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Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed

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Abstract. The influence of storm runoff processes on stream nitrogen dynamics was investigated in a headwater riparian swamp on the Oak Ridges moraine in southern Ontario. Hydrologic data were combined with analysis of an isotopic tracer ($^{18}0$) and nitrogen (NH_4^+, NO_3^-) concentrations in saturation overland flow and stream discharge. Storm runoff was separated into its event and pre-event components using $^{18}0$ in order to examine the effect of water source on nitrogen chemistry. Laboratory experiments were also used to study nitrogen transformation associated with storm runoff-surface substrate interactions in the swamp. In most storms NO_3-N and NH_4-N concentrations in the initial 3—4 mm throughfall increment were 10—20x and 20—100x higher respectively than stream base flow concentrations. Maximum stream NO_3-N concentrations were <2x to 6x higher than base flow concentrations and preceded or coincided with peak stream discharge. Storm-to-storm variations in stream NO_3-N behaviour also occurred during the hydrograph recession phase. NH_4-N concentrations attained an initial peak on the rising hydrograph limb, or at peak stream discharge. A second NH_4-N increase occurred during the late recession phase 3—5 h after maximum stream discharge. Inorganic-N concentrations in surface runoff were similar to peak streamflow.

The close agreement between observed NO_3-N concentrations and values predicted from a chemical mixing model indicate that stream NO_3-N variations were controlled mainly by the mixture of throughfall and groundwater in surface stormflow from the swamp. Laboratory experiments also indicated that NO_3-N in surface runoff behaved conservatively when mixed with swamp substrates. With the exception of the late hydrograph recession phase, observed stream NH_4-N concentrations were much lower than concentrations predicted by the chemical mixing model. The rapid loss of NH_4-N from mixtures of surface stormflow and swamp substrates in laboratory experiments and the absence of uptake in sterilized substrates indicated that NH_4-N retention in surface storm runoff was due to biotic processes.

Introduction

Recent reviews of stream biogeochemistry reveal major gaps in our knowledge of the processes regulating stream nutrient dynamics (Likens 1984;

Meyer et al. 1988). Although within-stream transformation processes influence stream element dynamics (Meyer & Likens 1979; Mulholland et al. 1985), watershed-scale processes frequently define the overall supply and availability of nutrients to streams (Hynes 1975). Likens (1984) has suggested that scientists should focus on how water chemistry is altered during passage through watersheds to streams in order to understand or predict stream biogeochemistry. Water moves from hillslopes into headwater streams by various surface and subsurface routes during and between precipitation events. Contrasts in residence time and in the environment encountered along these flow paths can produce large differences in the chemistry of water reaching the stream by various pathways. Relationships between these hydrologic pathways and stream nutrient patterns have been largely neglected by ecologists.

Hydrologists identify several mechanisms of storm runoff generation in humid forested watersheds. Subsurface flow on hillslopes is produced by rapid infiltration of rain which flows to the stream through interconnected large pores (macropores) or through saturated soil horizons (Beven & Germann 1982; Anderson & Burt 1990). Partial-area overland flow occurs on certain portions of a watershed where rainfall rates are greater than soil infiltration rates (Betson & Marius 1969). A third important storm flow mechanism is saturation overland flow which is generated by rain or snowmelt on near-stream areas that have become saturated from below by a rising water table (Dunne & Black 1970; Bonell & Gilmour 1978). Tracer studies using stable isotopoes (^{2}H, $^{18}0$) indicate that 'pre-event water' (water stored in the soil prior to the storm event) usually dominates storm discharge in streams (Sklash & Farvolden 1979; Sklash et al. 1986). An 'event water' (rainfall, snowmelt) component of stream discharge can be generated by direct precipitation onto saturated areas (Rodhe 1987).

Differences in the origin and flow path of storm runoff may greatly control stream water chemistry. However, few studies have directly identified hydrologic pathways and measured their associated element transformation processes. Pionke et al. (1988) have related the chemistry of saturation overland flow and subsurface flow in the near-stream zone to stream N and P dynamics during a summer storm event in a Pennsylvania agricultural catchment. Recently, the influence of the solute chemistry of subsurface stormflow on stream element exports has been investigated in a forested eastern Tennessee catchment (Mulholland et al. 1990; Wilson et al. 1991b).

Most studies of storm runoff have focused on upland forested catchments in which wetlands are absent (Hooper & Shoemaker 1986; Sklash et al. 1986; Wilson et al. 1991a). Riparian wetlands may play an important role in contributing to storm runoff and stream chemistry (Wels et al. 1990). Although saturation overland flow is an important mechanism for generating storm runoff in wetlands (Taylor 1982; Roulet 1991), information is currently lacking on how throughfall chemistry and biogeochemical processes associated with surface storm runoff in wetlands regulate stream water composition.

The major objective of the present study was to investigate stream nitrogen variations during storms in relation to element transformations associated with saturation overland flow in a forested riparian wetland. Hydrologic data were combined with observations of a natural isotope oxygen-18, and nitrogen concentrations in saturation overland flow and stream discharge to assess the influence of storm runoff sources on stream nitrogen dynamics. I also used laboratory experiments to analyze nitrogen transformations associated with storm runoff-surface substrate interactions in zones of saturation overland flow in the wetland.

Study area

The study was conducted in a headwater riparian swamp located in a 1.57 km^2 watershed approximately 50 km northeast of Toronto, Canada (44°00′N, 79°05′W) on the southern flank of the Oak Ridges moraine, a major topographic feature composed of sands and gravels, locally covered by till. An extensive regional aquifer with calcium bicarbonate type water, approximately 218 km^2 in area and 15 m thick underlies the moraine (Howard & Beck 1986). The headwater swamp is representative of valley bottom wetlands in groundwater discharge zones that are widespread in regions of North America and Europe where aquifers occur in glacial and fluvio-glacial deposits (Calles 1985; Carter & Novitski 1988; Roulet 1990).

The watershed is drained by two first-order streams that join and flow to the second-order outlet. Slopes are moderate to steep (10—20%) and elevations vary from 280 m at the outlet to 346 m at the northern perimeter of the watershed (Fig. 1). Upland soils are well-drained Ochreptic Hapludalfs, and the vegetation is primarily mature (80—100 yr) sugar maple (*Acer saccharum*) and American beech (*Fagus grandifolia*) interspersed with younger stands of white pine (*Pinus strobus*) and paper birch (*Betula papyrifera*) and old field communities of grasses and forbs with scattered patches of trees.

The riparian swamp occupies 2% of the watershed and is located in a 20—100 m wide zone along the perennial streams (Fig. 1). The swamp soils are peaty Histosols which increase in thickness from a few cms at the

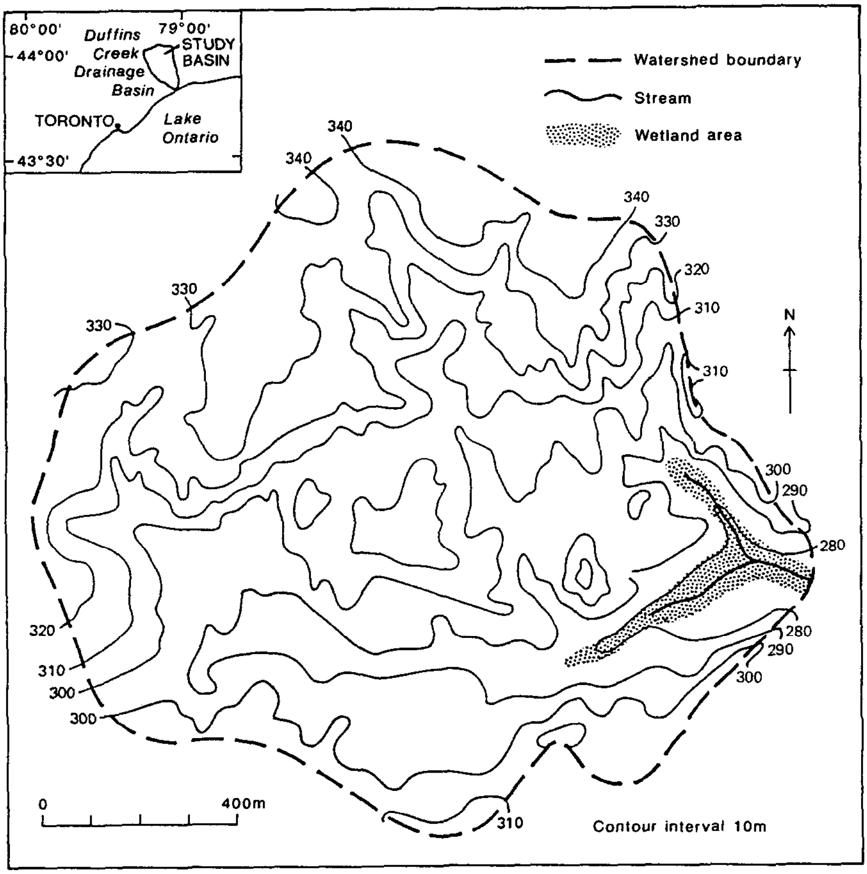

Fig. 1. Location of the study swamp and topographic map of the catchment.

wetland perimeter to >2 m in the near-stream zone. The forest cover consists of 100—120 yr old eastern hemlock (*Tsuga canadensis*) and northern white cedar (*Thuja occidentalis*) with an understorey composed mainly of striped maple (*Acer pensylvanicum*) and red maple (*Acer rubrum*).

The swamp receives a constant large groundwater input of >45 mm/d (Roulet 1990). Geochemical analysis indicates that shallow local groundwater enters the swamp as springs and seeps at the upland margins, whereas deeper groundwater from a regional flow system flows upwards through the organic soils within the swamp (Hill 1990). These groundwater systems have created many diffuse saturated zones that are joined together by small streamlets which transport groundwater rapidly (<30 min.

during baseflow) across the swamp surface to the first and second order streams (Fig. 2). Surface flow in the streamlets often passes into shallow underground pipes formed by the decay of buried logs and roots and into cavities under partially uprooted trees. The surfaces of the saturated areas are characterized by small depressions and rills containing 1—2 cm of water and intervening areas of exposed organic soil covered with leaf and fine woody litter. The areal extent of the saturated areas does not vary temporally and is controlled by the swamp microtopography and the constant groundwater input (Routlet 1990).

Previous hydrologic studies on the swamp indicate that saturation overland flow dominates storm runoff production, and increased subsurface flow produced by a rapid rise in the water table (groundwater

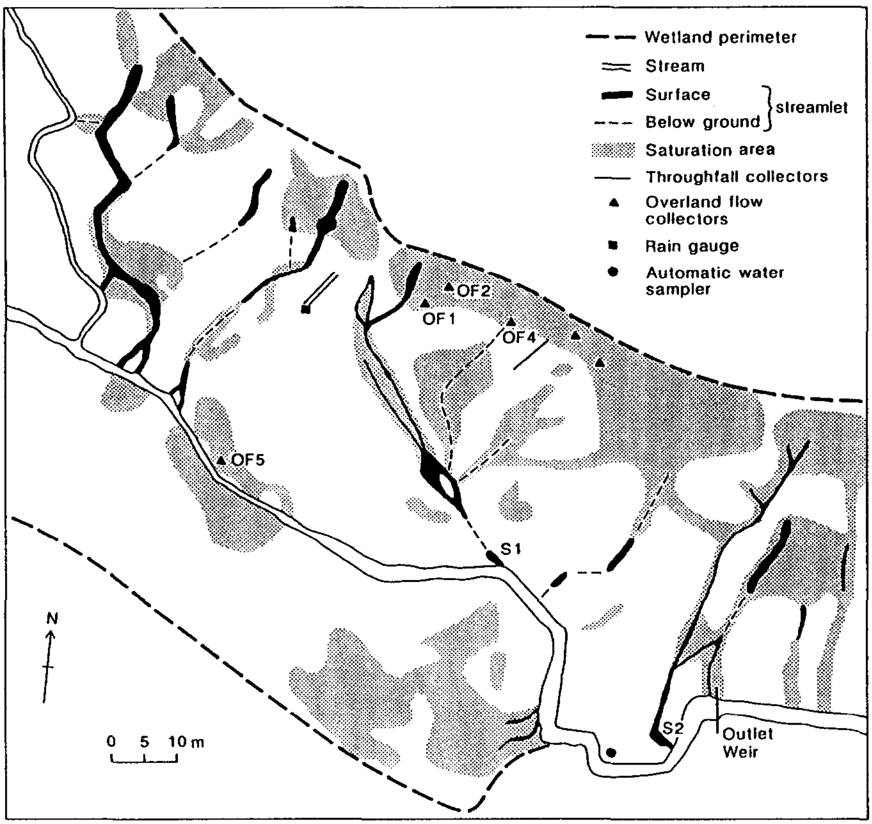

Fig. 2. Portion of the swamp located between the junction of the north and south tributary streams and the outlet weir showing the distribution of permanently saturated areas and instrument locations.

ridging) adjacent to the stream is not important (Roulet 1991; Waddington et al. 1992). The surrounding moraine slopes do not contribute storm runoff to the swamp. Hydrograph separation using oxygen −18 showed that pre-event water formed 80—90% of the outlet stream hydrograph volume in most storms (Hill & Waddington 1992). However, instantaneous event water contributions had considerable storm-to-storm variability with maximum values in the range of 20—63%. Waddington et al. (1992) suggested that rapid mixing of event water with a larger reservoir of pre-event water on the surface of the permanent saturated areas within the swamp accounts for the dominance of pre-event water during storms.

Methods

Field methods

Throughfall precipitation was collected using a sequential rainfall sampler (Kennedy et al. 1979) at two sites in the swamp (Fig. 2). The throughfall collectors consisted of 5 m long plastic troughs connected to polyethylene bottles which sampled successive 4.2 mm increments. After July 8, 1990 the troughs were increased in length to 6.65 m and each bottle then collected a 3.2 mm increment. Connectors were arranged so that each bottle filled before precipitation flowed to the next bottle in the sequence. An air outlet pipe prevented siphoning between bottles. Sample volume was related to the timing and intensity of throughfall using a tipping bucket rain gauge linked to a trough collector located adjacent to one of the throughfall samplers. The tipping bucket rain gauge was connected to a datalogger. Discharge in the second order stream at the basin outlet was measured at a 53° thin-plate V notch weir using a Stevens type F recorder and an electronic potentiometer water level recorder linked to the datalogger. During storms, stream samples were collected at 15—20 minute intervals using a stage activated sampler installed upstream of the pond behind the weir. Water samples were also collected manually during several storms from two streamlet outlets (S1, S2) discharging into the second order stream (Fig. 2).

Overland flow collectors (e.g. Abdul & Gillham 1989) were used to sample storm runoff on the permanently saturated areas of the swamp (Fig. 2). The collectors, which consisted of 4 cm ID PVC pipe capped at the lower end, were positioned on the surface a few mm above the saturated peat so that they would only collect water during periods of peak runoff. Water samples were usually removed from throughfall samplers, overland flow collectors and the stream sampler within 24 h after a storm and filtered through cellulose acetate membrane filters (0.45 μm).

Hydrograph separation techniques

Stable environmental isotopes are frequently used as tracers to separate the storm runoff hydrograph into its event water and pre-event water components (Sklash & Farvolden 1979; Kennedy et al. 1986). The event and pre-event water contributions can be calculated using a simple chemical mixing equation:

$$Q_P = [(C_T - C_E)/(C_P - C_E)]Q_T \tag{1}$$

where Q is discharge, C is the tracer concentration and P, E and T refer to pre-event, event and steam water respectively.

The reliability of hydrograph separation depends mainly on the magnitude of difference between event and pre-event water signatures and the documentation of areal and temporal variations of event and pre-event water tracer values (Sklash & Farvolden 1979). Hill & Waddington (1992) found that the $^{18}0$ content of surface water on saturated areas was similar to groundwater indicating that pre-event water had a uniform isotope value. They also used the incremental intensity mean method to evaluate temporal variations in the isotopic content of throughfall (event water) from the beginning of the storm up to the time of taking each stream sample (McDonnell et al. 1990). This method expresses the isotopic value of event water as:

$$\delta_E = \sum_{i=1}^{n} Ii\,\delta i \bigg/ \sum_{i=1}^{n} Ii \tag{2}$$

where Ii is the average intensity (mm/h) during the sampling increment and δi is the corresponding isotope value. This method gives greater weighting to episodes of higher intensity rain within storms which may produce a large runoff response.

The chemical mixing equation was used to examine nitrogen dynamics in storm runoff. If NO_3-N and NH_4-N were to behave in a conservative manner, patterns of variation in stream water N concentations during storms could be explained in terms of the mixture of event and pre-event water entering the stream. Deviations from the pattern of chemistry predicted on the basis of source water nitrogen concentrations can provide useful information about biogeochemical transformations in storm runoff.

Observed NO_3-N and NH_4-N concentrations in the swamp outlet stream during storms were compared to predicted concentrations which were calculated as:

$$C_T = \frac{C_E Q_E + C_P Q_P}{Q_T} \tag{3}$$

The quantity of event and pre-event water at specific times during storm runoff was calculated using the $^{18}0$ data for the storm event. Nitrogen variations in throughfall (event water) were evaluated using the incremental intensity mean method. Nitrogen concentrations in the outlet stream base flow prior to each storm were used to represent the pre-event water concentration throughout the event. This approach assumes that sources of groundwater flow to the stream during storms are the same as during baseflow conditions. Waddington et al. (1992) showed that water table response in the swamp was minor during storms suggesting that the relative contribution of local and regional groundwater remained similar to baseflow.

Laboratory experiments

Changes in NO_3-N and NH_4-N concentrations that result from interaction between swamp substrates and mixtures of throughfall and groundwater in saturation overland flow were examined in a laboratory experiment. Surface peat and litter from five separate areas of permanent saturation were mixed to form a composite sample. Approximately 20 g of this mixed substrate was placed in flasks with 200 ml mixtures of groundwater collected from saturated areas during base flow periods and throughfall obtained from collector troughs after storm events. Laboratory experiments were begun within 2 hours after collection to surface substrates and groundwater.

Water mixtures containing 5, 10 and 20% throughfall were shaken continously for 0.3, 0.6, and 1 h respectively with swamp substrates. After each time interval the water mixtures were filtered (0.45 μm) for analysis of NO_3-N and NH_4-N. Hydrograph separation using $^{18}0$ indicated that the throughfall (event water) component increases from 5% in the initial phase to 20% at peak flows in most storms (Hill & Waddington 1992). Vigorous mixing of water and swamp substrates reproduces the high concentrations of particulate organic matter which were observed in surface runoff prior to peak discharge. Swamp substrates which had been shaken for 1 hour with water mixtures containing 20% throughfall were retained after filtration. One set of these substrates was immediately incubated with water mixtures containing 15 and 5% throughfall for an additional 0.5 and 1 h respectively with occasional stirring. This procedure simulated the recession phase of storm runoff which had a smaller event water component and low quantities of particulate transport. A second set of substrates was incubated with groundwater under static conditions for 2—4 h to simulate the late recession phase of the storm. Triplicate sets of each groundwater-throughfall mixture were incubated with substrates for each time interval. Flasks containing the various water mixtures without substrates were also run separately to provide a measurement of the initial NO_3-N and NH_4-N concentrations in the water.

A second experiment was designed to separate biological transformation of nitrogen from abiotic mechanisms of sorption. Flasks containing 20 g of swamp substrate were amended with 0.8 ml of chloroform. Bacteriological analysis showed that this treatment was effective in eliminating cell growth. Sets of sterile and living substrates were incubated using the procedures described previously.

Laboratory analysis

Concentrations of $(NO_3 + NO_2)$-N were measured by Cd—Cu reduction followed by automated colorimetry using a Technicon AutoAnalyzer II system (Technicon 1977). Concentrations of nitrite in periodic tests were below detection limit. NH_4-N was analyzed by Technicon (1978) procedures. Isotope analyses for $^{18}0$ were done in the Environmental Isotope Lab at the University of Waterloo. Stable isotope composition is reported in the conventional delta (δ) notation using units of parts per thousand (‰) relative to the standard SMOW (Standard Mean Ocean Water).

Results

Groundwater and throughfall nitrogen concentrations

Local groundwater at depths of 1—3 m adjacent to the perimeter of the swamp had NO_3-N concentrations of 100—180 μg/l, whereas NO_3-N concentrations in regional groundwater beneath the swamp were $<$ 10 μg/l (Hill 1990). Both groundwater systems had similar NH_4-N concentrations of 20—60 μg/l.

Spatial variations in surface water nitrogen concentrations in swamp saturated areas and streamlets were examined during base flow in late June and July 1990. Springs along the swamp edge had NO_3-N concentrations of 100—140 μg/l, whereas saturated areas within the swamp had NO_3-N concentrations of $<$ 20 μg/l. Compared to spring sources, most streamlets entering the main stream had lower NO_3-N concentrations of 50—80 μg/l. These NO_3-N variations result from the emergence of local groundwater at the swamp edge and the entry of regional groundwater into saturated areas and streamlets within the swamp (Hill 1990). Surface water NH_4-N concentrations were < 10 μg/l throughout the riparian swamp. These low NH_4-N concentrations in comparison to the higher values in local and regional groundwater entering the swamp are due mainly to microbial immobilization in the surface peat of the saturated areas (Hill & Warwick 1987). Stream samples collected at the watershed outlet during base flows on 25 dates between June and November 1990 revealed seasonally constant NH_4-N concentrations; mean $\pm$SE $= 7 \pm 2$ μg/l, whereas NO_3-N concentrations declined gradually from 120—130 μg/l in June to 90—100 μg/l in October. These base flow nitrogen concentrations in the outlet stream represent an integration of the spatial variations in groundwater nitrogen within the swamp.

Incremental throughfall chemistry was analyzed for 11 storms between June and November 1990. Variations in NO_3-N and NH_4-N in successive throughfall increments are shown for a number of representative storms (Fig. 3). Concentrations shown for individual increments are joined for visual interpretation. Inorganic N concentrations showed large storm to storm differences; however, a similar pattern of high concentrations in the initial throughfall increment followed by a decline to lower concentrations was evident in all storms. In some storms for example, July 15 and October 12, 1990, the final one or two increments had higher nitrogen concentrations than the mid-storm period. In most storms, NO_3-N and NH_4-N concentrations in the initial throughfall increment were 10—30x and 20—100x higher respectively than stream base flow concentrations. During the mid-storm period, NO_3-N and NH_4-N concentrations were sometimes similar to, or considerably lower than stream base flow values (Fig. 3).

Storm nitrogen variations in overland flow and the outlet stream

Variations in NO_3-N and NH_4-N concentrations were observed for 26 storms between November 1987 and November 1990 in the outlet stream. During the period June—November 1990, $^{18}0$ was also measured in 11 storm hydrographs. Seven of these storms had a sufficient difference between event and pre-event isotopic signatures to allow hydrograph separation (Hill & Waddington 1992). These hydrograph separations indicated that the event water contributions to storm runoff varies in relation to precipitation intensity and duration. Maximum instantaneous event water contributions were 20—25% for moderate intensity-short duration storms,

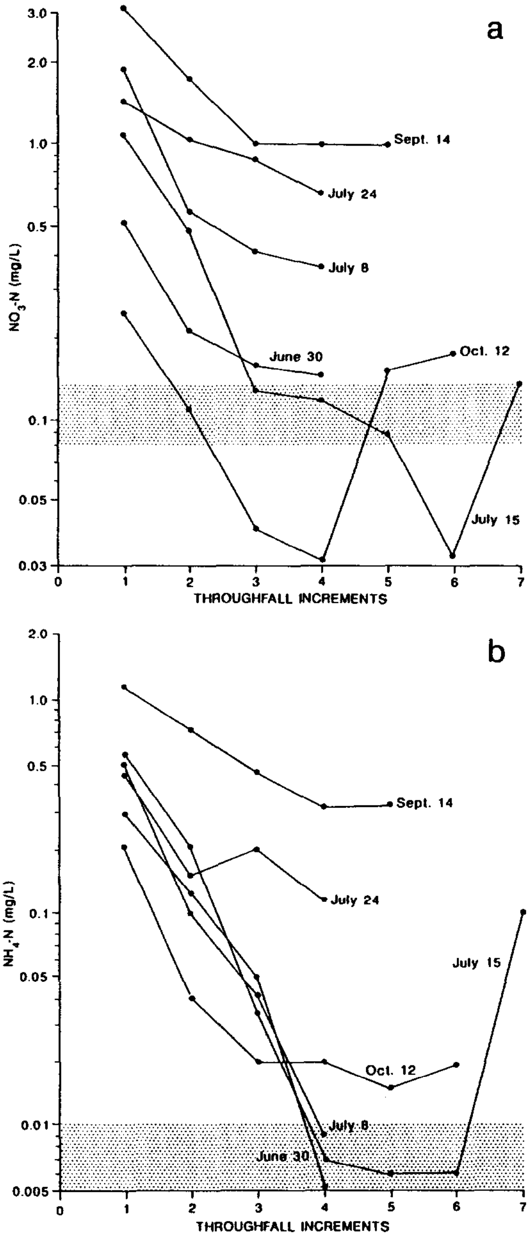

Fig. 3. NO_3-N and NH_4-N concentrations in sequential throughfall increments for storms in 1990. Increments are 4.2 mm for June 30 and July 8 and 3.2 mm for storms after July 8. The horizontal band indicates the range of NO_3-N and NH_4-N concentrations during base flows in the swamp outlet stream.

39—44% for low intensity-long duration events and exceeded 60% for a high intensity-short duration storm (Hill & Waddington 1992).

Several patterns were evident in the temporal variation of stream NO_3-N concentrations during storms (Figs. 4—6). Nitrate-N concentrations increased with maximum values varying from < 2x to 6x higher than base flow concentrations. There was also variation between storms in the timing of the concentration peak that led or coincided with the peak discharge. Complex hydrogaphs that exhibit more than one peak are characteristic of low intensity-long duration storms in the watershed. The behaviour of NO_3-N during these events shows contrasts between the first and second phases of the storms. Maximum NO_3-N concentrations fre-

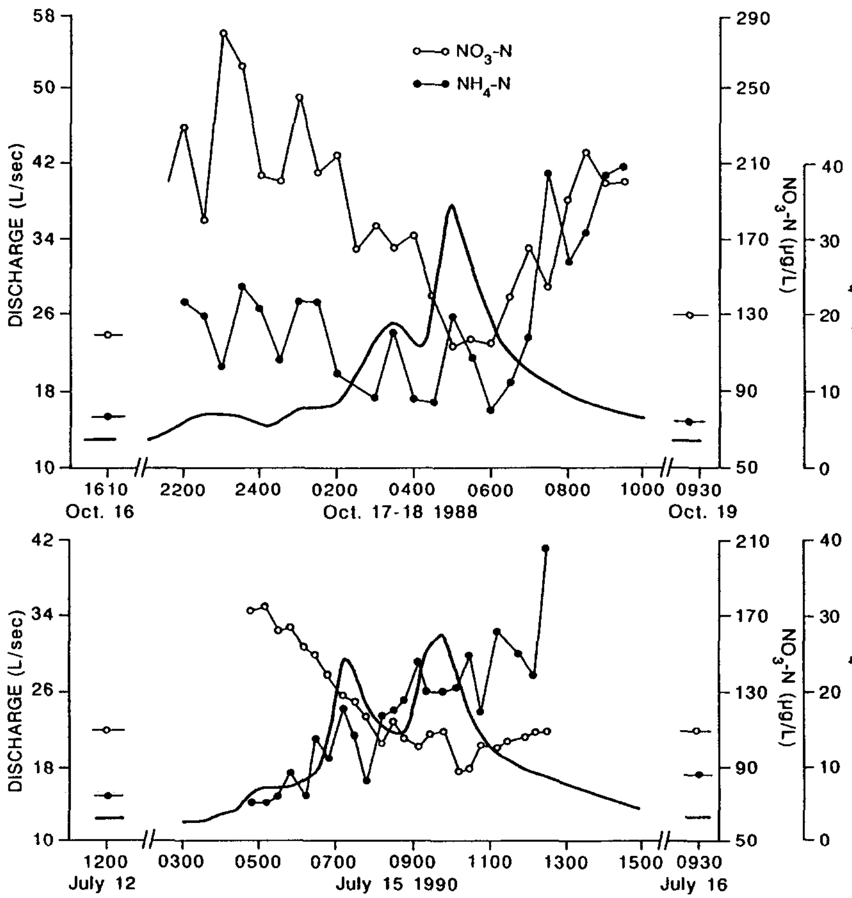

Fig. 4. NO_3-N and NH_4-N concentrations in relation to stream discharge for storms on Oct. 17—18, 1988 and July 15, 1990.

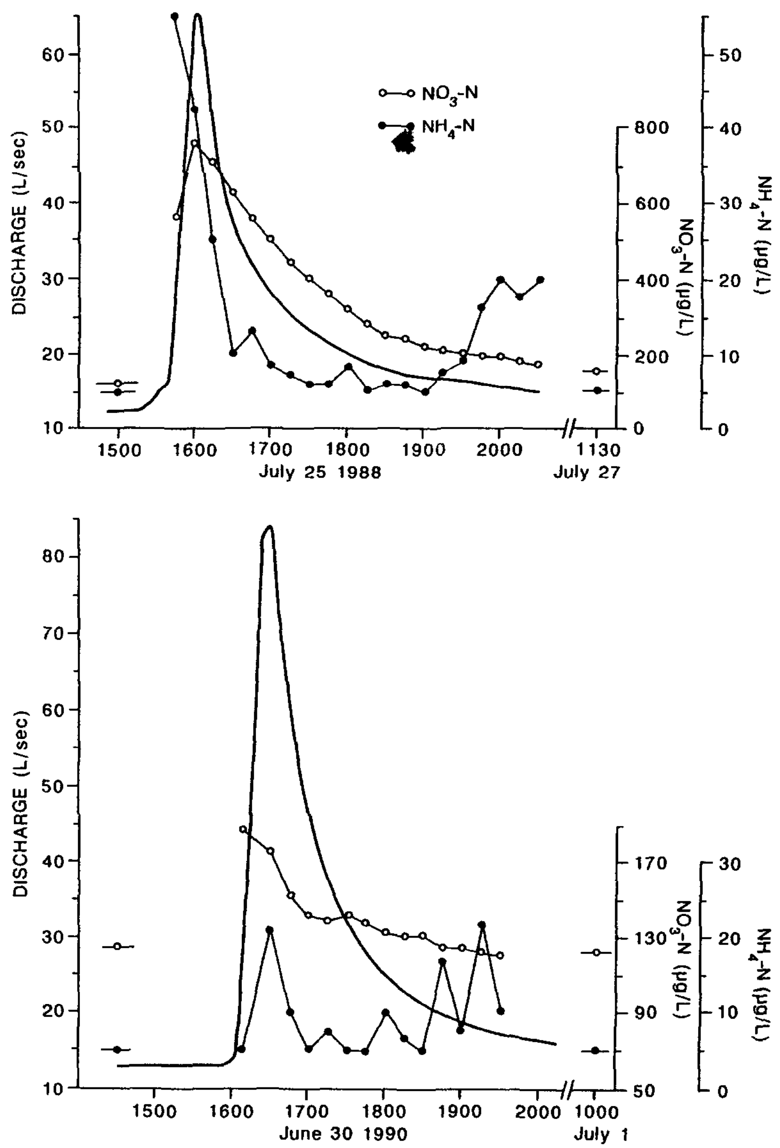

Fig. 5. NO_3-N and NH_4-N concentration in relation to stream discharge for storms on July 25, 1988 and June 30, 1990. Note the difference in scale for NO_3-N on July 25, 1988.

quently occurred at an early stage on the ascending hydrograph limb, several hours before the first discharge peak (Fig. 4). This concentration effect during the first phase of the storm was replaced by a NO_3-N dilution response associated with the second discharge peak.

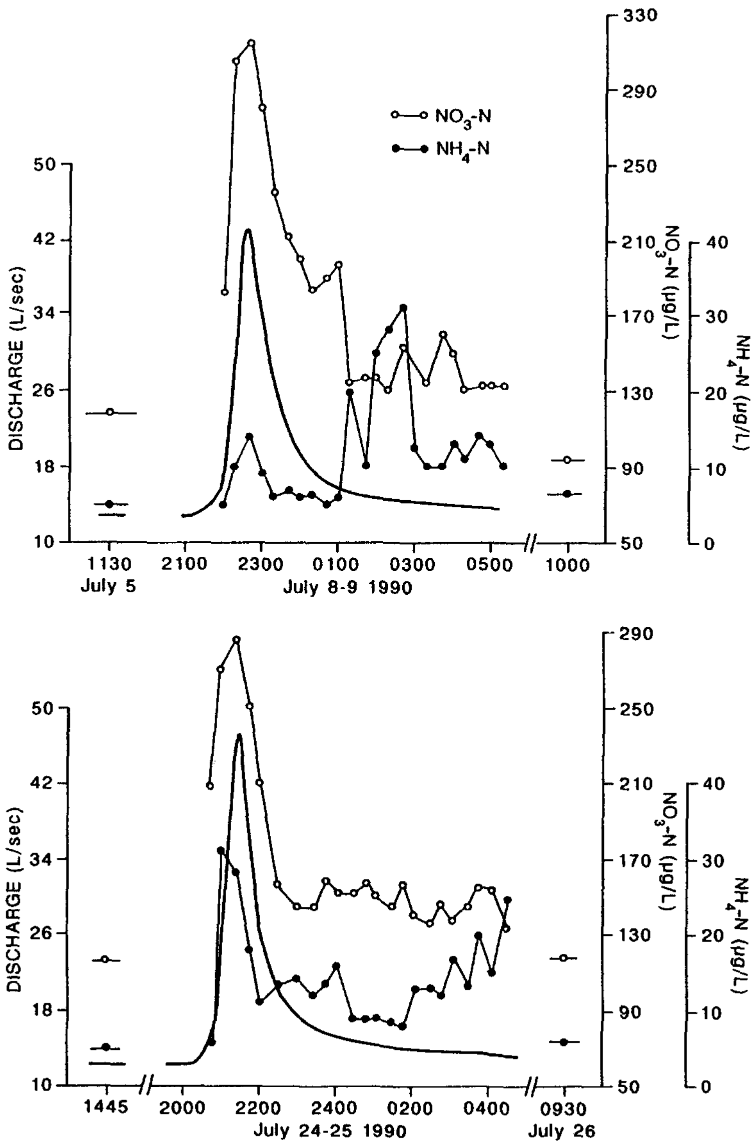

Fig. 6. NO_3-N and NH_4-N concentrations in relation to stream discharge for storms on July 8—9, and July 24—25, 1990.

During the storm recession phase, NO_3-N concentration declined progressively towards base flow values in some storms (Fig. 5). In other storms NO_3-N declined rapidly in the early recession phase and then remained relatively constant for 4—6 h at concentrations higher than base flow values (Fig. 6). A third pattern evident during the second phase of the Oct. 17—18, 1988 and June 15, 1990 storms was characterized by NO_3-N dilution below base flow concentrations during the early recession, followed by a gradual return to, or an increase above base flow concentrations late in the hydrograph recession (Fig. 4).

Concentration-discharge relationships for NH_4-N during storms were less variable than for NO_3-N in the swamp outlet stream. In most storms NH_4-N concentrations attained an initial peak on the rising limb of the hydrograph, or at peak discharge (Figs. 4—6). This initial peak was followed by a decline to values near base flow concentrations in the early recession phase. A consistent feature of storm period NH_4-N behaviour was the occurrence of a second increase in concentration to levels which were sometimes higher than the initial peak during the late recession stage 3—5 h after the peak in stream discharge.

Overland flow from saturated areas was sampled for a number of storms in 1990. Visual observations were made and water samples were taken manually from streamlet outlets 1 and 2 during a high intensity-short duration thunderstorm on June 30, 1990, which produced the highest stream discharge of 1990 with $<2\%$ of discharge peaks since 1987 exceeding this magnitude. Rapid increases in runoff occurred on saturated areas throughout the swamp in this storm. Visual observations suggested that large amounts of particulate organic matter, consisting of surface vegetation detritus (needles, wood fragments) and peat soils fragments, were transported by this surface runoff. Particulate transport declined rapidly after peak discharge. Inorganic nitrogen concentration in overland flow collectors and at the streamlet outlets showed a concentration increase relative to base flow values (Table 1). A concentration effect was also found for NO_3-N and NH_4-N in runoff from saturated areas during other storm events.

Storm runoff sources in relation to stream nitrogen dynamics

The July 8—9 storm event shows how a significant difference between the stream base flow (pre-event water) $^{18}0$ value of $-12.0‰$ and the throughfall (event water) values of -3.2 to $-5.1‰$ can be used to calculate the quantity of these two water sources in the stream at specific times during the storm event (Fig. 7). A comparison of observed NO_3-N concentrations with those predicted from the mixture of event and pre-event water in the outlet stream shows a reasonable agreement (Fig. 8). Predicted and observed maximum NO_3-N concentrations are similar for moderate intensity-short duration storms on July 8—9 and August 12 and the high intensity storm on June 30. However, observed NO_3-N concentrations

Table 1. Base flow and storm runoff NO_3-N and NH_4-N concentrations in saturated areas and streamlets within the swamp. Location of overland flow collectors (OF1—OF5) and streamlets (S1, S2) shown in Figure 2.

Site	Base flow range	Storm runoff				
		June 30	July 8—9	July 15	July 24	Aug. 12
				NO_3-N (μg/L)		
OF1	14—16	230	470	100	70	196
OF2	10—20	170	420	40	220	
OF4	7—10		520		400	258
OF5	10—15		230			
S1	35—50	130				
S2	65—75	150				
				NH_4-N(*mg*/L)		
OF1	5	25	4	10	20	
OF2	5	10	10	8	16	
OF4	5	20	29		16	
OF5	5—10	15	10			
S1	5—10	23				
S2	5	12				

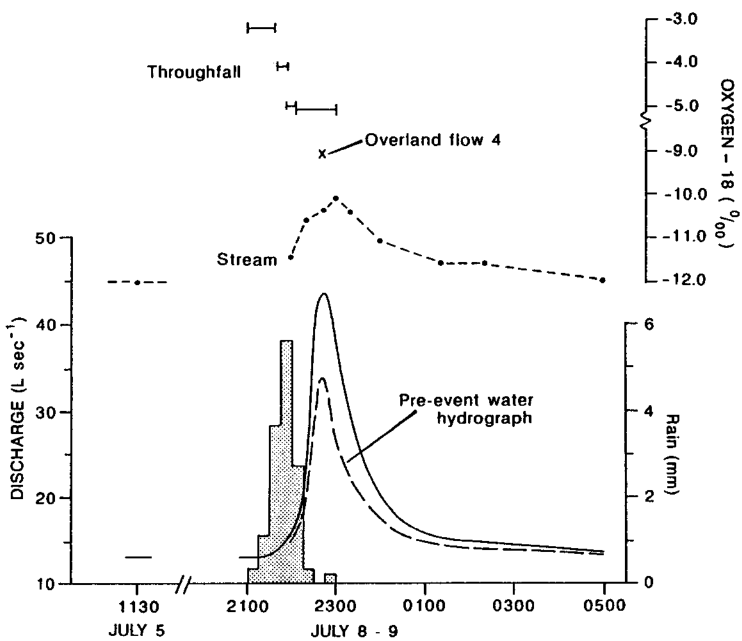

Fig. 7. Variations in stream discharge and $\delta^{18}O$ for the July 8—9, 1990 storm.

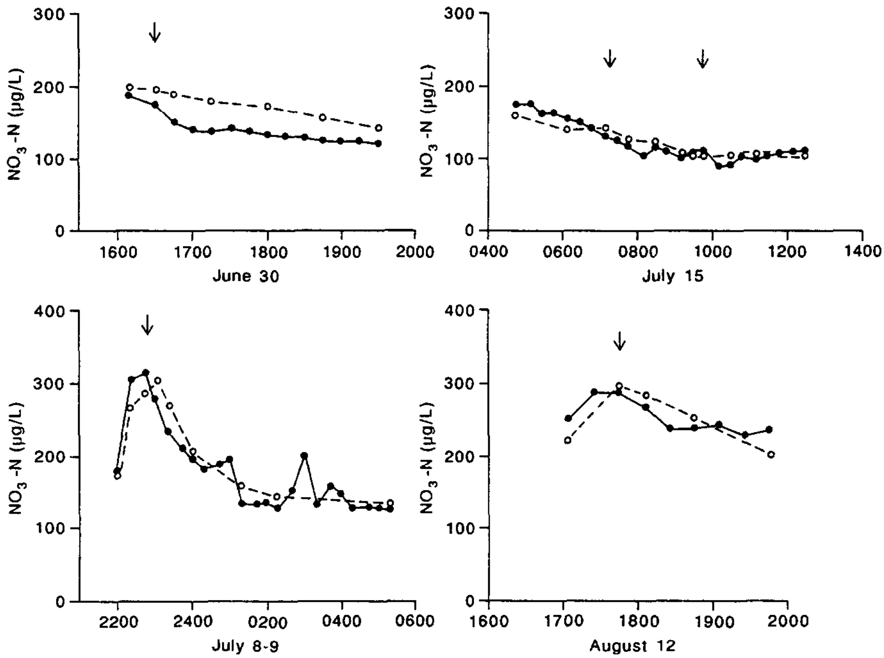

Fig. 8. Comparison of observed stream NO_3-N concentrations (●) and predicted values (○) based on the conservative mixing of pre-event and event water components for four storms in 1990. The vertical arrows indicate the time of peak stream discharge.

declined more rapidly than predicted concentrations during the hydrograph recession on June 30. For the July 15 low intensity-long duration storm predicted NO_3-N concentrations successfully reproduce the initial observed NO_3-N concentration peak on the rising limb of the first hydrograph peak and the observed NO_3-N decline to below baseflow concentrations during the second discharge peak (Fig. 8). In contrast, predicted NH_4-N concentrations are much higher than observed values particularly on the rising limb of the hydrograph and at maximum discharge (Fig. 9).

Predicted and observed inorganic-N concentrations were also compared for saturation overland flow in the swamp using data from overland flow collectors. The ^{18}O values indicated that event water formed 50% of storm runoff in a composite water sample from collectors 1 and 2 for the June 30 storm and 36% of the runoff sample for collector 4 in the July 8—9 storm. On the basis of these event water contributions predicted and observed NO_3-N concentrations were 220 vs 200 μg/l for June 30 and 400 vs 520 μg/l for July 8—9. In contrast predicted and observed NH_4-N

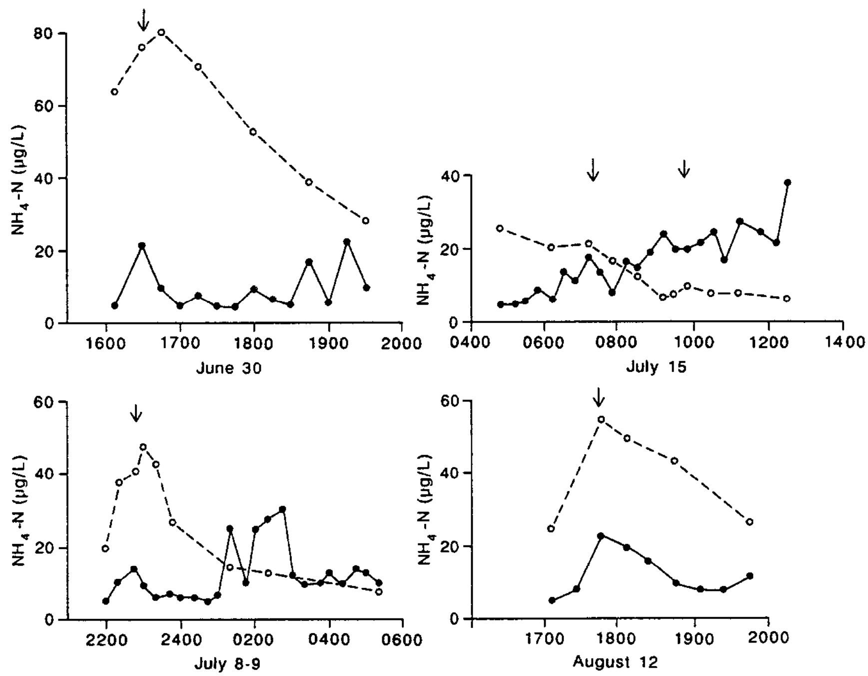

Fig. 9. Comparison of observed stream NH_4-N concentrations (●) and predicted values (O) based on the conservative mixing of pre-event and event water components for four storms in 1990. The vertical arrows indicate the time of peak stream discharge.

concentrations were 120 vs 18 µg/l (June 30) and 82 vs 29 µg/l (July 8—9).

Laboratory experiments

There was no difference between NO_3-N concentrations in mixtures of throughfall and groundwater incubated with saturated area swamp substrates and the water mixtures without substrates during experiments, when peak NO_3-N concentrations were 200 and 400 µg/l (Fig. 10). NH_4-N concentrations in water mixtures shaken with swamp substrates for up to 1 h to simulate the rising hydrograph limb and peak discharge were significantly lower than concentrations in controls (Fig. 10). Replacement of water mixtures after 1 h with mixtures containing a smaller event water component for an additional 0.5—1 h also showed a significant decline in NH_4-N concentrations relative to controls. However, flasks in which water mixtures were replaced after 1 h with groundwater and incubated for an additional period of 2.5—3.5 h to simulate the late

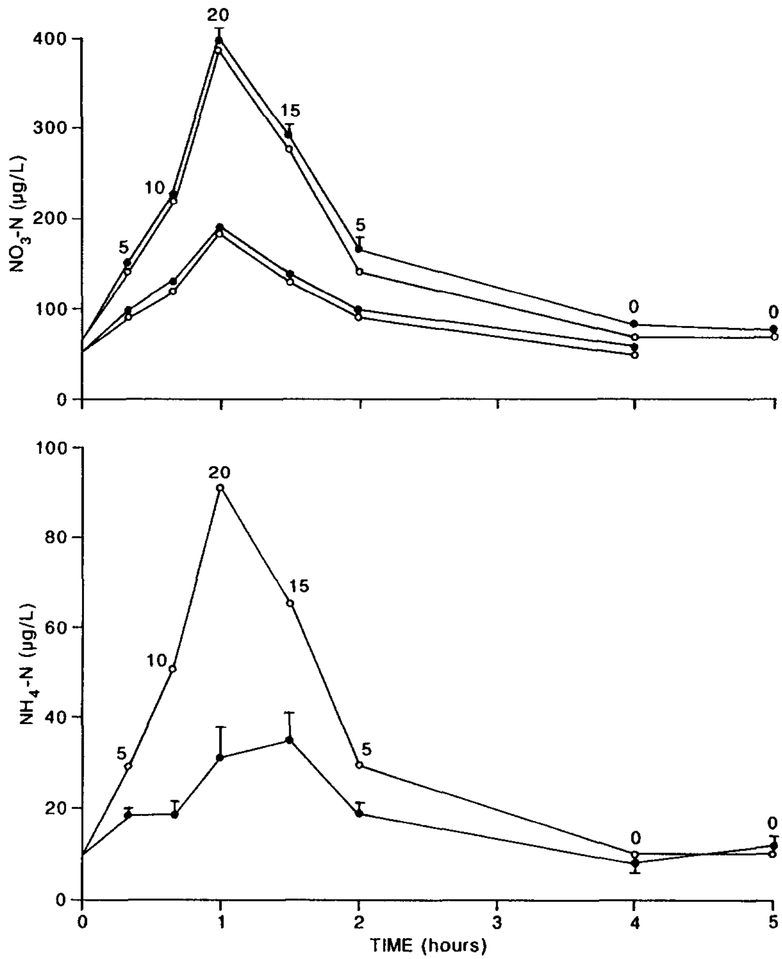

Fig. 10. Concentrations of NO_3-N and NH_4-N over time in flasks containing throughfall-groundwater mixtures with swamp substrates (●), and without substrates (O). Values are means of three replicates ±SE. Points without error bars indicate SE smaller than the symbol itself. Numbers indicate the throughfall component (%) in the water mixture.

recession phase of the storm had NH_4-N concentrations which were similar to flasks without substrates (Fig. 10). NH_4-N concentrations in flasks containing water mixtures and sterilized substrates were similar to concentrations in flasks without substrates, whereas flasks with untreated substrates showed NH_4-N uptake suggesting that biotic processes are responsible for NH_4-N loss from water mixtures (Fig. 11).

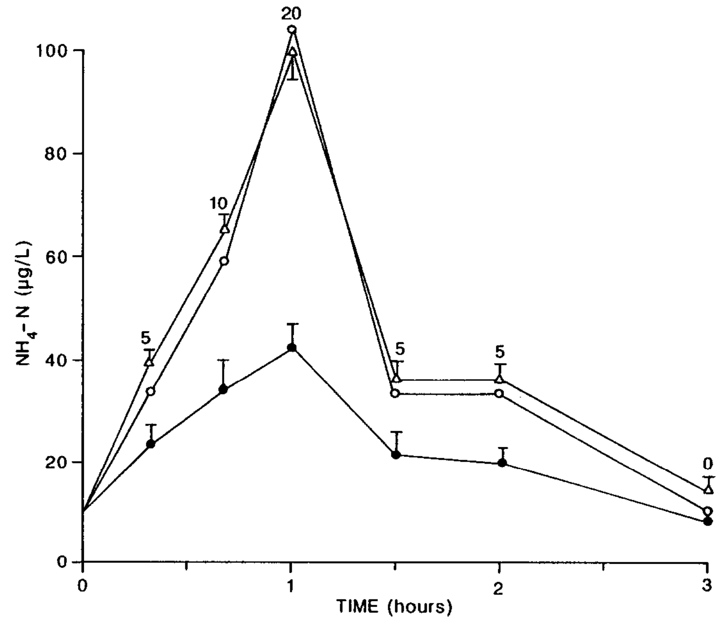

Fig. 11. Concentrations of NH_4-N over time in flasks containing throughfall-groundwater mixtures with untreated substrates (●), with chloroform-sterilized substrates (Δ) and without substrates (O). Values are means of three replicates of ± SE. Numbers indicate the throughfall component (%) in the water mixture.

Discussion

The dominant features of NO_3-N concentration dynamics during storms in the swamp outlet stream include variability in maximum NO_3-N concentrations and in the timing of the concentration peak relative to peak stream discharge. The close agreement between observed NO_3-N concentrations in storm runoff and concentrations predicted from the chemical mixing model suggests that temporal variations in NO_3-N are regulated by the mixture of throughfall and groundwater transported by saturation overland flow to the stream. The laboratory experiments also indicate that NO_3-N behaves in a conservative manner when mixtures of throughfall and groundwater are shaken with swamp substrates.

Although the maximum instantaneous contribution of throughfall is $<25\%$ in most storms, this small component strongly influences stream NO_3-N concentrations. The frequent occurrence of maximum stream NO_3-N concentrations on the rising limb of the hydrograph or at peak discharge can be attributed to the high NO_3-N concentrations which occur in the first 3—4 mm of throughfall. Declines in streamwater NO_3-N concentrations during storms to levels below base flow concentrations appear to be associated with very low NO_3-N concentrations in later throughfall increments e.g. July 15, 1990 (Figs. 3 and 4). The variable behaviour of NO_3-N during the hydrograph recession e.g. the progressive decline to base flow values on June 30, 1990 (Fig. 5) and the maintenance of higher NO_3-N concentrations on July 8—9 and July 24—25, 1990 (Fig. 6) can also be related to throughfall NO_3-N variations in the later phase of these storms (Fig. 3).

Considerable storm-to-storm differences in the temporal behaviour of NO_3-N have also been found in streams draining grassland watersheds in England and New Zealand (Webb & Walling 1985; Cooke & Cooper 1988). This complexity of NO_3-N behaviour in streams has been attributed to interactions between several factors including storm characteristics, runoff processes and antecedent soil moisture and nitrogen status (Webb & Walling 1985). In several watersheds a dilution of NO_3-N with minimum concentrations at peak stream discharge occurred in storms dominated by saturation overland flow which had low NO_3-N concentrations. In other storms a concentration effect, with maximum NO_3-N concentrations on the falling limb of the hydrograph, was observed when runoff was dominated by subsurface storm flow which had high NO_3-N content (Webb & Walling 1985; Cooke & Cooper 1988). In contrast, my results indicate that considerable differences in NO_3-N dynamics between individual storm events can occur in watersheds which have a single dominant storm runoff mechanism, provided that this pathway delivers a temporally variable mixture of event and pre-event water.

Peaks in NO_3-N concentrations during the early stages of a storm hydrograph have frequently been attributed to a soil flushing effect (Walling & Foster 1978). Flushing effects are often important following periods of drying in which nitrogen accumulates in surface soil horizons from dry fallout deposits and soil N mineralization. However, flushing of NO_3-N in the Oak Ridge moraine watershed mainly involves the removal of inorganic N from the riparian forest by throughfall in the early storm phase rather than soil flushing. Dry fallout does not accumulate on the saturated areas of the swamp even during drought periods because of the constant groundwater discharge. Hill & Shackleton (1989) measured negative rates of annual N mineralization and negligible nitrification in the top 0—8 cm zone of peat in the saturated areas, indicating that NO_3-N is unlikely to be flushed from these sites during storms.

Peaks in NH_4-N which frequently preceded the storm hydrograph peak, are probably also linked to high NH_4-N concentrations in the initial throughfall increments. However, in contrast to NO_3-N, observed stream

NH_4-N concentrations from the initial rise of the storm hydrograph to the early recession phase were substantially lower than concentrations predicted from the mixture of throughfall and groundwater delivered to the stream. Microbial processes appear to be responsible for the maintenance of relatively low NH_4-N concentrations in the stream during storms. Removal of NH_4-N from mixtures of storm runoff and swamp substrates resulted from biotic uptake of N, as shown by the low NH_4-N concentrations for untreated swamp substrates when compared with concentrations for sterilized substrates. The close agreement between NH_4-N concentrations in sterilized substrate treatments and in treatments containing only throughfall-groundwater mixtures indicates that abiotic adsorption is not important. The pH of the mixtures was not altered by the addition of chloroform which suggests that the absence of abiotic NH_4 uptake was not caused by protonation of the sorption sites.

A progressive increase in stream concentrations during the late recession phase of the storm hydrograph is a consistent feature of NH_4-N behaviour. The laboratory experiments suggest that these higher NH_4-N concentrations are not caused by desorption of NH_4-N which was taken up by swamp substrates earlier in the storm event. Substrates which reduced NH_4-N concentrations in water from 90 to 30 μg/l when shaken for 1 h did not subsequently release NH_4-N into the water column when incubated for periods of 2.5—3.5 h with groundwater containing 10 μg/l NH_4-N.

Higher streamwater NH_4-N concentrations during the late recession period may result from a decline in the rate of microbial N uptake. The relatively small difference between observed NH_4-N values and concentrations predicted from the chemical mixing model during the late recession stage of storms on June 30 and July 8—9, 1990 is consistent with reduced microbial uptake, whereas large differences between observed and predicted NH_4-N values for the July 15, 1990 storm appears to contradict this hypothesis. However, predicted NH_4-N values are based on a method of calculating the NH_4-N concentration of event water which includes all throughfall increments prior to each stream sampling time. During long duration storms such as the July 15 event the chemistry of the event water component during the late recession period may be influenced more strongly by the most recent throughfall increment than by earlier increments. Throughfall NH_4-N concentrations during the July 15, 1990 event increased sharply from 6 μg/l to 104 μg/l in the final 3.2 mm increment which fell between 0900—1100 h (Fig. 3). If the event water component of stream discharge in the recession phase after 1000 h consisted mainly of the final throughfall increment then the observed and predicted NH_4-N values would be similar.

Storm event NH_4-N behaviour has not been investigated in most previous studies. Pionke et al. (1988) found that NH_4-N concentrations increased to a maximum at high stream flows and declined progressively during the hydrograph recession in a small agricultural watershed. High NH_4-N concentrations (250—350 μg/l) in surface runoff derived from plant and soil washoff were similar to peak concentrations in stream discharge. Groundwater and precipitation NH_4-N concentrations were 170 and 100 μg/l respectively which suggests that NH_4-N was released rather than removed in the riparian zone of this watershed.

Studies which indicate effective retention of mineral elements, particularly NO_3-N in the riparian zone of small agricultural watersheds have focused mainly on groundwater fluxes during periods of stream baseflow (Lowrance et al. 1984; Peterjohn & Correll 1984; Cooper 1990). High NO_3-N concentrations, anaerobic soils and the considerable water residence time of subsurface water favour rapid denitrification in these watersheds. In contrast, a groundwater mass balance indicated that the Oak Ridges moraine swamp was an efficient sink for NH_4-N, but did not retain NO_3-N (Hill 1991). The absence of NO_3-N removal during base flow and storm runoff periods in this swamp may be related to the short residence time and high 0_2 concentrations of surface water.

Nitrogen transformations involving the mixing of throughfall and groundwater in saturation overland flow may also influence storm runoff chemistry in other headwater riparian wetlands which occur in zones of permanent groundwater discharge. Riparian zones which are ephemerally connected to groundwater systems have a fluctuating water table and may exhibit different mechanisms of storm runoff generation and nitrogen dynamics than those observed in the Oak Ridges moraine swamp. Saturation overland flow may only be an important runoff pathway when the water table is near the ground surface, whereas at other times stormflow may follow a subsurface path (Bonell et al. 1990). Periods of lower water table may produce episodes of nitrification in surface soils which contribute to NO_3-N release in subsequent storms (Reddy & Patrick 1984).

The results of the present study reveal the value of research that uses hydrologic, chemical and isotope measurements to study both streams and storm runoff pathways within watersheds. In combination with laboratory analysis of interactions between storm runoff and watershed substrates, such integrated studies can provide important insights into the processes controlling stream nutrient dynamics during storms.

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