

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.

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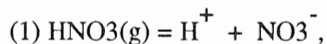
Nitrate in the Ecosystem

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 (Altwickler, 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:



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). Stottlemeyer 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). Stottlemyer 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.

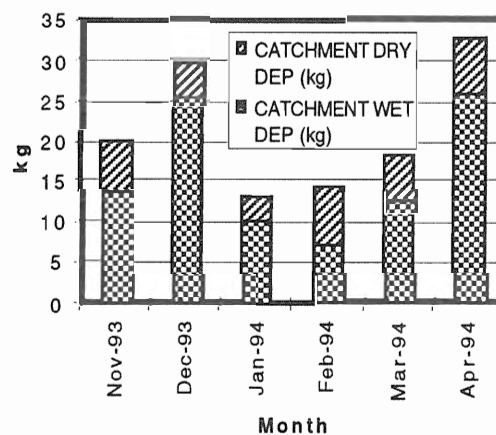


FIGURE 1. Nitrate deposition into the Nettle Brook catchment.

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 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 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 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.

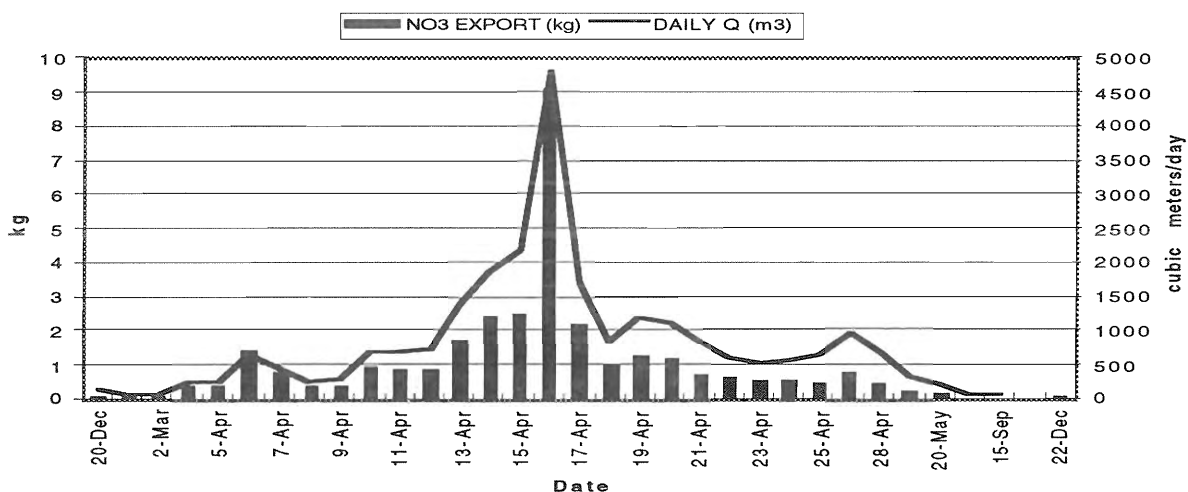
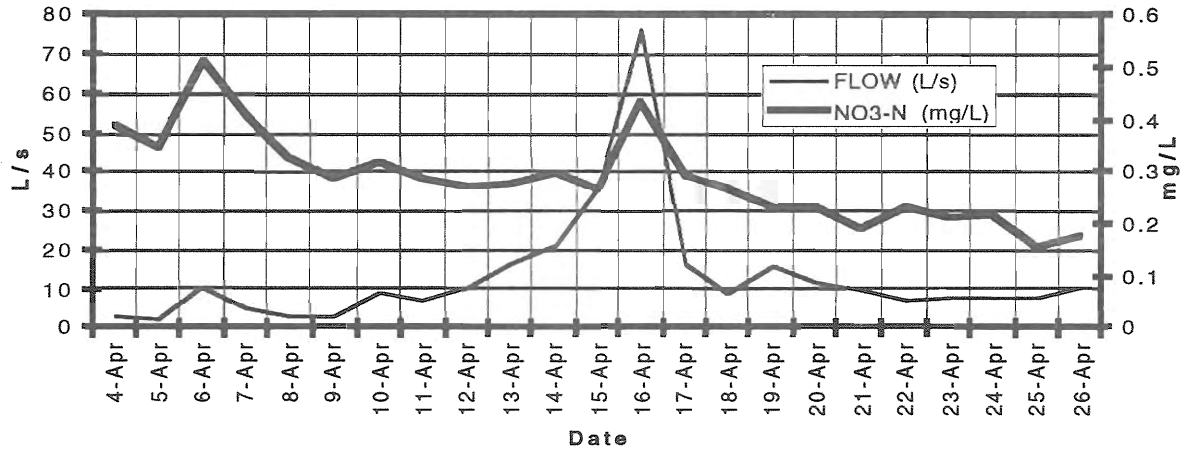


FIGURE 2. Nettle Brook nitrate export. Note that sample intervals are daily during Spring snowmelt and monthly during the rest of the year.



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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.

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.

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

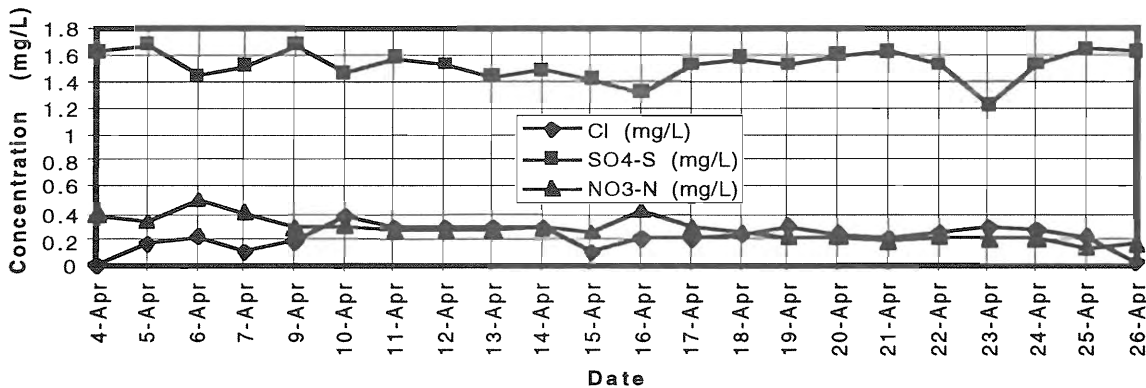


FIGURE 4. Anion concentrations at Nettle Brook during Spring snowmelt. No evidence of preferential elution of ions appears evident.

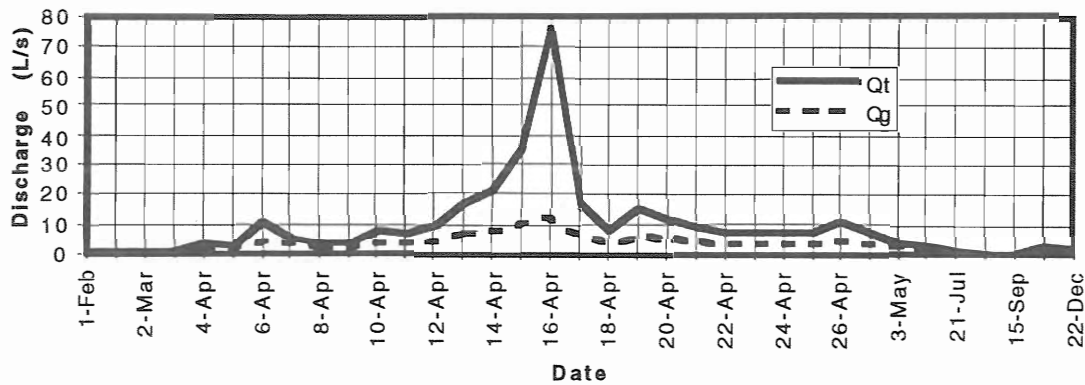


FIGURE 5. The hydrograph separation developed from the procedure described by Hendershot *et al.* (1992) using modifications described in the text showing the relative contributions of ground water (Q_g) and solum water ($Q_s = Q_t - Q_g$) to Nettle Brook streamflow.

$$(3) C_{t,pred} = (Q_g \times C_g + Q_s \times C_s) / Q_t$$

where

$C_{t,pred}$ = Predicted total conc of Si (mg/L)
 C_g = Si conc of groundwater (mg/L)
 C_s = Si conc of solum (soil) (mg/L)
 Q_g = flow from groundwater (L/s).

The value for C_g may be obtained from the Si concentration at baseflow (0.17 L/s) and C_s from the Si concentration observed from soil pore-water samples. A hydrograph plot of Q_t and Q_g 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 C_g 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 (Q_s) during peak flow and 100% groundwater (Q_g) 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 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 of spring melt as a result of increased biological activity as streamwater warms. Johnson *et al.* (1969) note that

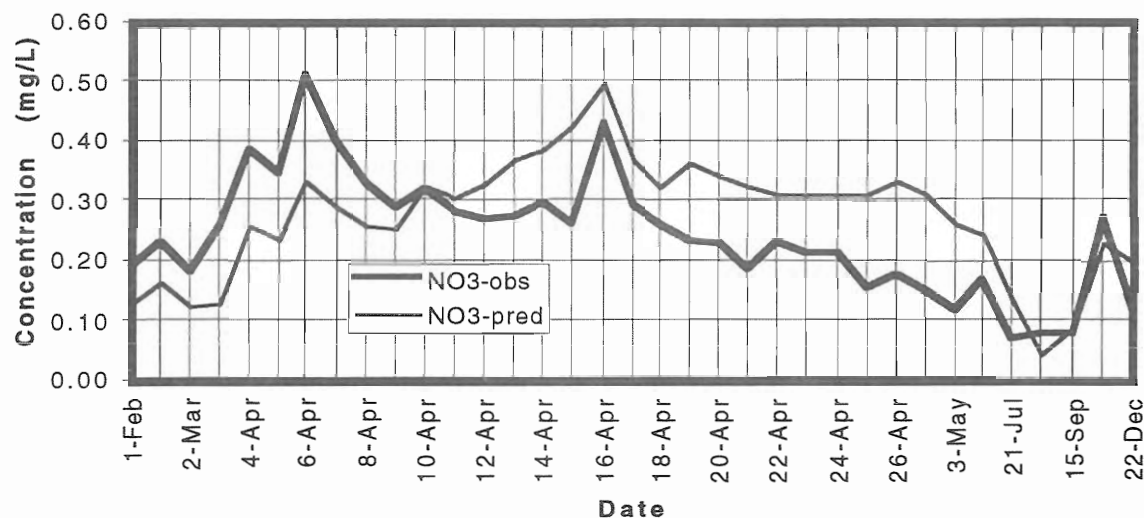


FIGURE 6. Predicted and observed nitrate concentrations based on the hydrograph separation discussed in the text and nitrate concentrations determined from soil sample analyses. Inputs for predicted nitrate were 0.58 mg/L (Cs) and 0.04 mg/L (Cg).

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.

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