, 669), (8.00, 1443), (9.00, 1373), (10.0, 1971), (11.0, 2182), (12.0, 2077), (13.0, 10278), (14.0, 0.00), (15.0, 0.00), (16.0, 0.00), (17.0, 0.00), (18.0, 0.00), (19.0, 0.00), (20.0, 0.00)
DOCUMENT: Snowpack melt values (m3) were derived by converting the daily average of snowpack depth recorded every 30 minutes by an snow depth sensor located at the Nettle Brook V-notch weir to water equivalent by multiplying 0.3 * snowpack depth (m) * 110000 (m2) and subtracting the value obtained for the previous day. SEE SP TABLE 1.1

**Q_Precip_m3d** = GRAPH(TIME)
(0.00, 1254), (1.00, 0.00), (2.00, 0.00), (3.00, 2156), (4.00, 1591), (5.00, 0.00), (6.00, 0.00), (7.00, 528), (8.00, 0.00), (9.00, 0.00), (10.0, 979), (11.0, 0.00), (12.0, 0.00), (13.0, 2761), (14.0, 55.0), (15.0, 33.0), (16.0, 55.0), (17.0, 110), (18.0, 330), (19.0, 33.0), (20.0, 0.00)
DOCUMENT: Daily precipitation values collected 2 km from Nettle Brook (PMRC) were used to calculate precipitation input values into the Nettle Brook catchment. Precipitation is reported as water equivalent (m3). 422 m3 of snow (snow depth sensor) occurred in 2013 m3 of precipitation (rain/snow) on Apr 7, therefore the amount of precipitation for that date entered is 1591. SEE SP TABLE 1.1

## SECTOR 2 (SOLUM MODULE)

*STOCK:*
**MOBILE_SOLUM_NO3_kg(t)** = MOBILE_SOLUM_NO3_kg(t - dt) + (Storage_Flux_NO3_kgd + M_and_P_NO3_kgd - Solum_to_Stream_kgd) * dt
INIT MOBILE_SOLUM_NO3_kg = 5.8
DOCUMENT: This stock combines snowmelt and/or rain NO3 and NO3 released from the immobile solum stock. The initial value is approximated by multiplying the streamwater sample concentration for the day previous to the simulation period by the estimated water quantity in the solum water stock (1.15mgL x 2829m3/1000 =3.25kg ).

*INFLOW:*
**Storage_Flux_NO3_kgd** = LOGIC
DOCUMENT: Release of nitrate from the immobile stock into the mobile stock exhibits a positive exponential corollation with increase in Q solum (flushing effect). Movement of nitrate into the immobile stock from the mobile stock (storage) exhibits a positive linear corrolation with the estimated saturation height of the solum.

**M_and_P_NO3_kgd** = (Qm_and_Qp_m3d * PRED_C_Melt_and_Precip_mgL) / 1000

*OUTFLOW:*
**Solum_to_Stream_kgd** = (Q_Solum_m3d*Pred_C_Solum_mgL) / 1000
DOCUMENT: This flow represents lateral subsurface flow through the solum to the stream.

*STOCK:*
**SOLUM_WATER_m3**(t) = SOLUM_WATER_m3(t - dt) + (Infiltration_m3day - To_Stream_m3d) * dt
INIT SOLUM_WATER_m3 = 2829
DOCUMENT: This stock contains an approximated water quantity (m3) stored in the solum. The approximation was derived from Table 1 for the day prior to snowmelt (Q precip-+Qmelt-Qstreamflow, day 0 = 2829 m3) Solum water loss to groundwater has been ignored because of lack of data.

*INFLOW:*
Infiltration_m3day = Qm_and_Qp_m3d
DOCUMENT: This flow represents infiltration of snowmelt or rain into the solum. Overland flow to the stream is considered insignificant.

*OUTFLOW:*
To_Stream_m3d = Q_M_and_S_m3d
DOCUMENT: During high flow events, such as spring melt, flow from the solum is assumed to be primarily lateral subsurface flow to the groundwater dominated stream with little net loss to groundwater although some exchange occurs.

*STOCK:*
**STORED_SOLUM_NO3_kg**(t) = STORED_SOLUM_NO3_kg(t - dt) + (-Storage_Flux_NO3_kgd) * dt
INIT STORED_SOLUM_NO3_kg = 29.7
DOCUMENT: This stock contains the estimated NO3 lost from the snowpack to the solum prior to Spring snowmelt (29.7 kg).

*OUTFLOW:*
**Storage_Flux_NO3_kgd** = LOGIC
DOCUMENT: Release of nitrate from the immobile stock into the mobile stock exhibits a positive exponential corollation with increase in Q solum (flushing effect). Movement of nitrate into the immobile stock from the mobile stock (storage) exhibits a positive linear corrolation with the estimated saturation height of the solum.

***CONVERTERS:***
**Depth_to_lat_trans** = 66.79 - SAT_SOL_cm
Flush = ((-0.096*(SAT_SOL_cm))+5.394)*(EXP(0.001*Q_M_and_S_m3d))
DOCUMENT: This equation describes flushing of nitrate in the deepest strata in the soil.

**LOGIC** = (IF (Sol_Trend > SAT_SOL_cm) THEN (Solstoinc) ELSE (Solstodec)) + (IF (Q_Trend > Q_M_and_S_m3d) THEN (Flush) ELSE (0))
DOCUMENT: Different behavior is exhibited in nitrate retention and release in three distinct layers in the subsurface soil horizons. It is hypothesized that lateral flowpaths change as solum saturation increases. Movement into the immobile phase in all three strata is described by one linear equation (with an anomalous increase in the middle strata) and is a function of solum saturated height or water content. Movement (flushing) of nitrate into the mobile phase is described by similar but different exponential equations as a function if solum flow rate (increasing Q results in increasing release). The flushing effect equations decrease as saturation level nears the soil surface. It may be that this is a result of available nitrate having been removed by percolating water and transported to the lower horizons.

**Pred_C_Solum_mgL** = (MOBILE_SOLUM_NO3_kg/SOLUM_WATER_m3) * 1000
DOCUMENT: This converter calculates the concentration of solum water by dividing the mobile nitrate stock by the solum water volume.

**Q_Solum_m3d** = Q_M_and_S_m3d
DOCUMENT: This flow represents the fraction of streamflow determined by the hydrograph separation in Module 3.

**Q_Trend** = FORCST(Q_M_and_S_m3d,0.0625,0.0625,0)
DOCUMENT: This converter in used to detect increasing or decreasing flow in the solum.

**SAT_SOL_cm** = ((SOLUM_WATER_m3/110000)*100) *3.3
DOCUMENT: Water retained in the solum (input from melt and precipitation and not output to the stream) is converted to solum saturation elevation (centimeters).

**Solstodec** = (0.0043*(SAT_SOL_cm^2))-(0.276 * (SAT_SOL_cm))-0.0042
Solstoinc = (0.0029*(SAT_SOL_cm^2))-(0.276*(SAT_SOL_cm))-0.0007
DOCUMENT: This equation describes the movement of nitrate into the immobile phase and applies to all strata.

**Sol_Trend** = FORCST(SAT_SOL_cm,0.0625,0.0625,0)
FLUX = GRAPH(TIME)
(0.00, 0.00), (1.00, 5.00), (2.00, 0.00), (3.00, 7.00), (4.00, 0.00), (5.00, 0.00), (6.00, -8.00), (7.00, 0.00), (8.00, 0.00), (9.00, -5.00), (10.0, 0.00), (11.0, 0.00), (12.0, 0.00), (13.0, 30.0), (14.0, -15.0), (15.0, 0.00), (16.0, 0.00), (17.0, 0.00), (18.0, 0.00), (19.0, 0.00), (20.0, 0.00)
DOCUMENT: This graph was used to input discrete quantities (kgs) of nitrate to and from the mobile solum to make the solum concentration reflect as closely as possible the concentration necessary to produce the observed streamwater nitrate concentrations. This

is the first step in deriving equations to replace the discrete addition or removal of nitrate simulating flux between mobile and immobile solum components. The quantities are plotted against variables such as flow rates or solum water content and regression analysis used to derive equations.

## SECTOR 3

*CONVERTERS:*

**C_GW_mgL** = 0.11

DOCUMENT: Groundwater NO3-N was below detection limits (< 0.05 mg/L). Half of the detection limit was converted to NO3 and used as the input for the GW concentration..

**PRED_C_Stream_NO3_mgL** = (((Q_M_and_S_m3d * 1000) * (Pred_C_Solum_mgL)) + ((Q_GW_m3d * 1000) * (C_GW_mgL))) / ((Q_M_and_S_m3d * 1000) + (Q_GW_m3d * 1000))

Q_GW_m3d = OBS_Q_Stream_m3d - Q_M_and_S_m3d

DOCUMENT: This flow represents the groundwater contribution to streamflow.

**Q_M_and_S_m3d** = 0.3 * ((OBS_Q_Stream_m3d - 21)^1.13)

DOCUMENT: This equation is derived by a method similar to that used by Hendershot et al. (1992) SEE MODEL WRITE-UP.

**OBS_C_Stream_NO3_mgL** = GRAPH(TIME)

(0.00, 1.15), (1.00, 1.71), (2.00, 1.54), (3.00, 2.25), (4.00, 1.79), (5.00, 1.46), (6.00, 1.27), (7.00, 1.40), (8.00, 1.26), (9.00, 1.20), (10.0, 1.21), (11.0, 1.31), (12.0, 1.17), (13.0, 1.90), (14.0, 1.29), (15.0, 1.16), (16.0, 1.03), (17.0, 1.02), (18.0, 0.84), (19.0, 1.01), (20.0, 0.93)

DOCUMENT: Observed NO3 concentrations derived from samples obtained at the Nettle Brook weir were averaged from 2 samples collected daily during the 20 day Spring melt period. SEE SP TABLE 3.

**OBS_Q_Stream_m3d** = GRAPH(TIME)

(0.00, 220), (1.00, 234), (2.00, 220), (3.00, 631), (4.00, 409), (5.00, 253), (6.00, 265), (7.00, 663), (8.00, 662), (9.00, 703), (10.0, 1397), (11.0, 1837), (12.0, 2141), (13.0, 4801), (14.0, 1701), (15.0, 834), (16.0, 1164), (17.0, 1097), (18.0, 809), (19.0, 593), (20.0, 507)

DOCUMENT: These streamflow values were derived from the daily sum of values recorded every 5 minutes by instrumentation located at the Nettle Brook V-notch weir during the 20-day Spring melt period. SEE TABLE 1.

## NOT IN A SECTOR (USED FOR SIMULATION ANALYSIS)

***STOCK:***

Meltwater_NO3_out_kg(t) = Meltwater_NO3_out_kg(t - dt) + (Melt_and_Precip_NO3_to_Solum_kgd) * dt

INIT Meltwater_NO3_out_kg = 0

*INFLOW:*
**Melt_and_Precip_NO3_to_Solum_kgd** =
(PRED_C_Melt_and_Precip_mgL*Qm_and_Qp_m3d)/1000
**OBS_EXPORT_NO3_kg**(t) = OBS_EXPORT_NO3_kg(t - dt) +
(Stream_NO3_Export_kgd) * dt
INIT OBS_EXPORT_NO3_kg = 0

*INFLOW:*
**Stream_NO3_Export_kgd** =
(OBS_C_Stream_NO3_mgL*OBS_Q_Stream_m3d)/1000

***STOCK:***
**PRED_EXPORT_NO3_kg**(t) = PRED_EXPORT_NO3_kg(t - dt) +
(Pred_Stream_NO3_kgd) * dt
INIT PRED_EXPORT_NO3_kg = 0

*INFLOW:*
**Pred_Stream_NO3_kgd** = (OBS_Q_Stream_m3d * PRED_C_Stream_NO3_mgL) / 1000

***STOCK:***
**W_and_D_DEP_NO3_kg**(t) = W_and_D_DEP_NO3_kg(t - dt) +
(Dep_and_Melt_NO3_kgd) * dt
INIT W_and_D_DEP_NO3_kg = 0

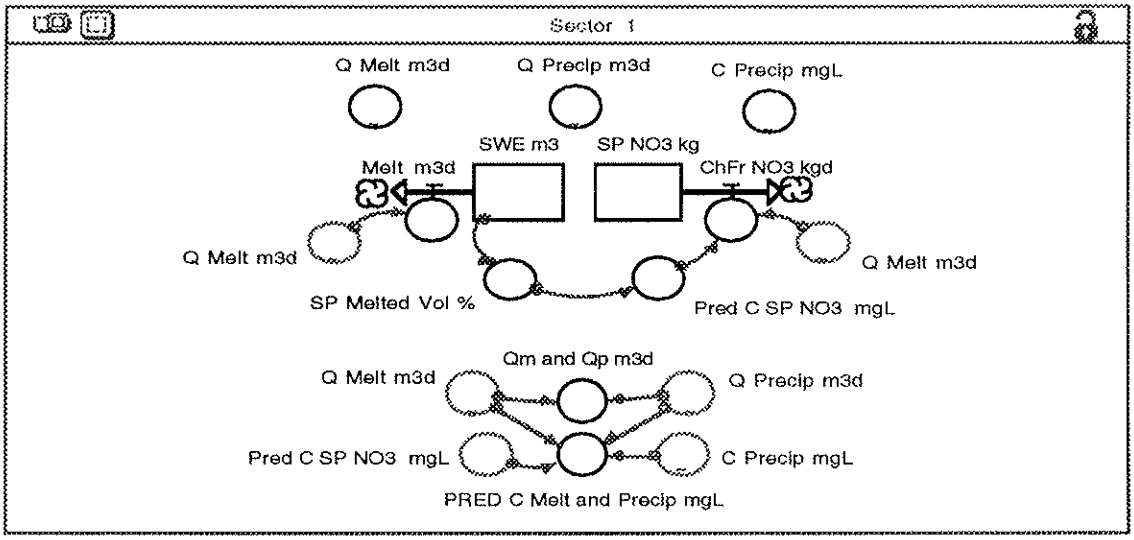
*INFLOW:*
**Dep_and_Melt_NO3_kgd** = M_and_P_NO3_kgd

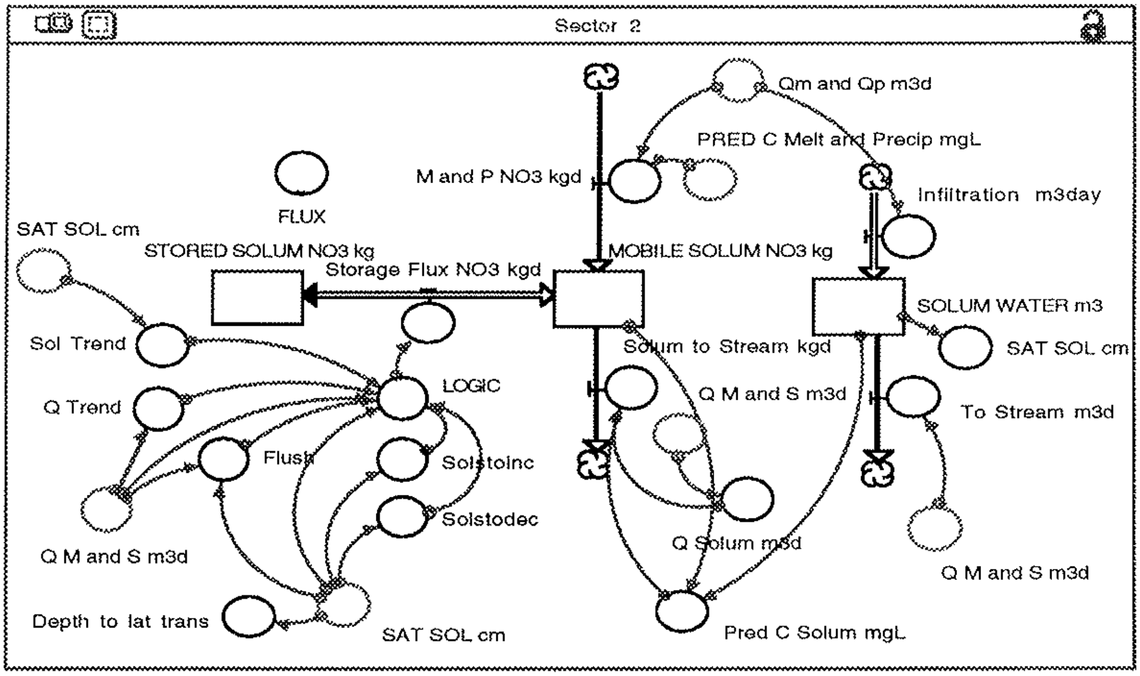
## APPENDIX C2: MODEL WATER BALANCE (SNOWPACK DENSITY = 0.32)

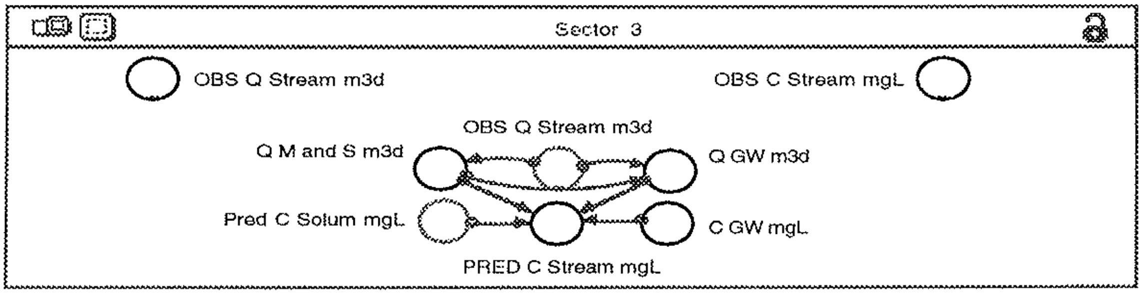
| Date (2330) | melt day # | SP Depth (mm) | WS SWE (m3) | Q melt (m3) | Q stream (m3 | Q precip (m3) |
|---|---|---|---|---|---|---|
| 30-Mar | | 702 | 24710 | XXX | XXX | unk |
| 31-Mar | | 691 | 24323 | 387 | 83 | unk |
| 1-Apr | | 679 | 23901 | 422 | 68 | 0 |
| 2-Apr | | 664 | 23373 | 528 | 67 | 33 |
| 3-Apr | 0 | 613 | 21578 | 1795 | 220 | 1254 |
| 4-Apr | 1 | 595 | 20944 | 634 | 234 | 0 |
| 5-Apr | 2 | 585 | 20592 | 352 | 220 | 0 |
| 6-Apr | 3 | 576 | 20275 | 317 | 631 | 2156 |
| SNOW 7-Apr | 4 | 557 | 19606 | 669 | 409 | 1591 |
| 8-Apr | 5 | 569 | 20029 | -422 | 253 | 0 |
| 9-Apr | 6 | 568 | 19994 | 35 | 265 | 0 |
| 10-Apr | 7 | 549 | 19325 | 669 | 663 | 528 |
| 11-Apr | 8 | 508 | 17882 | 1443 | 662 | 0 |
| 12-Apr | 9 | 469 | 16509 | 1373 | 703 | 0 |
| 13-Apr | 10 | 413 | 14538 | 1971 | 1397 | 979 |
| 14-Apr | 11 | 351 | 12355 | 2182 | 1837 | 0 |
| 15-Apr | 12 | 292 | 10278 | 2077 | 2141 | 0 |
| 16-Apr | 13 | 0 | 0 | 10278 | 4801 | 2761 |
| 17-Apr | 14 | 0 | 0 | 0 | 1701 | 55 |
| 18-Apr | 15 | 0 | 0 | 0 | 834 | 33 |
| 19-Apr | 16 | 0 | 0 | 0 | 1164 | 55 |
| 20-Apr | 17 | 0 | 0 | 0 | 1097 | 110 |
| 21-Apr | 18 | 0 | 0 | 0 | 809 | 330 |
| 22-Apr | 19 | 0 | 0 | 0 | 593 | 33 |
| 23-Apr | 20 | 0 | 0 | 0 | 507 | 0 |
| 24-Apr | | 0 | 0 | 0 | 573 | 55 |
| 25-Apr | | 0 | 0 | 0 | 631 | 165 |
| 26-Apr | | 0 | 0 | 0 | 923 | 1089 |
| 27-Apr | | 0 | 0 | 0 | 843 | 759 |
| 28-Apr | | 0 | 0 | 0 | 661 | 0 |

**NOTE:** On melt day 4 (Apr 7) 2013 m3 of precipitation occurred of which 422 m3 was calculated as snow (SP depth sensor) hence 1591 was entered for Q precip m3 and 422 was added to the SWE.

# APPENDIX C3: SCATS STELLA DIAGRAM.







## APPENDIX D: METHOD USED TO DETERMINE SOLUM EQUATIONS.

The amount of $NO_3^-$ required to be added or subtracted from mobile solum stock to bring predicted streamwater nitrate concentrations as close as possible to observed streamwater nitrate concentrations is determined by inputs into the Flux object in SCATS and entered into a spreadsheet (Table D1).

**Table D1.**

| DATE | MELT DAY # | C PRED | C OBS | Q sol | Q str | SOL cm | FLUX kg | INC | DEC |
|---|---|---|---|---|---|---|---|---|---|
| 3-Apr | 0 | 1.34 | 1.15 | 109 | 220 | 15 | 0 | | |
| 4-Apr | 1 | 1.37 | 1.71 | 118 | 234 | 17 | 0 | | |
| 5-Apr | 2 | 1.54 | 1.54 | 109 | 220 | 19 | 2 | 2 | |
| 6-Apr | 3 | 2.14 | 2.25 | 359 | 631 | 22 | 11 | 11 | |
| 7-Apr | 4 | 2.01 | 1.79 | 222 | 409 | 29 | -7 | | -7 |
| 8-Apr | 5 | 1.49 | 1.46 | 129 | 253 | 32 | -6 | | -6 |
| 9-Apr | 6 | 1.34 | 1.27 | 136 | 265 | 32 | 0 | | |
| 10-Apr | 7 | 1.48 | 1.4 | 378 | 663 | 32 | 0 | | |
| 11-Apr | 8 | 1.42 | 1.26 | 378 | 662 | 34 | -4 | | -4 |
| 12-Apr | 9 | 1.23 | 1.2 | 404 | 703 | 37 | -6 | | -6 |
| 13-Apr | 10 | 1.16 | 1.21 | 849 | 1397 | 41 | 1 | 1 | |
| 14-Apr | 11 | 1.2 | 1.31 | 1140 | 1837 | 46 | 2 | 2 | |
| 15-Apr | 12 | 1.23 | 1.17 | 1343 | 2141 | 48 | 3 | 3 | |
| 16-Apr | 13 | 1.79 | 1.9 | 3179 | 4801 | 62 | 45 | 45 | |
| 17-Apr | 14 | 1.54 | 1.29 | 1049 | 1701 | 75 | -40 | | -40 |
| 18-Apr | 15 | 0.91 | 1.16 | 486 | 834 | 73 | 0 | | |
| 19-Apr | 16 | 0.93 | 1.03 | 698 | 1164 | 71 | 0 | | |
| 20-Apr | 17 | 0.94 | 1.02 | 654 | 1097 | 70 | -2 | | -2 |
| 21-Apr | 18 | 0.93 | 0.84 | 470 | 809 | 69 | -4 | | -4 |
| 22-Apr | 19 | 0.92 | 1.01 | 335 | 593 | 68 | 0 | | |
| 23-Apr | 20 | 0.91 | 0.93 | 282 | 507 | 67 | 0 | | |
| | | | | | | | | | |
| | | | | | | | | | |

The Flux quantities are then input to scatter plots such as Q solum vs solum water content to determine if a mathematical relationship exists (Figure D1). The equations describing the relationships are then used to manipulate nitrate flux between mobile and immobile nitrate stocks replacing the Flux object.

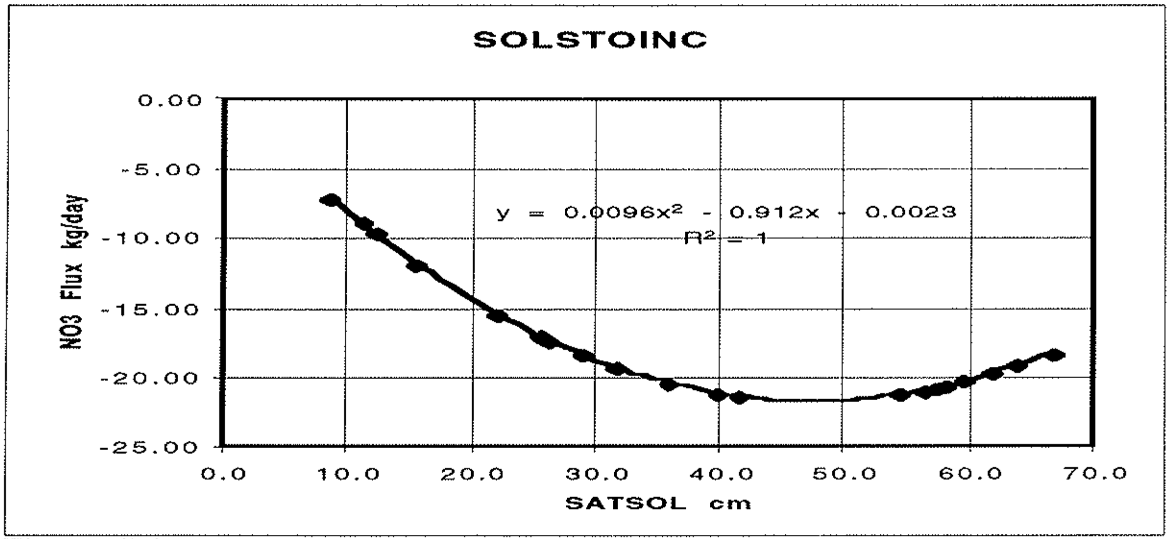


**Figure D1.**

# APPENDIX E: METHOD USED TO DETERMINE HYDROGRAPH SEPARATION.

In Table E1, Qt is equal to observed streamflow (Q m3/day), Qg is Qt - Qs, and Qs is determined by the equation that allows the closest fit between observed Si concentrations (Si-obs) and predicted Si concentrations (Ct-Sipred). Ct-Sipred is calculated as

$$((Qg \times CgSi) + (Qs \times CsSi)) / Qt$$

The plots of observed and predicted Si (Figure E1) and the resulting hydrograph separation (Figure E2) are observed as the equation describing Qs is manipulated. In this case

$$Qs = 0.34(Qt - 21)^{1.13}$$

The value for Cs-Si was determined at peak flow and is assumed to be representative of solum Si concentration. The value for Cg-Si was determined from soil pore water samples in the saturated zone and is assumed to be representative of groundwater Si concentration.

**Table E1.**

| DATE | Q(m3/day) | Si-obs(mg/L) | Qt | Qs | Qg | Ct-Sipred(mg/L) | Cs-Si(mg/L) | Cg-Si(mg/L) |
|---|---|---|---|---|---|---|---|---|
| 1-Feb | 50 | 2.51 | 50 | 15 | 35 | 2.21 | 0.96 | 2.76 |
| 23-Feb | 69 | 1.84 | 69 | 27 | 42 | 2.06 | 0.96 | 2.76 |
| 2-Mar | 41 | 2.42 | 41 | 10 | 31 | 2.32 | 0.96 | 2.76 |
| 21-Mar | 51 | 2.31 | 51 | 16 | 35 | 2.20 | 0.96 | 2.76 |
| 4-Apr | 234 | 1.53 | 234 | 145 | 89 | 1.64 | 0.96 | 2.76 |
| 5-Apr | 220 | 1.75 | 220 | 135 | 85 | 1.66 | 0.96 | 2.76 |
| 6-Apr | 631 | 1.16 | 631 | 477 | 154 | 1.40 | 0.96 | 2.76 |
| 7-Apr | 409 | 1.32 | 409 | 286 | 123 | 1.50 | 0.96 | 2.76 |
| 8-Apr | 253 | 1.485 | 253 | 160 | 93 | 1.62 | 0.96 | 2.76 |
| 9-Apr | 265 | 1.485 | 265 | 170 | 95 | 1.61 | 0.96 | 2.76 |
| 10-Apr | 663 | 1.135 | 663 | 506 | 157 | 1.39 | 0.96 | 2.76 |
| 11-Apr | 662 | 1.24 | 662 | 505 | 157 | 1.39 | 0.96 | 2.76 |
| 12-Apr | 703 | 1.205 | 703 | 542 | 161 | 1.37 | 0.96 | 2.76 |
| 13-Apr | 1397 | 1.12 | 1397 | 1197 | 200 | 1.22 | 0.96 | 2.76 |
| 14-Apr | 1837 | 1.18 | 1837 | 1638 | 199 | 1.16 | 0.96 | 2.76 |
| 15-Apr | 2141 | 1.135 | 2141 | 1951 | 190 | 1.12 | 0.96 | 2.76 |
| 16-Apr | 4801 | 0.96 | 4801 | 4889 | -88 | 0.93 | 0.96 | 2.76 |
| 17-Apr | 1701 | 1.145 | 1701 | 1500 | 201 | 1.17 | 0.96 | 2.76 |
| 18-Apr | 834 | 1.215 | 834 | 661 | 173 | 1.33 | 0.96 | 2.76 |
| 19-Apr | 1164 | 1.165 | 1164 | 971 | 193 | 1.26 | 0.96 | 2.76 |
| 20-Apr | 1097 | 1.19 | 1097 | 907 | 190 | 1.27 | 0.96 | 2.76 |
| 21-Apr | 809 | 1.22 | 809 | 638 | 171 | 1.34 | 0.96 | 2.76 |
| 22-Apr | 593 | 1.27 | 593 | 444 | 149 | 1.41 | 0.96 | 2.76 |
| 23-Apr | 507 | 1.23 | 507 | 369 | 138 | 1.45 | 0.96 | 2.76 |
| 24-Apr | 573 | 1.28 | 573 | 426 | 147 | 1.42 | 0.96 | 2.76 |
| 25-Apr | 631 | 1.27 | 631 | 477 | 154 | 1.40 | 0.96 | 2.76 |
| 26-Apr | 923 | 1.21 | 923 | 743 | 180 | 1.31 | 0.96 | 2.76 |
| 28-Apr | 661 | 1.23 | 661 | 504 | 157 | 1.39 | 0.96 | 2.76 |
| 3-May | 318 | 1.32 | 318 | 212 | 106 | 1.56 | 0.96 | 2.76 |
| 20-May | 199 | 2.02 | 199 | 119 | 80 | 1.69 | 0.96 | 2.76 |
| 21-Jul | 32 | 2.56 | 32 | 5 | 27 | 2.47 | 0.96 | 2.76 |
| 26-Jul | 21 | 2.72 | 21 | 0 | 21 | 2.76 | 0.96 | 2.76 |
| 15-Sep | 27 | 2.39 | 27 | 3 | 24 | 2.59 | 0.96 | 2.76 |
| 29-Nov | 173 | 1.47 | 173 | 99 | 74 | 1.73 | 0.96 | 2.76 |
| 22-Dec | 103 | 1.7 | 103 | 49 | 54 | 1.90 | 0.96 | 2.76 |

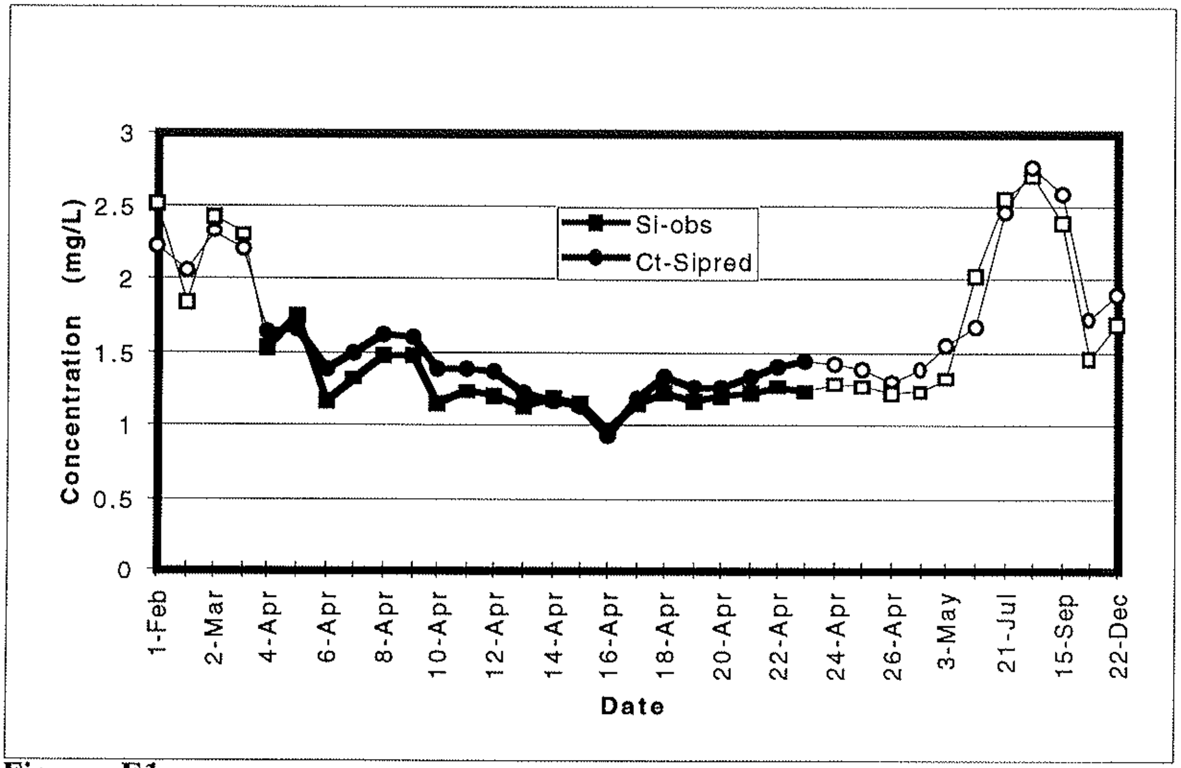


**Figure E1.**

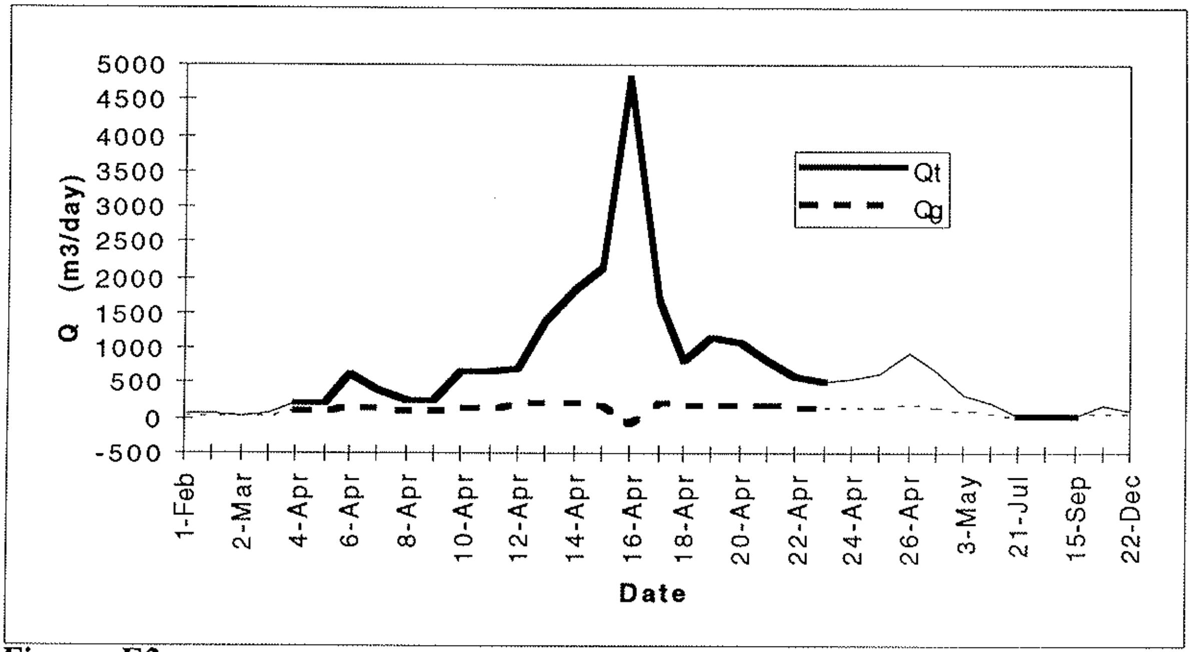


**Figure E2.**