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ABSTRACT

Stream riparian zones are landscape features that retain nutrients and enhance water quality. However, little is known about winter controls on nutrient transport in riparian zones. In this study we examine the distribution and movement of nitrate (NO_3^-) between snowpack, underlying soils and groundwater in a riparian zone to quantify processes which control NO_3^- transport through seasonally–frozen surface soils. Soils and vegetation in buffer zones attenuate nitrate during the growing season. However, this ability is uncertain with vegetation senescence, and when soils freeze and seasonal snowcover can contain an important nitrate load and later release it to surface waters during melt. At our study site snowcover reached a maximum depth of 32 cm following the major snowfall event from Julian Day (JD) 41 to 47, 2000. During this event, the snow water equivalent (SWE) increased twofold to 4.7 cm. A melt event starting on JD 53 resulted in a SWE loss of 2 cm. Snowpack NO_3^- concentrations reached a maximum value of 1.4 mg L^{-1} and a maximum loading of 51.7 mg m^{-2}. During the main melt event, snowpack loading reduced to 36.9 mg m^{-2} and concentrations of NO_3^- in the snow decreased to 0.55 mg L^{-1}. Over the study period, groundwater NO_3^- concentrations were relatively constant near 0.25 mg L^{-1}. However, evidence of mixing of groundwater with stream water is strongly suggested by higher NO_3^- concentrations in near–stream groundwater (0.75 mg L^{-1}), which was under hydrostatic pressure caused by the stream ice–cover. No identifiable NO_3^- pulse was observed during the main snowmelt period because persistent soil frost promoted depression storage, overland flow and shallow throughflow. Our results indicate that overland flow and shallow throughflow were the likely pathways for NO_3^- export from this system. Clearly these processes cannot be ignored when quantifying snowpack NO_3^- through riparian buffers with frozen soils.

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RÉSUMÉ

Les zones riveraines des cours d'eau sont des caractéristiques terrestres qui retiennent les substances nutritives et accroissent la qualité de l'eau. Toutefois, on sait peu de choses à propos du contrôle qu'exerce l'hiver sur le transport des substances nutritives dans les zones riveraines. Dans cette étude, nous examinons la distribution et le mouvement du nitrate (NO_3^-) entre la neige accumulée, les sols sous–jacents et les eaux souterraines dans une zone riveraine pour quantifier les processus qui contrôlent le transport du NO_3^- à travers les sols de surface temporairement gelés. Les sols et la végétation dans les zones tampons atténuent le nitrate pendant la saison de croissance. Cependant, cette capacité est incertaine quand la végétation vieillit; les sols gèlent et l'enneigement saisonnier peut contenir une importante charge en nitrate puis la libérer plus tard vers les eaux de surface en période de fonte. Au site d'étude, l'enneigement atteignait une profondeur maximale de 32 cm après la chute de neige majeure du jour julien (JJ) 41 à 47; 2000. Au cours de cet événement, l'équivalent en eau de la neige (ÉEN) a doublé pour atteindre 4,7 cm. Une fonte ayant commencé au JJ 53 s'est traduite par une perte ÉEN de 2 cm. Les concentrations NO_3^- de la neige accumulée ont atteint une valeur maximale de 1,4 mg L^{-1} et une charge maximale de 51,7 mg m^{-2}. Au cours du principal événement de fonte, la charge de l'enneigement a été réduite à 36,9 mg m^{-2} et les concentrations de NO_3^- dans la neige sont tombées à 0,55 mg L^{-1}. Pendant la période d'étude, les concentrations de NO_3^- dans les eaux souterraines sont demeurées relativement constantes, à près de 0,25 mg L^{-1}. Cependant, des signes de mélange des eaux souterraines avec les eaux de courant sont fortement manifestes compte tenu des concentrations de NO_3^- plus élevées dans les eaux souterraines à proximité des cours d'eau (0,75 mg L^{-1}), sur lesquelles des pressions hydrostatiques étaient exercées en raison du manteau glacial recouvrant le cours d'eau. Aucune impulsion NO_3^- identifiable n'a été observée au cours de la période principale de fonte des neiges du fait que le gel du sol permanent favorisait l'emmagasinement dans les dépressions du sol, l'écoulement terrestre et le débit peu profond. Nos résultats indiquent que l'écoulement terrestre et les débits peu profonds étaient les voies d'exportation probables du NO_3^- provenant du réseau. Manifestement, on ne peut pas faire fi de ces processus lorsqu'on cherche à quantifier le NO_3^- de la neige accumulée dans les zones tampons riveraines où l'on trouve des sols gelés.

INTRODUCTION

The annual atmospheric nitrate (NO_3^-) load to the snowpack in Ontario is 0.11 g m^{-2} (Ro *et al.*, 1988). In areas that experience seasonal snowcover, intermittent winter thaws or spring melt usually represent the major hydrological event of the year. High NO_3^- concentrations released from the snowpack during spring melt can cause acidification of surface waters and, at excessive concentrations, impact the health of humans and livestock (Jeffries, 1998).

The transport of nitrate from snowmelt through soils and into surface waters is a complex process. Solute movement in soil is controlled by several factors such as hydraulic gradient, hydraulic conductivity, soil texture, antecedent moisture conditions, unfrozen water content and solute concentration (Jones and Bedard, 1997; Williams *et al.*, 1996). The presence of frozen surface soil with moderate to high water content can limit infiltration and cause overland flow (Kane and Stein, 1983; Granger *et al.*, 1984). During freezing, water moves downward in soils towards the advancing freezing front. Segregation of ice from unfrozen water forms ice crystals and lenses. This creates regions of high solute concentration in mobile unfrozen water surrounding localized ice rich areas (Radke and Berry, 1998; Yershov, 1998).

Snow alters the thermal properties of underlying soils. Because of its low thermal conductivity and diffusivity, snow insulates the soil surface from large temperature fluctuations and generally moderates the freezing process. Consequently, the presence of a partially–thawed soil surface can significantly affect the transport dynamics and subsequent fate of NO_3^- in terrestrial and aquatic systems because of increased soil permeability.

In a study of the buffering capacity of soils in Michigan, Stottlemyer and Toczydlowski (1991) noted an increase in the initial concentration of NO_3^- in successive soil horizons during the infiltration of meltwater and attributed this to the mobilization of over winter mineralization/nitrification products. Stottlemyer and Toczydlowski (1999) studied the effect of successive snowmelt on chemical pulses and found that peak NO_3^- loss from the snowpack coincided with the final snowmelt pulse. This observation is consistent with related literature reviewed by Jones (1999). However, there is a lack of information regarding the infiltration of NO_3^- from upper soil horizons to below the root zone during this period (Jones, 1999).

Riparian zones are strips of natural vegetation located along the margins of streams that separate surface waters from adjacent lands. Although they comprise a small portion of the total catchment area, these landscape features improve the water quality of streams by reducing nutrient leaching in groundwater and surface runoff (Jacobs and Gilliam, 1985; Hill, 1996; Cey *et al.,* 1999). The majority of nutrient retention studies in riparian zones have been conducted during the growing season when plant biomass and soil microbial activity is high. Few studies have examined winter controls on nutrient transport in riparian zones, particularly the distribution and movement of NO_3^- between snowpack, underlying soils and shallow groundwater (Brooks *et al.,* 1998). This study examines the distribution and movement of nitrate in soils from snowpack in a stream riparian zone located in Waterloo, Ontario. Objectives of this study are 1) to quantify changes in NO_3^- concentrations between snowpack, soil and shallow groundwater; 2) to identify the processes which control the concentration of NO_3^- within soil and shallow groundwater and 3) estimate NO_3^- loading from the winter snowpack.

STUDY AREA

The Laurel Creek is located in south–central Ontario and drains an area of 74 km^2 (Figure 1). Mean annual precipitation in the watershed is 928.5 mm of which approximately 17% (161 mm) is snow (Environment Canada, 1998). During the winter, prevailing winds are from the southwest and atmospheric pollutant loads containing NO_x and S originate from the American midwest (Keith and Dillon, 1998).

The study site is located in the riparian zone on the west bank of Laurel Creek, approximately 1 km above Columbia Lake in Waterloo, Ontario (Figure 1). Land use upslope of the study site is predominantly parkland. Soils are silty and alluvial in origin with abundant surface litter (Presant and Wickland, 1971). The saturated hydraulic conductivity of the soil is 1.6 m d^{-1}. Vegetation at the site includes typical riparian species including willow (*Salix spp.*), sedges (*Carex spp.*) and goldenrod (*Solidago*).

METHODS

The study was conducted between Julian Day (JD) 13 and 64, 2000. A transect in the riparian zone was instrumented with four groundwater wells (Figure 1) constructed of 25 mm (ID) PVC slotted along their lengths. Wells GW4, GW2, and GW1 were installed to a depth of 1 m and GW3 to 0.9 m. Water table depth was recorded manually once a week but daily during melt periods.

Soil water samples were collected from two lysimeters. Surface lysimeter (LY1) was constructed from a 0.2 m^3 plastic container and sampled soil water to a depth of 0.2 m. A zero tension lysimeter (LY2), similar to the design described by Thompson and Scharf (1994), was installed laterally into the soil from an access pit leaving 0.40 m of overlying soil relatively undisturbed. Unfrozen soil moisture was determined for five depths (10, 20, 30, 40, 50 cm) with a Troxler™. Sentry TDR probe lowered into an access tube adjacent to GW3 and the lysimeters. Soil temperatures were recorded at depths of 5, 10 and 20 cm. Ambient air temperature was recorded every 15 minutes at the University of Waterloo weather station (located approximately 1 km southwest of the study site).

Snow samples were collected at the study site with a snow tube to determine density and snow water equivalence (SWE). All samples were stored in pre–washed Ziplock bags and returned immediately to the laboratory for analysis. A snowpack lysimeter (2 x 2 x 0.2 m) constructed of particle board frame was painted white (to reflect solar radiation) and lined with plastic sheeting to collect meltwater, which was directed into a 20 L bucket buried in an adjacent pit. A Solinst Levelogger™ pressure transducer was placed in the bottom of the bucket to automatically record changes in meltwater flux at 15–minute intervals. Sampling of groundwater, soil water, stream water and snow was conducted once a week but more frequently during events (snowfall, rain on snow and melt).

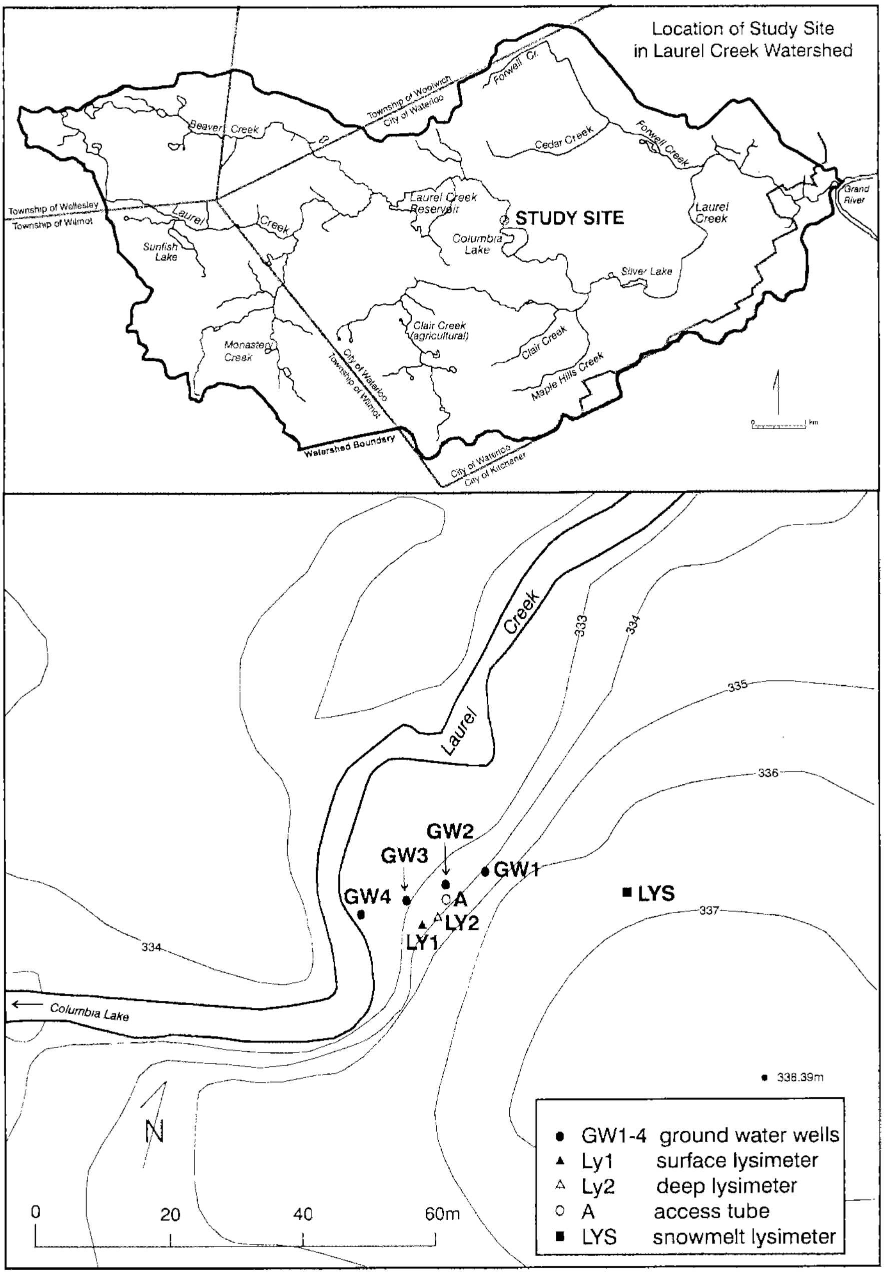

Figure 1. Study Location. Laurel Creek Watershed is Part of the Grand River System, Southern Ontario, Canada.

All water samples were collected in acid–washed, triple–rinsed 100 ml HDPE (polyethylene) bottles. Electrical conductivity, total dissolved solids and pH of water samples were measured in the laboratory. Nitrate concentration in water samples was determined with a Technicon Auto Analyzer according to the Cd reduction method (Environment Canada, 1979). The detection limit of the analytical method is 0.001 mg L^{-1}. Snow samples were aggregated for each sampling date for chemical analysis.

RESULTS AND DISCUSSION

Snowpack and Subsurface Hydrology

In 2000, Ontario experienced an extraordinarily warm winter (Figures 2a and 2b) with a departure of 1.7°C from normal for the Great Lakes Region (Environment Canada, 2000a). Snowcover at the study site reached a maximum depth of 32 cm following the major snowfall event from JD 41 to 47. This event doubled the SWE from 2.3 cm on JD 42 to a maximum of 4.7 cm on JD 53 (Figures 3a and 3b). During the peak snowfall (JD 42 and 43), the SWE increased from 2.3 cm to 3.8 cm (Figure 3a). The predominant wind direction during the event was from the NE and NNE whereas preceding snowfall events, originated from south and westerly direction (Environment Canada, 2000b). The daily mean air temperature exceeded 0°C up to a maximum of 4°C on JD 53, and remained above freezing for four days (Figure 2a), which triggered the major melt–event. An SWE of approximately 20 mm was lost from the snowpack between JD 53 and 55 (Figure 3b). This melt event caused significant depression storage as well as overland flow to occur from adjacent hillslopes. The remaining snowpack melted on JD 55 and 56 after 15.3 mm of rain.

Soil temperature data (Figure 2b) show that maximum depth of ground frost did not exceed 20 cm during the study period. The soil remained frozen to a depth of approximately 10 cm until JD 54 while the soil at 5 cm remained frozen until JD 60, seven days after the major melt event. Ground probing showed that the surface was completely thawed by JD 64. These results suggest that the soil thawed from bottom up, likely because insulation of the surface by grass and litter cover minimized the downward soil heat flux.

The water table rose slightly prior to melt (Figure 4). This corresponded to significant hydrostatic pressure of stream water, constrained by its ice cover as noted during drilling for stream water sampling. The maximum change in groundwater level was 34 cm in GW1 following melt.

During the study, unfrozen soil moisture in the top 20 cm decreased, corresponding to the estimated depth of freezing. Soil moisture in the unsaturated zone at 30 cm followed a similar trend until JD 55. At 50 cm depth, the soil moisture initially decreased but began to increase when the water table rose above the level of the sensor, and continued to increase while apparently at saturation (Figures 4, 5, 2b). This may correspond to swelling of the soil associated with the higher groundwater pressure and water table (Price and Schlotzhauer, 1999).

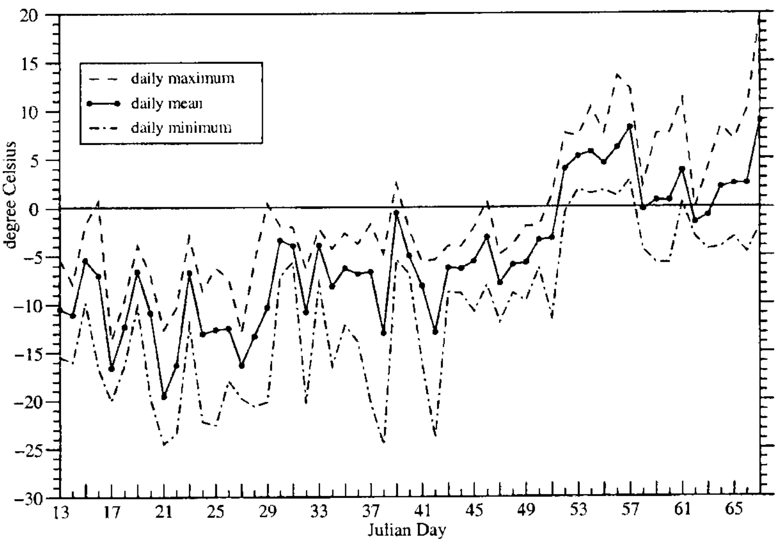

Figure 2a.

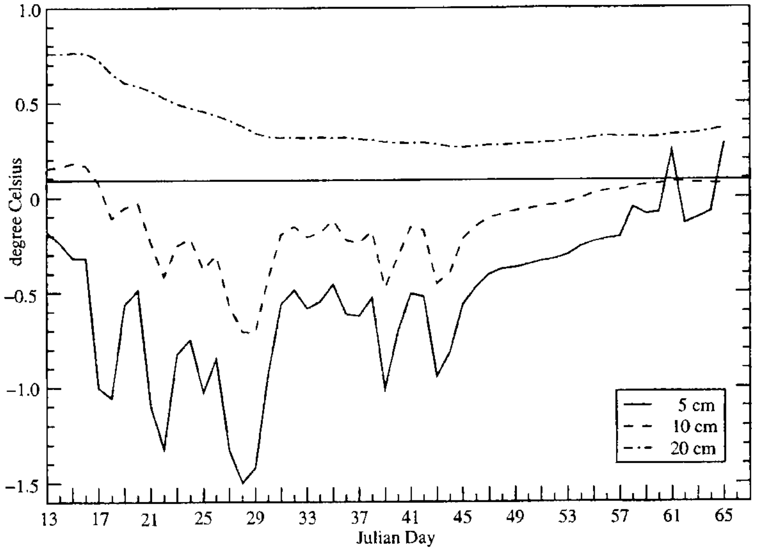

Figure 2b.

Figure 2a. Air Temperature (Daily Mean, Min., Max.).
Figure 2b. Soil Temperature at Depth 5 cm, 10 cm, 20 cm (Recorded by the University of Waterloo Weather Station, http://weather.uwaterloo.ca/).

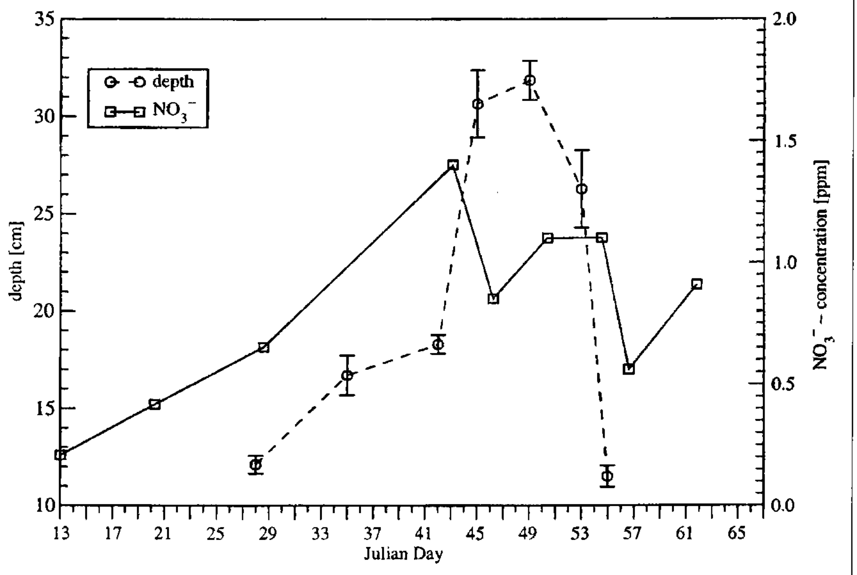

Figure 3a.

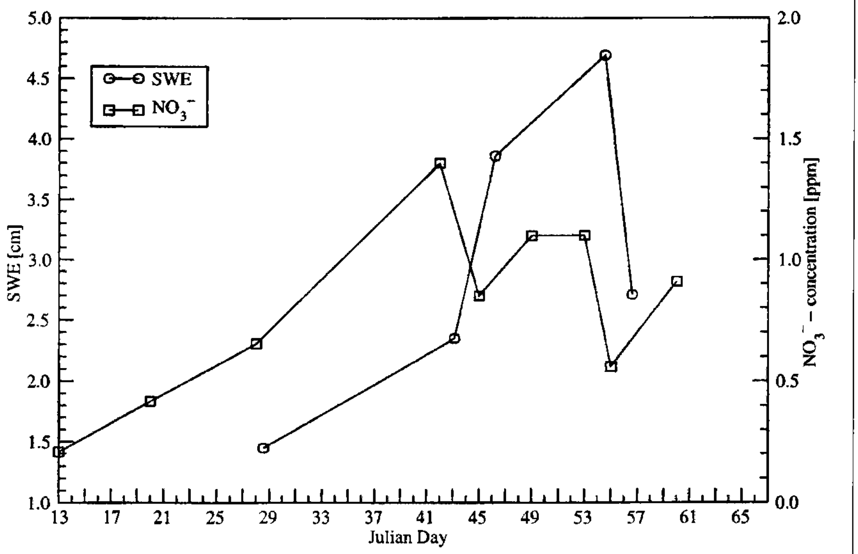

Figure 3b.

Figure 3a. Snow Depth [cm] and NO_3^- Concentration [ppm].
Figure 3b. Snow Water Equivalent [cm] and Snow NO_3^- Concentration [ppm].

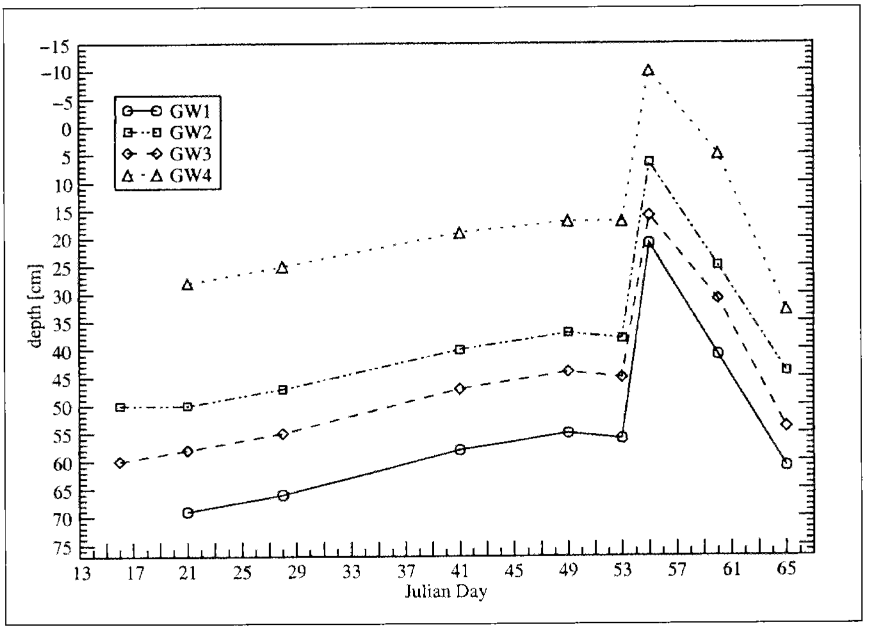

Figure 4. Groundwater Level [cm] Below Surface for Wells GW1, GW2, GW3 and GW4.

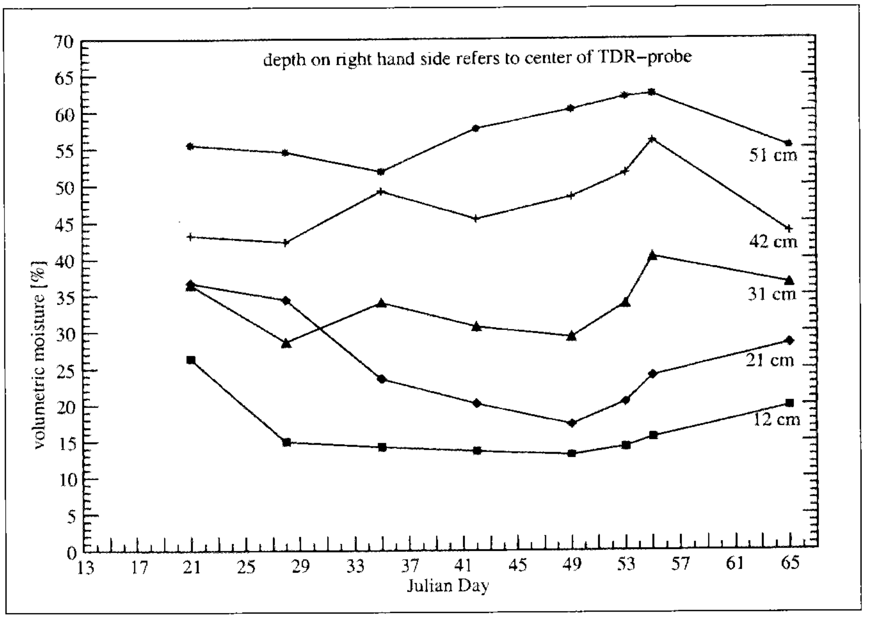

Figure 5. Unfrozen Volumetric Soil Moisture [%] at Depths 12, 21, 31, 42 and 51 cm.

Concentrations of total dissolved solids (TDS) in groundwater were greater than river water by approximately 60 mg L^{-1} (Figure 6a). After a stable period (JD 21 to 41), TDS decreased from approximately 500 to 250 mg L^{-1} on JD 55. The decrease in TDS started before the beginning of melt. Hydrostatic pressure under river ice likely reversed the hydraulic gradient in the riparian zone, thus causing river water to be stored in the soils.

The pH of groundwater, river water and snow was slightly basic over the study period (Figure 6b). Before melt, the pH of river and groundwater increased from 7.7 to 8.1 and from 7.3 to 7.85, respectively. The pH of the snow was generally higher than 8.3 (except JD 49) and rose with the melt event to 8.8 on JD 55. This may have resulted from the potential buffering capacity of carbonate rich soil particles that were transported by wind from the adjacent agricultural field and deposited in the snowpack. Correspondingly, the pH of the river water dropped from 8.1 before melt to 7.3 on JD 55, then increased above the pre–melt value on JD 65. The highest groundwater pH value of 8 coincided with peak groundwater levels.

The highest weekly total NO_3^- load in the snowcover was approximately 51.7 mg m^{-2}. The concentration of NO_3^- decreased to 0.55 mg L^{-1} between JD 53 and 55 which coincides with the major melt event. In the snowpack, NO_3^- concentrations increased until JD 42 and reached a maximum value of 1.4 mg L^{-1}. During the study period, NO_3^- concentrations in three groundwater wells (GW1, GW2, GW3) remained constant around 0.25 mg L^{-1} (Figure 7) and NO_3^- levels at GW4 were approximately 0.75 mg L^{-1}, with a maximum value of 1.8 mg L^{-1} on JD 55. On this day, GW4 was likely contaminated with river water. The NO_3^- concentrations in soil water did not differ markedly from those of the groundwater.

Ground thawing seemed to occur from the bottom of the frost layer to the surface, probably because of dead grasses insulating the ground surface. With regard to NO_3^- attenuation, Lewis and Grant (1980) found that the snowcover itself can protect the ground surface from freezing, thereby allowing microbial activity to take place. Our results suggest that the vegetation cover, which influenced the thermal regime before, during and after snowmelt also affected nitrate dynamics at the site.

The change in NO_3^- concentration during snowpack accumulation on JD 42 was attributed to the change in wind direction (Keith and Dillon, 1998). Differences in SWE and NO_3^- concentrations between JD 42 and 45 show that the 13 cm of snow accumulation contained only trace amounts of NO_3^-, compared with an average concentration of 1.4 mg L^{-1} for the preceding snowfall events (Figure 3a and 3b). Total wet NO_3^- deposition at the study site was strongly influenced by the timing and/or source of the snow.

The maximum accumulation of NO_3^- within the snowpack for the study period (cumulative up to JD 53) was 51.7 mg m^{-2}. This value is about half that (110 mg m^{-2}) reported for southern Ontario from December to March by Ro *et al.* (1988). A total of 36.9 mg NO_3^- per m^2 was released during the main thaw event (from day JD 53 to JD 55). Neither the NO_3^- concentration in the groundwater nor in

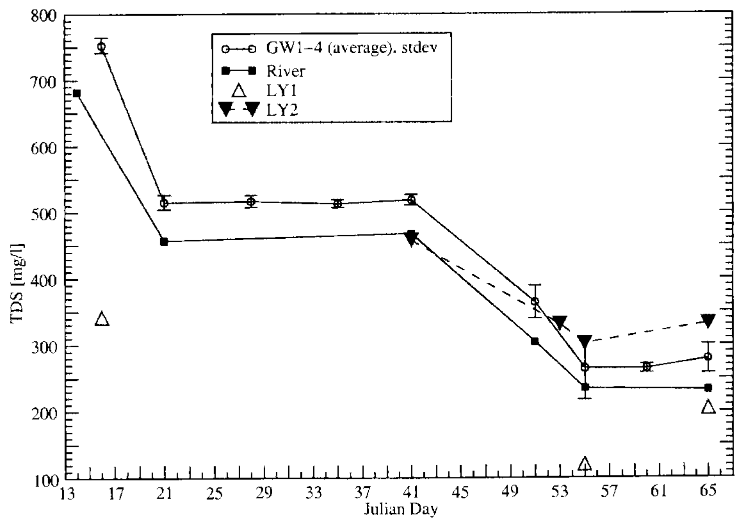

Figure 6a.

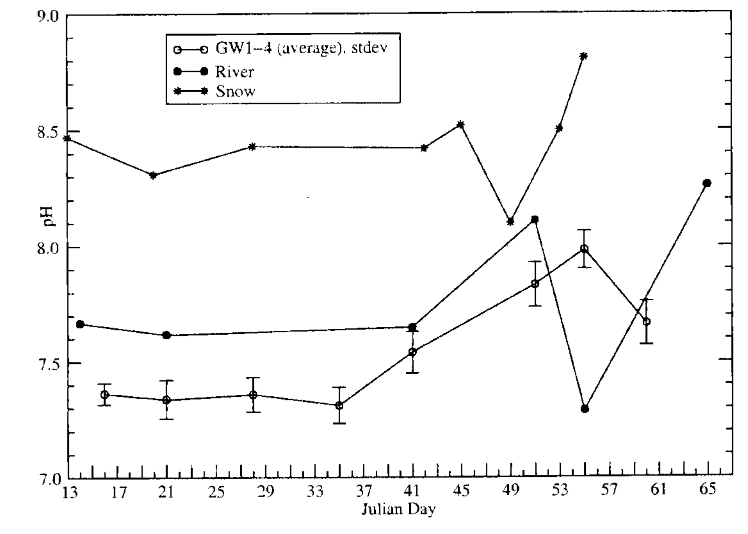

Figure 6b.

Figure 6a. Total Dissolved Solids (TDS) [mg/l] of Groundwater, River Water and Lysimeter Samples.
Figure 6b. pH of Groundwater, River Water and Snow.

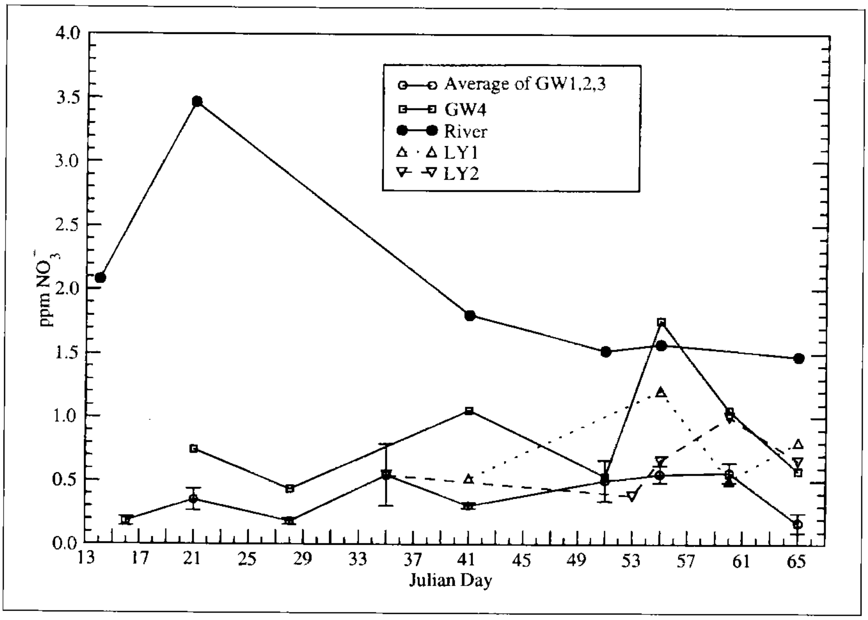

Figure 7. NO_3^- Concentration [ppm] of Groundwater, River Water and Lysimeter Samples.

the lysimeters changed significantly during the melt period. Nitrate export was primarily along shallow subsurface and overland flow pathways that were visible on JD 55, seeping from hillslopes adjacent to the site. These pathways were possible because of impermeable ground frost at shallow depth. Nitrate transport along these preferential pathways may explain why no nitrate pulse was observed in the wells and lysimeters. There was no evidence of increasing nitrate concentrations in the stream during the melt event.

The effectiveness of buffer strips for nutrient removal is a function of individual watershed hydrology, buffer width, location, slope, vegetation characteristics, soil type and degree of saturation (Gilliam *et al.*, 1997; Hill, 1996). At this location the buffer strip was typically wider than in many agricultural parts of the Laurel Creek watershed. In this situation, we anticipate riparian vegetation to reduce nutrient inputs from surface runoff via mechanical filtering of solids as well as the detention and assimilation of nutrients by riparian vegetation (Muscutt *et al.*, 1993; Dillaha *et al.*, 1989), although during the snowmelt period this latter process must be quite limited. Nitrate removal from shallow groundwater by denitrification is maximized when suitable redox conditions and energy sources for anaerobic bacteria exist in hydrogeologic settings where groundwater interacts with vegetation and organic sediments (Hill, 1996). During spring when rapid surface flow occurs, the potential influence of the riparian zone to attenuate NO_3^- is diminished.

CONCLUSION

The winter of 2000 was atypically warm, and the snowpack melted during a thaw with rain on snow in late February. During this period, the ground frost penetrated down to about 20 cm, and the unfrozen water decreased accordingly. Saturated and unsaturated soils in the riparian zone were inundated with stream water under hydrostatic pressure, due to ice cover. The snowpack had a total nitrate load of 51.7 mg m^{-2} prior to melt. Approximately 36.9 mg m^{-2} was released during the main melt event, but no nitrate pulse was observed in soilwater or groundwater. Surface flow over frozen soil, as well as shallow throughflow was observed during melt. These transient flowpaths are suggested as the probable pathway for nitrate export from this system. Consequently, riparian buffers will be ineffective for nitrate attenuation from the melting snowpack under these conditions.

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