

Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics

I. F. Creed¹ and L. E. Band²

Department of Geography, University of Toronto, Toronto, Ontario, Canada

Abstract. Considerable variation in the export of dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON) was observed among catchments located within an old-growth sugar maple forest in central Ontario. Although discharge was a strong predictor of N-export, rates of export were variable for each catchment, ranging from -50% to $+50\%$ from the catchment-average response for DIN and -25% to $+25\%$ from the catchment-average response for DON. Among the catchments, a unifying flushing behavior was apparent for NO_3^- -N, the dominant form of DIN in the discharge waters, providing a basis for explaining the variation in the export of DIN. Flushing occurs when a water table rises to the soil surface with subsequent mobilization of nutrients stored near or at the soil surface to surface waters. Catchment-specific flushing behaviors were captured in “flushing” characteristic time constants, defined as the time interval required for a decline in N concentrations in discharge waters to e^{-1} (37%) of their initial concentration. Variation in flushing behavior was linked to variation in N export; catchments with short flushing times (interpreted as catchments with source areas that are less variable) were observed to export less N than catchments with long flushing times (source areas that are more variable). A hypothesis was formulated in which catchment topography and its influence on variable source area dynamics accounts for variation in flushing behavior, hence variation in the export of NO_3^- -N among the catchments. The implication of this hypothesis is that to predict accurately the export of NO_3^- -N from catchments within a landscape, we need first to consider the influence of the topographic complexity of the catchments. Our understanding of the mechanisms of processing and export of DON is not sufficient for accurate prediction at this point, highlighting the need for additional research on DON.

1. Introduction

Significant variation in the export of N from certain forested catchments in Ontario has been observed [Creed, 1998]. We seek an understanding of the role of topography in regulating N export. A topographically based N flushing mechanism is identified, and the role of this mechanism in explaining the variation in N export from the catchments is considered. In a future paper (I. F. Creed et al., manuscript in preparation, 1998), the topographic properties that regulate the N flushing mechanism will be identified, providing the foundation for the development of topographic indices for incorporating topographic effects into catchment N export models.

There is a growing concern over increasing concentrations of N in surface and ground waters [Burt et al., 1988; Stoddard, 1991, 1994; Murdoch and Stoddard, 1992; Lepisto, 1995; Galloway et al., 1995], as it may have serious consequences for water quality and may contribute to the eutrophication of lakes and coastal waters [Carlsson et al., 1993; Lajtha et al., 1995;

Asman and Larsen, 1996]. Extensive areas of eastern North America are being exposed to increased levels of atmospheric N. The majority of this N is probably anthropogenic in origin [Galloway et al., 1984]. Until recently, it was assumed that N was tightly cycling in forests with little or no N export to surface waters. However, chronic atmospheric addition of N to forests has led to hypotheses concerning N saturation of these forests [Aber et al., 1989; Stoddard, 1994], resulting in the disruption of the N cycle and increased N export to surface waters. Since the export of N from forests to surface waters can be significant, it is important to be able to predict the flux of different nitrogenous species and the sources of variation in the magnitude of these fluxes [Lepisto, 1995; Lepisto et al., 1995].

Accurate prediction of N export is made difficult by the diversity of sources of variation in N export. Substantial variation exists in the concentrations of N in surface waters of forest ecosystems [e.g., Nicolson, 1988; Semkin et al., 1984; Creed, 1998]. Obvious sources of variation include a response to environmental change, such as the spatial variability associated with climatic or atmospheric acidic deposition gradients, or the temporal variability associated with drought-flood sequences or escalating atmospheric acidic deposition rates. These sources of variation may have a long-term effect on the concentrations of N in surface waters [Burt et al., 1988; Aber, 1992; Reynolds and Edwards, 1995]. Sources of variation may also be a response to ecological change. Nitrogen inputs through atmospheric deposition generally exceed N outputs,

¹Now at Departments of Plant Sciences and Geography, University of Western Ontario, London, Ontario, Canada.

²Now at Department of Geography, University of North Carolina, Chapel Hill.

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such that catchments act as net sinks for N [Stoddard and Murdoch, 1991; Kahl *et al.*, 1993; Mitchell *et al.*, 1996]. However, as forests mature, there is evidence indicating that forests become net sources of N, concomitant with reduced forest demand for N and enhanced mineralization of soil and litter N [Driscoll and Schaefer, 1989; Stoddard, 1991; Murdoch and Stoddard, 1992; Emmett *et al.*, 1993]. An increase in the export of N, independent of any change in N deposition in the region, reflects a decrease in the capacity of watersheds to retain N [Stoddard, 1991] or to release N by other mechanisms (e.g., denitrification). Disturbances, including harvesting, fire, or other land-use changes [Vitousek and Melillo, 1979; Reynolds and Edwards, 1995] will also enhance the release of N, although some of these increases may be transient [Reynolds and Edwards, 1995].

Prior to being able to predict these environmental and ecological sources of variation, however, we must understand the inherent sources of variation specifically related to the catchment's topographic characteristics. The relationship of catchment topography to the chemical composition of surface waters has been previously considered [e.g., Wolock *et al.*, 1989, 1990; Robson and Neal, 1991]. The chemistry of surface waters reflects the topographically influenced hydrological flowpaths traversed within the catchment from which the water originated. For example, similar catchments receiving the same amount of atmospheric acidic deposition have been observed to vary significantly in the acidity of their surface waters, due to different hydrological flowpaths of hillslope derived soil solution en route to the stream [Chen *et al.*, 1984; Schofield *et al.*, 1985; Nicolson, 1988].

Recent studies have highlighted the importance of variable source areas in the prediction of the chemical composition of surface waters [e.g., Govindaraju, 1996]. For catchments characterized by variable source area hydrology, subsurface flow is a dominant flowpath in runoff generation as it (1) contributes directly to runoff [Anderson and Burt, 1978] and (2) contributes to saturation overland flow and therefore indirectly to runoff [Freeze, 1974; Burt, 1989; Bonnell, 1993]. Saturation overland flow is the combination of direct precipitation onto saturated areas and return flow [Musgrave and Holtan, 1964] from the saturated areas [Dunne, 1978]. Return flow occurs when infiltrating water causes the water table to rise to the soil surface and to flow over the soil surface to the stream. These saturated areas become contributors of not only water [Betson, 1964; Ragan, 1968; Dunne and Black, 1970a, b] but also of those chemicals accumulated near or at the soil surface to discharge waters [Govindaraju, 1996]. Both field and modeling studies have demonstrated the effects of topography on variable source area dynamics [Dunne and Black, 1970a, b; Dunne *et al.*, 1975; Anderson and Burt, 1978; Beven, 1978; Beven and Kirkby, 1979; O'Loughlin, 1981]. For example, catchments dominated by steep, convex slopes will have smaller, less variable source areas than catchments dominated by gentle, concave slopes [Dunne, 1978].

Of particular interest in this study are topographic effects on variable source area hydrology [Hewlett and Hibbert, 1967; Freeze, 1972; Anderson and Burt, 1978; Dunne, 1978; Beven and Kirby, 1979]. In this paper, the potential importance of topography on N export mechanisms in catchments characterized by variable source area hydrology within the Turkey Lakes Watershed, central Ontario, Canada, is considered. The Turkey Lakes Watershed, a long-term monitoring site operated by Forestry Canada and Environment Canada in the Algoma

Highlands of central Ontario, is ideally suited for this study, since the potential sources of variation in N export are comparatively few. The watershed contains a forest in a stable stage of development, so that variations in forest physiological processes are due to environmental rather than developmental conditions. The forest is dominated by a single species with a constant genotype and the forest is not disturbed by harvesting practices. The catchments receive uniform amounts of N through atmospheric deposition; yet the catchments export variable amounts of DIN and DON [Nicolson, 1988; Creed, 1998]. This set of catchment conditions provides a unique opportunity to focus on topographic effects on the export of N.

The objectives of this research are (1) to determine if a common mechanism for N export exists among the catchments, (2) to identify the catchment properties that regulate this mechanism, and (3) to determine if variations in these catchment properties contribute to the observed variation in N-export. In this paper, empirical data are evaluated to determine if evidence exists for the hypothesized N flushing mechanism [Creed *et al.*, 1996] and if this mechanism is a significant source of the natural variation in N export among the catchments of the Turkey Lakes Watershed. In a future paper (I. F. Creed *et al.*, manuscript in preparation, 1998), we will explore the catchment properties that regulate the N flushing mechanism.

2. Test Area

The Turkey Lakes Watershed (TLW) is located in the Algoma Highlands of central Ontario, Canada (Figure 1). This Canadian Shield watershed (10.5 km²) contains a chain of lakes fed by small headwater catchments that ultimately drain into Batchawana Bay on the eastern shoreline of Lake Superior.

The climate is continental and strongly influenced by the proximity of Lake Superior. The topography is controlled by bedrock with 400 m of relief from the watershed's outlet (at 244-m a.s.l.) to its summit at Batchawana Mountain (at 644-m a.s.l.). A set of major faults control the higher order drainage patterns [Jeffries and Semkin, 1982]. The bedrock is composed of generally insoluble, mafic metavolcanic rock ranging from andesite to basalt, with granite present near the summit of Batchawana Mountain [Giblin and Leahy, 1977]. Overlying the bedrock is a thin and discontinuous till, ranging in depth from <1 m at higher elevations (with infrequent surface exposure of bedrock) to 1–2-m at lower elevations [Jeffries and Semkin, 1982]. Till deposits up to 65 m deep occasionally occur in local bedrock depressions and/or along bedrock fault lines [Elliot, 1985]. Soil maps indicate that Orthic Ferro-Humic and Humo-Ferric podzols have developed within the tills, with dispersed pockets of highly humified organic deposits (Ferric Humisols) found at all elevations in bedrock-controlled depressions and adjacent to streams and lakes [Canada Soil Survey Committee, 1978; Cowell and Wickware, 1983]. However, field inspection indicates that the soils follow a catenary sequence of regosols, brunisols, podzols, and organics from the ridge to the stream. In general, soils, if present, are thin and undifferentiated near the ridge, gradually thickening, differentiating, and perhaps increasing in organic content on topographic benches and toward the stream.

The landscape is completely covered by an uneven-aged (120–180 years) mature forest composed of 90% sugar maple (*Acer saccharum* Marsh.), 7% yellow birch (*Betula alleghaniensis*

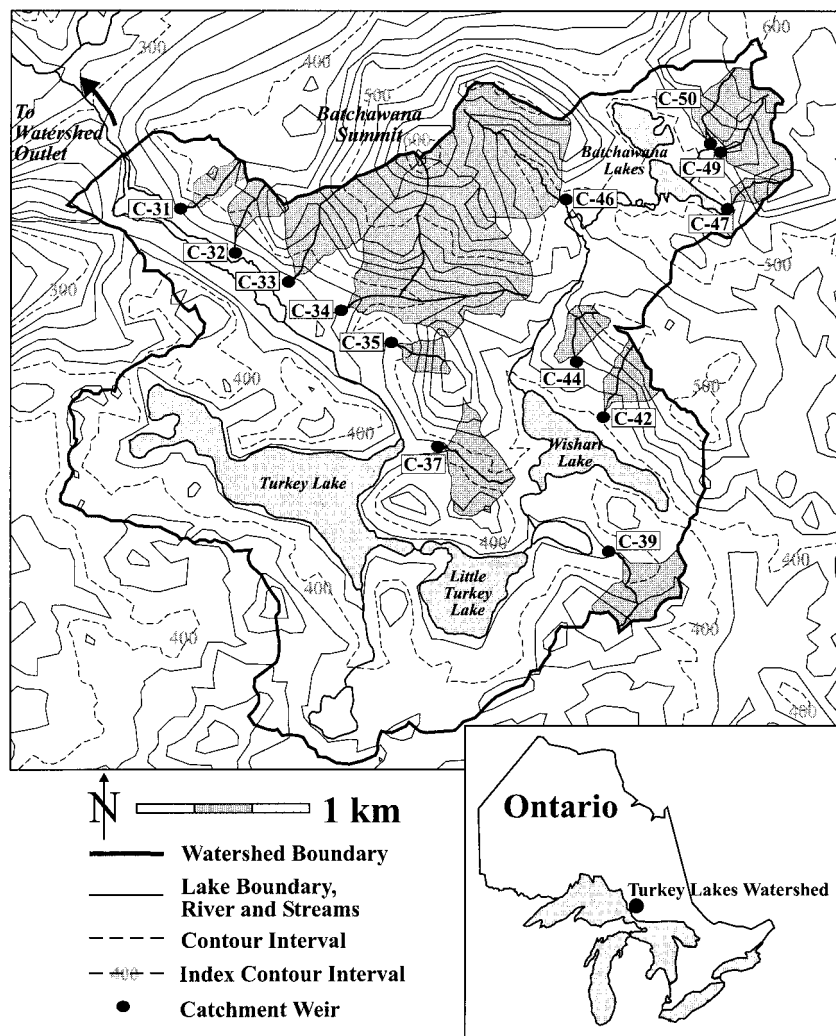


Figure 1. Location of the Turkey Lakes Watershed (centered at 47°03'00"N and 84°25'00"W). The analyses presented in this paper focuses on the continuously gauged catchments (c31 to c50) which represent the range in topographic conditions within this region.

sis Britton), and other minor species (including red maple, *Acer rubrum* L.; ironwood, *Ostrya virginiana* (Mill.) K. Koch; and white spruce, *Picea glauca* (Moench) Voss.) [Wickware and Cowell, 1983, 1985]. With the exception of a light harvest of yellow birch (~35 years ago), the watershed remains essentially undisturbed. The growing season is about 175 days, roughly late April through mid-October. Leaf flushing generally occurs in late May and leaf fall occurs from late September to early October. The dominant sugar maple trees are generally shorter and poorer quality at higher elevations (>460 m a.s.l.), indicating a combination of climatic and nutrient stresses at some topographic positions within the landscape [Nicolson, 1988].

Since the autumn of 1980, the TLW has served as a continuous monitoring site for the study of the biogeochemistry of land and lake systems. Through this monitoring effort, a network of strategically located sampling stations within the watershed was established. Data collected from the sampling stations were selected to examine sources of variation in the export of N (Figure 1). The period 1981–1990 forms the basis of this study.

3. Methods

A full description of the methods used in determining N budgets has been described in a previous paper [Creed, 1998]. This paper focuses on methods for computing the concentrations and fluxes of N in discharge waters. For each catchment, discharge and the concentrations and fluxes of DIN and DON in discharge were measured. Total daily discharges were derived from continuously monitored stream gauge stations equipped with a 90° or 120° V-notch weir on the catchments. Missing data (usually small winter discharges) were estimated by linear regression with an adjacent catchment for which there was a complete record [Nicolson, 1988].

The concentrations of total N, DIN, and DON were determined from stream water samples collected every 2 weeks during the winter, daily during spring snowmelt, and weekly or every 2 weeks during the summer and autumn. Samples were collected at the same sampling point, in the center of the stream, during each visit. From each sample, particulate matter was removed by filtering the sample through a Whatman no. 41 filter that had been rinsed with distilled water. For the deter-

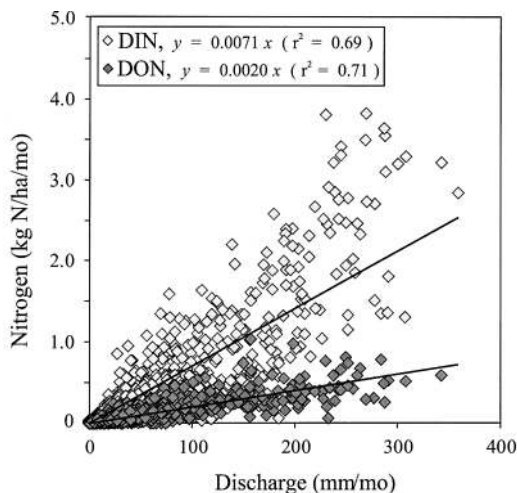


Figure 2. Regressions describing the linear relationship of the catchment flux of DIN ($\text{kg N ha}^{-1} \text{ month}^{-1}$) and DON ($\text{kg N ha}^{-1} \text{ month}^{-1}$) as a function of discharge (millimeters per month) based on data collected for all catchments during the period from 1981 to 1990.

mination of the concentration of DIN in mg L^{-1} , a 100-mL subsample was filtered through a $0.45\text{-}\mu\text{m}$ millipore membrane filter that had been washed with distilled water and stored without preservative at 2°C in glass containers that had been washed with acid-water ($0.1 \text{ N H}_2\text{SO}_4$) and rinsed with distilled water. All samples were analyzed within 48 hours of collection for $\text{NO}_3^- \text{-N}$ (cadmium reduction procedure) and $\text{NH}_4^+ \text{-N}$ (indophenol blue procedure) using a Technicon AutoAnalyzer II-C+. Total DIN was calculated by the addition of the concentration of the $\text{NO}_3^- \text{-N}$ and $\text{NH}_4^+ \text{-N}$ species. For the determination of the concentration of DON in mg L^{-1} , a 100-mL subsample was preserved with the addition of 1 mL 30% H_2SO_4 per 100 mL and stored at 2°C in glass containers that had been washed with acid-water ($0.1 \text{ N H}_2\text{SO}_4$) and rinsed with distilled water. These subsamples were analyzed within 48 hours of collection for total N (Kjeldahl procedure), which represents the sum of organic N-containing compounds, plus residual inorganic $\text{NH}_4^+ \text{-N}$. DON was calculated by the difference between the concentration of total N and $\text{NH}_4^+ \text{-N}$ in the sample.

We studied patterns of N export from the catchment by two methods: (1) N measured as a mass flux and (2) N measured as a concentration. Consideration of the mass flux of N from the catchment provides an indication of the mass export of N from the catchment. The monthly fluxes ($\text{kg ha}^{-1} \text{ mo}^{-1}$) of the N species were calculated as the monthly sum of the products of the total weekly discharge and the average weekly concentrations of N in the discharge. Total weekly discharges were obtained by accumulating the daily measurements for 7-day periods. Average weekly concentrations of the N species in the discharge were obtained by (1) averaging the daily measurements for weeks with multiple sampling dates and (2) averaging adjacent weeks for weeks with no sampling dates. Similarly, the seasonal and annual fluxes were calculated as the sum of the appropriate monthly fluxes. In contrast to mass flux, consideration of the variations in the concentrations and speciation of N in catchment discharge waters provides insights to the extent of microbial processing of N within the catchment and into the mechanism of release of N from the catchment. The monthly volume-weighted average concentrations (mg N/L) of

the N species were calculated as the monthly sum of the products of the concentration of N (c_i) and the total daily discharge (q_i) divided by the monthly sum of the total daily discharge (q) (i.e., $(\sum c_i q_i)/q$).

4. Results

4.1. N-Export Relationships

To explore the natural variation in N export from catchments within the Turkey Lakes Watershed, N flux-discharge and N concentration-discharge relationships were examined.

4.1.1. Flux-discharge relationships. Discharge (millimeters per month) was a strong predictor of the flux ($\text{kg N ha}^{-1} \text{ month}^{-1}$) of DIN and DON in the discharge waters of the catchments (Figure 2). The input flux of TDN occurred uniformly over the year but the output flux of DIN and DON occurring during the spring melt period (March–May) and a secondary peak occurring during the autumn storm period (September–November), these periods coinciding with the dominant hydrological activity within the year [Creed, 1998]. Significant relationships were observed between discharge and the flux of DIN and DON for each catchment (Table 1) and for the average of the catchments (Table 1, Figure 2). However, an analysis of the residuals between the catchment-specific and the catchment-average responses indicated that there was a broad range in the rate of N export among the catchments. For DIN, three catchments had significant residuals from the catchment-average rate of N export. Catchment c33 had a 50% higher rate of DIN export and c37 and c50 had a 50% lower rate of DIN export than predicted from the catchment-average response (Figure 3). Therefore, while discharge was a strong predictor, there appeared to be other catchment-specific mitigating factors that controlled the output flux of DIN. This is in contrast with the prediction of the output flux of DON, which showed less deviation from the catchment average (-25% to $+25\%$ from the catchment average, Figure 3) and could be modeled by catchment discharge with a more reasonable degree of confidence.

Table 1. Summary Statistics for Catchment-Specific and -Average Regressions Describing the Linear Increase in the Export of DIN and DON as a Function of Discharge

Code	DIN		DON	
	Regression Coefficient	r^2	Regression Coefficient	r^2
c31	0.0081	0.82	0.0024	0.66
c32	0.0085	0.81	0.0017	0.60
c33	0.0111	0.81	0.0019	0.70
c34	0.0093	0.81	0.0019	0.66
c35	0.0087	0.83	0.0018	0.68
c37	0.0036	0.77	0.0025	0.83
c39	0.0077	0.84	0.0020	0.86
c42	0.0062	0.78	0.0021	0.88
c44	0.0080	0.70	0.0021	0.72
c46	0.0065	0.70	0.0018	0.71
c47	0.0063	0.72	0.0015	0.59
c49	0.0059	0.69	0.0018	0.76
c50	0.0039	0.61	0.0024	0.73
Catchment average	0.007		0.002	

DIN and DON export in $\text{kg ha}^{-1} \text{ month}^{-1}$ and discharge in millimeters per month.

4.1.2. Concentration-discharge relationships. In contrast to the estimation of the flux of N from catchments, discharge was not a strong predictor of the concentration of DIN or DON in the discharge waters of the catchments. No significant relationship was observed between monthly discharge and monthly discharge-weighted average concentration of DIN or DON (Figure 4). One explanation for why significant concentration-discharge relationships were not observed is because the monthly data are composites of discrete hydrologic events. In any given hydrologic event, the concentration-discharge relationship may be significant, but shifted in its regression coefficient from the hydrologic event that occurred before or after because of the changing nature of the conditions within the catchments. Therefore, data taken from several hydrologic events may result in concentration-discharge relationships that are obscured by the change in the regression coefficient from one hydrologic event to the next. It may be because of the hypothesized flushing mechanism described below that no concentration-discharge relationship can be detected when combining data from multiple hydrologic events. Other studies have reported significant correlation between NO_3^- -N concentration and discharge; however, these relationships were variable, both negative [Arheimer *et al.*, 1996] and positive [Burt *et al.*, 1988], and the explained variances were small.

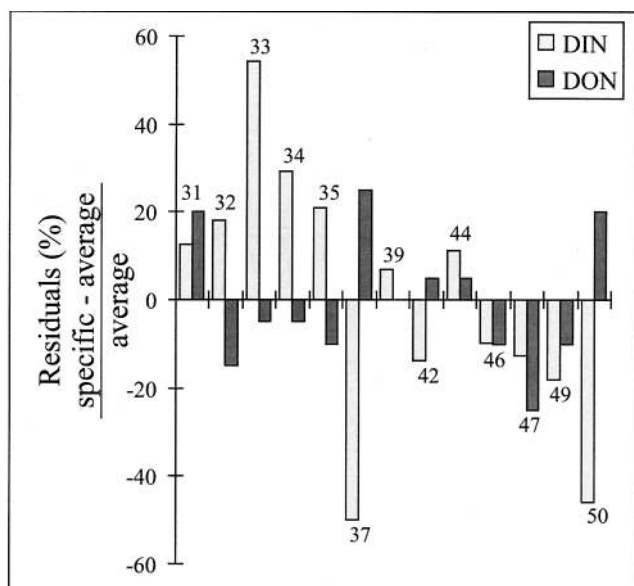


Figure 3. Residuals of catchment-specific versus catchment-average N flux-discharge relationships. Residuals (in percent) are based on the normalized difference between catchment-specific values versus catchment-average values (refer to Table 1). Positive residuals indicate the catchment has greater N export than the catchment-average response. Negative residuals indicate the catchment has lesser N export than the catchment-average response. There appears to be a geographic pattern to the residuals, with export that is less than the average occurring in the higher elevation catchments and more than the average occurring in the lower elevation catchments. Elevation influences the precipitation regime within the watershed, with less precipitation occurring at low elevation sites. However, while elevation introduces variations of the order of 15% in precipitation, variations of the order of 100% in N export are observed, indicating that some other variable has an overriding influence on N export.

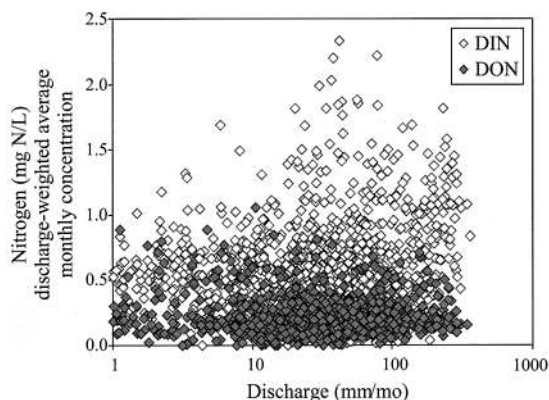


Figure 4. Relationship of discharge-weighted average monthly concentration of DIN (mg N L^{-1}) and DON (mg N L^{-1}) as a function of monthly discharge (millimeters per month).

A monthly time series of discharge and discharge-weighted average concentrations of NO_3^- -N (Figure 5), the dominant form of DIN, and DON (Figure 6) are presented for each catchment. In the case of the concentrations of NO_3^- -N, peak concentrations in the discharge waters occurred just prior to the peak spring hydrologic activity (i.e., snowmelt). For each catchment, the peak concentration of NO_3^- -N occurred in March, on the ascending limb of the discharge hydrograph, while the peak discharge occurred in April. Since this temporal pattern was found in each of the catchments, a unifying mechanism of NO_3^- -N export was suggested. Even with a unifying mechanism of DIN export, variations or differences existed among the catchments. For example, the spring peak in the concentration of NO_3^- -N was catchment-specific and ranged from 0.5 mg L^{-1} (for c37) to 1.6 mg L^{-1} (for c33). In addition, although the summer was generally the period with the smallest concentrations of NO_3^- -N, the concentrations were highly variable among the catchments, ranging from close to the limits of detection (approximately $<0.1 \text{ mg L}^{-1}$) of our procedures for c50 up to 1 mg L^{-1} for some of the other catchments. While in other streams, differences in summer base flow concentrations of NO_3^- -N are interpreted as differences in the phases of N saturation as per Stoddard [1994], this interpretation would clearly be inappropriate for the streams of the Turkey Lakes Watershed.

In contrast to NO_3^- -N, the concentrations of DON in the discharge waters were more uniform over the year, regardless of the hydrological activity (Figure 6). Although the catchment discharge waters showed seasonality in the flux of DON [Creed, 1998], there was no seasonality in the concentrations of DON. There was no indication of an increase in concentrations following the small discharge period of the winter and prior to the large discharge period of the spring and there was no reduction in concentrations during the summer months. The average concentrations of DON ranged from 0 to 0.5 mg N L^{-1} and the variability of concentrations of DON within each month appeared to be greater than the variability in the concentrations of NO_3^- -N (based on range in standard errors), particularly in the summer season.

4.2. Sources of Residuals in N-Export Relationships

To gain insights into the potential sources of the observed residuals in the N flux-discharge relationship (Figure 3), we

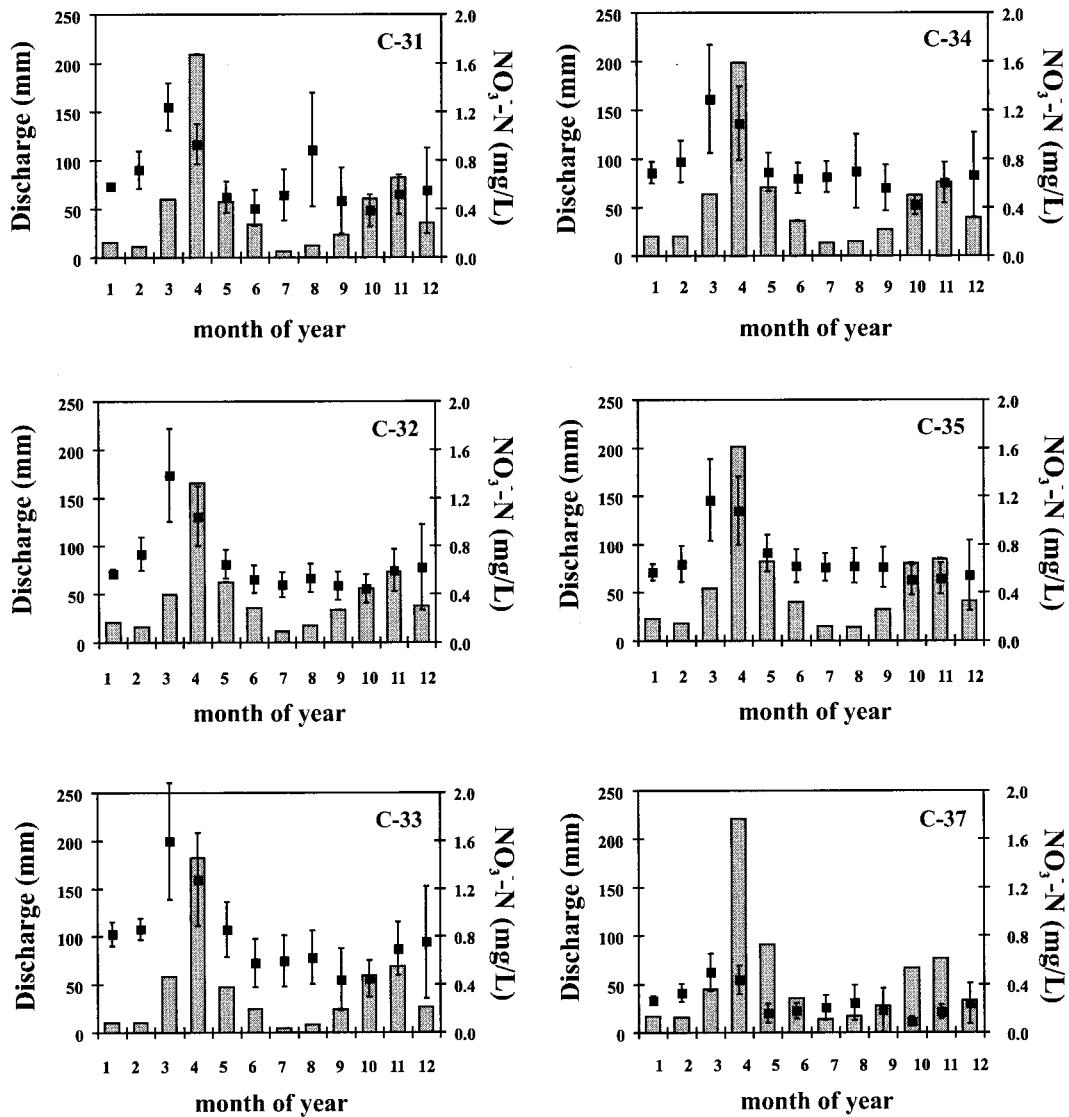


Figure 5. Monthly time series of discharge (bar, millimeters per month) and the discharge-weighted average concentration of DIN (point, $\text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N}$) (mg N l^{-1}) in the discharge. The peak concentration of DIN occurs prior to the peak discharge.

focused on $\text{NO}_3^- \text{-N}$ export dynamics. During the spring discharge period (the period for which data were collected on a daily basis), the $\text{NO}_3^- \text{-N}$ concentration-discharge relationship was characterized by a hysteresis; at equivalent discharge volumes, the $\text{NO}_3^- \text{-N}$ concentrations were larger on the rising limb of the discharge hydrograph than on the receding limb (Figure 7), indicating that the supply of $\text{NO}_3^- \text{-N}$ accumulated near or at the soil surface was quickly depleted in response to the discharge hydrograph. A time series of discharge and the concentration of $\text{NO}_3^- \text{-N}$ in discharge highlights the export behavior of $\text{NO}_3^- \text{-N}$ from the catchments. Before the spring discharge hydrograph, baseline concentrations of $\text{NO}_3^- \text{-N}$ were recorded. On the rising limb of the discharge hydrograph, there was a rapid increase in the concentration of $\text{NO}_3^- \text{-N}$, followed by an exponential decline as the discharge event proceeded (Figure 8). The exponential decline in the concentration of $\text{NO}_3^- \text{-N}$ during the discharge periods can be described by

$$N_t = N_0 e^{-kt} \quad (1)$$

- N_t concentration of $\text{NO}_3^- \text{-N}$ in the discharge waters at time = t , in mg L^{-1} .
- N_0 concentration of $\text{NO}_3^- \text{-N}$ in the discharge waters at $t = 0$, the time that peak concentration of $\text{NO}_3^- \text{-N}$ is observed, in mg L^{-1} .
- t time, in days.
- k constant proportionality factor, 1 day^{-1} .

The export behavior of $\text{NO}_3^- \text{-N}$ was not restricted to the spring discharge period, since a similar exponential decline in $\text{NO}_3^- \text{-N}$ concentrations occurred during both summer and autumn discharge periods. This observation has particular relevance, since it indicates that the export behavior of $\text{NO}_3^- \text{-N}$ during the spring discharge period was not a sole function of snowpack N or whatever mechanisms control snowmelt N; the same behavior is depicted during the nonsnowpack period.

Even though the catchments showed similarity in the export behavior of $\text{NO}_3^- \text{-N}$, variation in this behavior was present and may provide the foundation for explaining the observed resid-

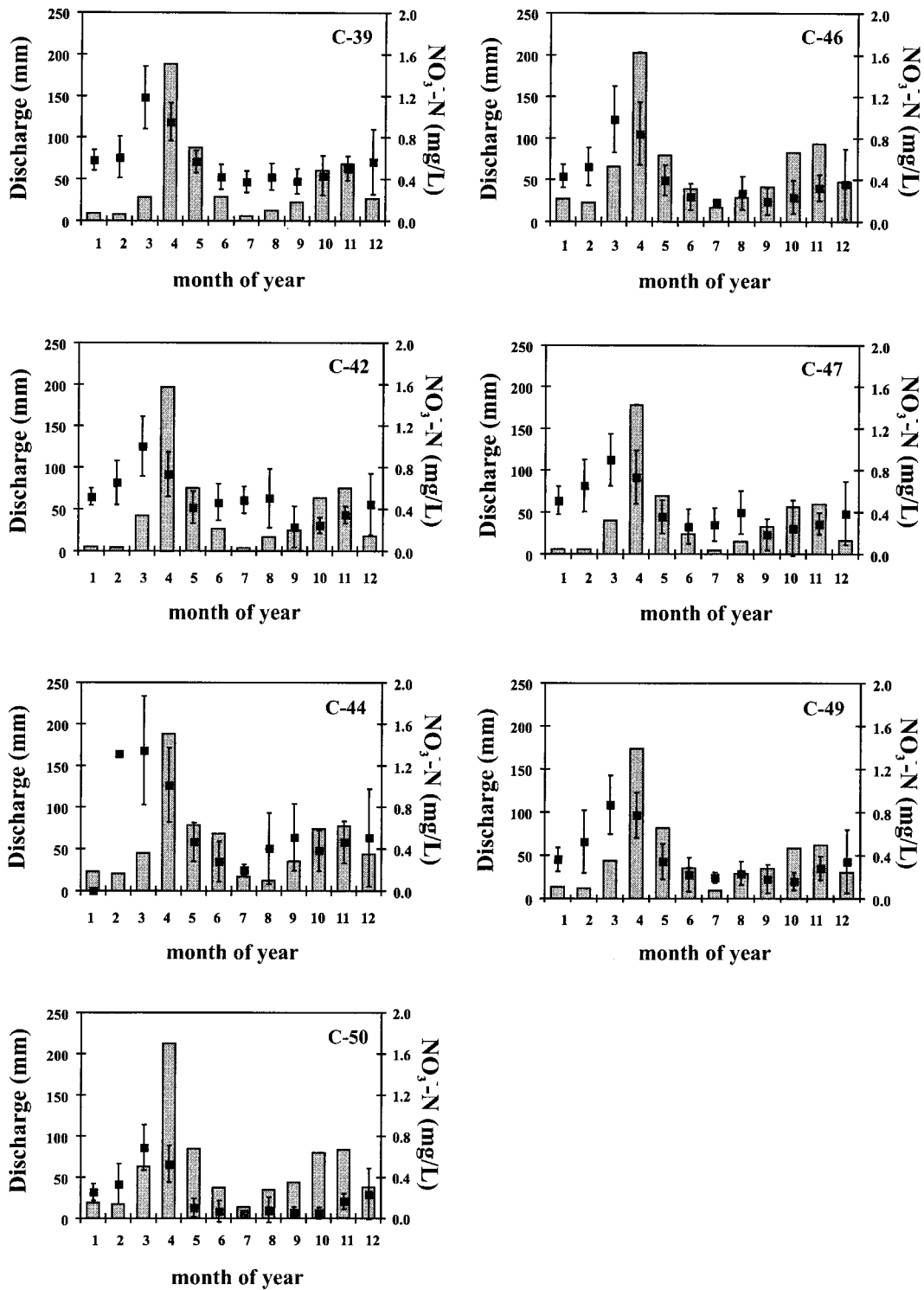


Figure 5. (continued)

uals in the catchment-average rate of N export. Specifically, variation was found in the characteristic time constants for the exponential decline in NO_3^- -N concentration in the discharge waters of the catchments. A time constant was defined as the time interval that must elapse in order for the concentrations of N in the discharge waters to decline to e^{-1} (37%) of their initial concentration:

$$N_0 e^{-1} = N_0 e^{-k t_e} \quad \text{or} \quad t_e = 1/k \quad (2)$$

where t_e is the time for concentration of NO_3^- -N to drop to 37% (e^{-1}) of its initial concentration, in days. For each catchment, a characteristic time constant was defined as the 10-year average of the time constants for the spring melt period. For those years in which multiple peaks in NO_3^- -N concentrations occurred during the spring melt period (e.g., the 1983 spring melt period may have had multiple freeze-thaw cycles), the average of multiple peaks were assumed to be representative

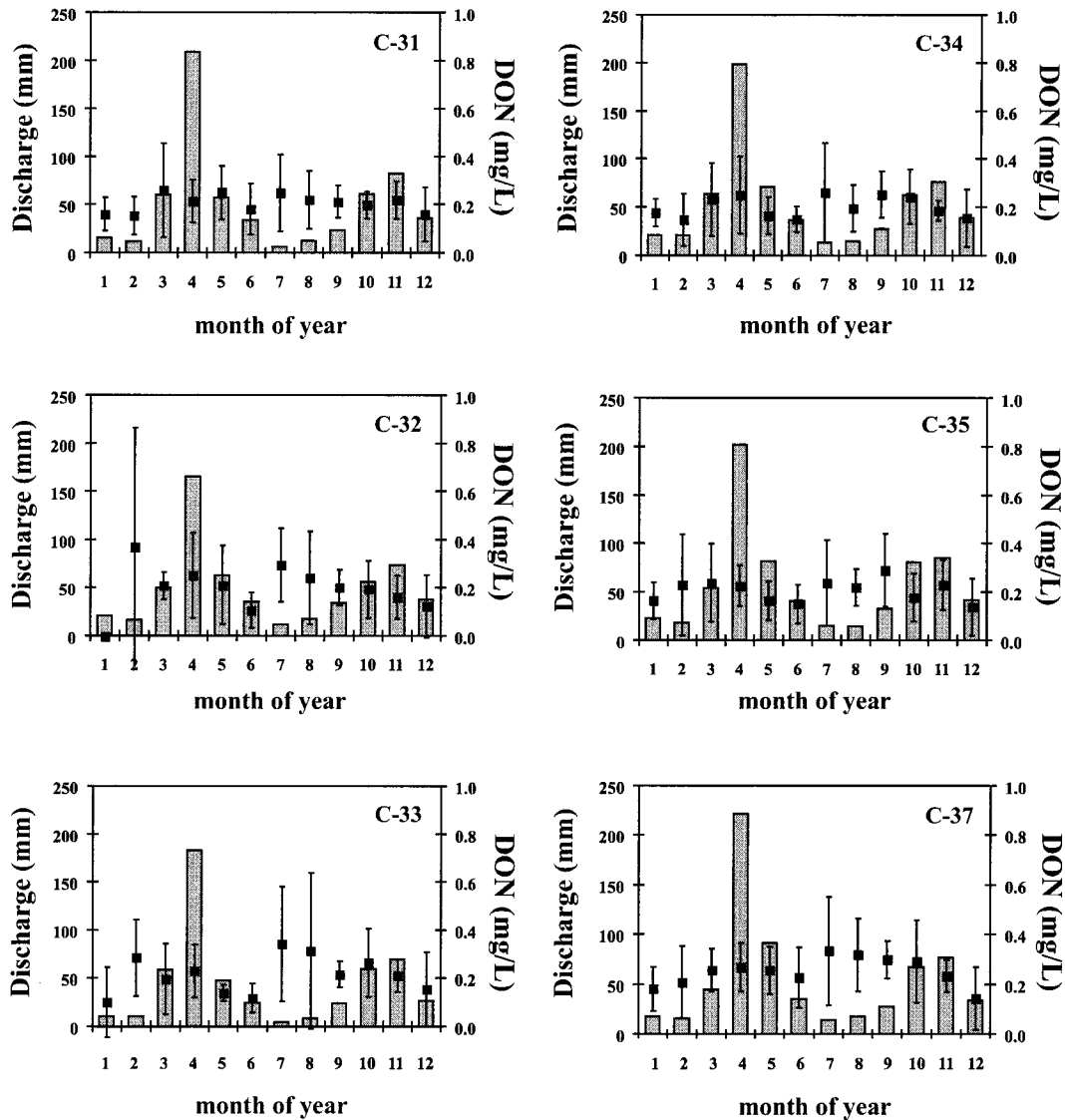


Figure 6. Monthly time series of discharge (bar, millimeters per month) and the discharge-weighted average concentrations of DON (point, mg N/L) in the discharge. In contrast to DIN, the concentrations of DON show no relationship with the discharge hydrograph.

of the time constant for that particular year. Using the average of multiple peaks assumes that the exponential decay is independent of the peak N concentration. It would have been interesting to see if there was a serial correlation to the rates of exponential decay conditional upon the time lapse between peaks and their sequence. However, this was beyond the scope of this study as the occurrence of multiple peaks in the data record was rare.

A summary of the statistics describing the characteristic time constants is presented in Table 2. The catchments' characteristic time constants showed a substantial range. Among the catchments, the time for the concentration of NO_3^- -N in the discharge waters to be reduced to 37% of its initial concentration ranged from 13 to 72 days. Even catchments that were situated next to each other (Figure 1) showed substantial differences in their characteristic time constants (e.g., c33 versus c34; c49 versus c50) (Table 2).

A strong relationship exists between the characteristic time constant and the observed residuals in the catchment average

discharge-DIN flux relationship (Figure 9). Catchments with shorter time constants exported less DIN than catchments with longer time constants. The catchment-specific rates of N export that showed the greatest residuals from the catchment-average rate of N export represented the extremes in the characteristic time constants. The shortest time constants were observed for c37 (18 days) and c50 (13 days) and the longest time constant was observed for c33 (72 days).

5. Discussion

The ability to predict, with reasonable precision and accuracy, the export of N from the land to adjacent waters is essential for establishing and reviewing resource management policies. One of the challenges of developing predictive models is the identification and incorporation of significant sources of variation in the export of N. Given the comparatively homogeneous TLW landscape, we anticipated that the rate of N-export from a single catchment would be representative of the

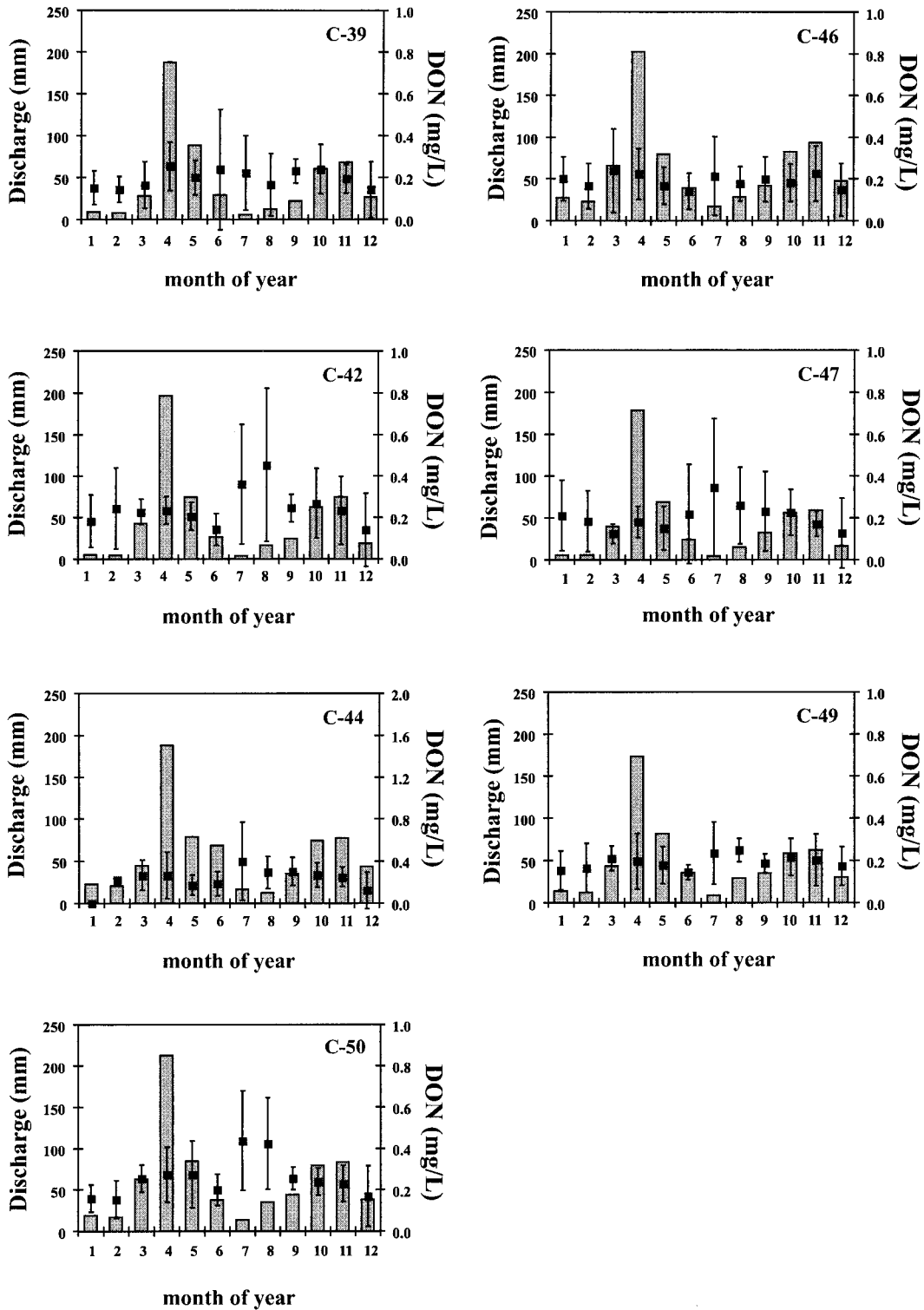


Figure 6. (continued)

landscape. The TLW catchments, however, showed significant variability in their rates of N-export (Table 1, Figure 3). The rates of export of these N compounds from each of the catchments ranged from -50% to $+50\%$ from the catchment-average response for DIN and -25% to $+25\%$ from the catchment-average response for DON. For the TLW catchments, which are regulated by variable source area (VSA) hydrology

[Hewlett and Hibbert, 1967], an explanation of the variation in the export of NO_3^- -N, the dominant form of N in the discharge waters, that is based on VSA dynamics, is presented.

5.1. Flushing Export of NO_3^- -N

A unifying mechanism for export of NO_3^- -N from the catchments was indicated by the observations in this study. A char-

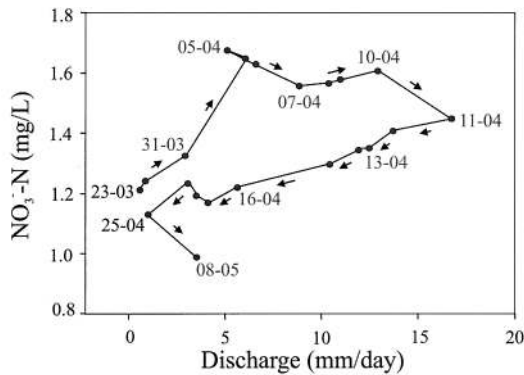


Figure 7. A representative example (c33, 1984) of hysteresis in the concentrations of NO_3^- -N (mg N L^{-1}) over the spring discharge period.

acteristic peak in the concentration of NO_3^- -N in the discharge on the rising limb of discharge hydrographs was observed for both spring melt and autumn storm events for each of the catchments. This characteristic behavior has been termed the “flushing effect” [Edwards, 1973; Walling, 1974; Walling and Foster, 1975]. The flushing effect has been observed for major nutrients, including DOC [Lewis and Grant, 1979; Foster and Grieve, 1982; Fiebig et al., 1990; Baron et al., 1991; Denning et al., 1991; Hornberger et al., 1994; Boyer et al., 1995] and NO_3^- -N [Murdoch and Stoddard, 1992; Stoddard, 1994]. Flushing implies that the export of N is regulated by a saturated throughflow process that is either coupled to the groundwater system (e.g., rising water table) or not coupled to the groundwater system (e.g., rising perched water table). When saturated throughflow is deep below the soil surface, N accumulates in the soil resulting in small export of N into adjacent waters. As saturated throughflow rises, N is flushed from the soil to the stream. As saturated throughflow intersects the soil surface, N formed in the highly bioactive surface of the soil is flushed resulting in large export of N into adjacent waters [Hornberger et al., 1994; Creed et al., 1996].

Saturated throughflow processes that could cause a rise of water to flush N have been observed in field studies [Anderson and Burt, 1982; Bottomley et al., 1984, 1986; Cooke and Dons, 1988]. Anderson and Burt [1982] described a rapid growth of a saturated wedge, as infiltrating water through matrix and/or macropore flowpaths was rapidly transmitted down, deepening and enlarging the wedge, causing an increase in the discharge of saturated throughflow to the stream. As the saturated wedge grows to intersect the N-enriched portion of the soil subsurface and/or surface, N is flushed and discharged to the stream. In the catchments of the Turkey Lakes, Bottomley et al. [1984, 1986] provided evidence to support the rapid growth of a saturated wedge. During melt runoff, the observed peak in N prior to the peak in discharge could have been attributed to the rapid generation of overland flow produced by the melting of a snowpack overlying frozen, impermeable soils [Bottomley et al., 1984]. In this case, the N would have originated exclusively from the preferential elution of N from the snowpack to the first melt waters [e.g., Semkin and Jeffries, 1988] with no flushing of N from the soil to the stream. However, using environmental isotopic evidence, Bottomley et al. [1984, 1986] showed that over 50% of the melt runoff was actually premelt in origin. They concluded that during the melting of a snowpack, melt waters infiltrate rapidly down to the saturated wedge, raise the

saturated wedge, and displace premelt water in storage to the stream. Melt waters could reach the saturated wedge through matrix and/or macropore flows. For matrix flow, melt waters could slowly pass through the N source areas and reach the saturated wedge. Although infiltration of melt waters to the saturated wedge could occur even when soils are frozen [Price and Hendrie, 1983], at the TLW, the soils rarely freeze, and thus do not impede infiltration processes. Gillham [1984] and Abdul and Gillham [1984] have shown that even a small amount of water to the capillary fringe can cause a rapid and disproportionately large rise in the saturated wedge resulting in large discharges of preevent, subsurface water to streams. In contrast, for macropore flows [McDonnell, 1990], melt waters could bypass N source areas within the matrix and rapidly reach the saturated wedge. Observations by McDonnell [1990] and Peters et al. [1995] suggest that macropore flow could be a dominant contributor to the rise in the saturated wedge. For the TLW catchments, as the saturated wedge rises to the soil surface, nutrients, such as NO_3^- -N, that have accumulated near or at the soil surface, will be transported to receiving waters.

It is noteworthy that although we observed a flushing effect for NO_3^- -N (Figure 5, 7, 8), the effect was not observed for DON (Figure 6). In a recent study, Northup et al. [1995] observed that the behaviors of DIN and DON are distinct, since DON strongly adsorbs to soil surfaces, rarely leaches below the rooting zone [Fahey et al., 1985], and is not subject to gaseous loss by denitrification. In contrast to inorganic forms of N, DON is not readily available to most soil organisms and cannot easily be converted to a form that might be lost from the catchment [Northup et al., 1995]. These characteristics support the conclusion that the exports of DIN and DON are either regulated by similar mechanisms but have differential resistance to transport or are not regulated by similar mechanisms.

5.2. VSA Regulation of Flushing Mechanism

With the appearance of a unifying flushing mechanism for the export of NO_3^- -N from the catchments (Figure 5), possible controls on this mechanism were considered. If the flushing export of NO_3^- -N is regulated by the intersection of the rising saturated throughflow with the soil surface mosaic of N-rich (supply NO_3^- -N to the rising waters) and N-poor (do not sup-

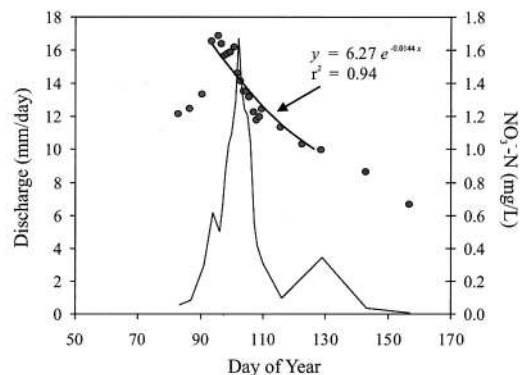


Figure 8. A representative example of a daily time series of discharge (millimeters per day) and the concentration of NO_3^- -N in the discharge (mg N L^{-1}). The peak concentration of NO_3^- -N occurs on the ascending limb of the melt and/or storm hydrograph. On a semilogarithmic plot (not shown), a linear regression describes the exponential decline in concentration of NO_3^- -N over the period of the melt or storm event.

Table 2. Summary Statistics for Regressions From Semilog Plots Describing the Exponential Decline (k) in the Concentrations of NO_3^- -N in the Stream During the Spring Melt Period

Code	k	r^2	Sample Size, number	Time Constant, days	Relative Rate of Flush
c31	-0.023 ± 0.0045	0.92 ± 0.054	17 ± 5.5	46 ± 7.8	long
c32	-0.020 ± 0.0050	0.91 ± 0.053	15 ± 4.7	52 ± 12.2	long
c33	-0.015 ± 0.0031	0.92 ± 0.045	18 ± 5.1	72 ± 14.0	very long
c34	-0.028 ± 0.0092	0.90 ± 0.060	12 ± 5.8	40 ± 13.6	long
c35	-0.027 ± 0.0132	0.88 ± 0.090	12 ± 4.8	45 ± 20.6	long
c37	-0.065 ± 0.0303	0.82 ± 0.139	10 ± 4.9	18 ± 6.9	very short
c39	-0.028 ± 0.0134	0.91 ± 0.090	12 ± 5.8	42 ± 16.6	long
c42	-0.047 ± 0.0220	0.90 ± 0.058	11 ± 6.5	25 ± 8.7	short
c44	-0.036 ± 0.0113	0.95 ± 0.054	12 ± 7.1	30 ± 11.1	moderate
c46	-0.029 ± 0.0063	0.96 ± 0.028	10 ± 3.7	36 ± 7.2	moderate
c47	-0.029 ± 0.0105	0.95 ± 0.043	16 ± 5.7	38 ± 11.7	moderate
c49	-0.035 ± 0.0203	0.93 ± 0.060	13 ± 5.8	34 ± 10.1	moderate
c50	-0.097 ± 0.0431	0.91 ± 0.053	8 ± 4.7	13 ± 7.1	very short

ply NO_3^- -N to the rising waters) areas, then the inherent variation in the rate of NO_3^- -N export from the catchments is related to the extent to which these intersections occur within the catchments. On the basis of this rationale, it is hypothesized that variation in the export of NO_3^- -N is tightly linked to variation in variable source area (VSA) dynamics (representing the intersection of the saturated wedge with N near or at the soil surface) among the catchments.

In a conceptual model of the flushing mechanism, the export of NO_3^- -N is regulated not by the total VSA but by the rate of expansion of the VSA. As a surface saturating event proceeds, the newly saturated annuli of the variable source areas become the dominant sources of the flushing export of NO_3^- -N as these annuli represent areas where saturated throughflow is rising to the soil surface and is flushing N from the soil to the stream for the first time. In other portions of the catchment, either saturated throughflow is rising to the soil surface but the available N has previously been flushed or the saturated throughflow is descending below the soil surface. A catchment's characteristic flushing time (Table 2) is an integration of the time that the rate of change in VSA (i.e., $d\text{VSA}/dt$) is positive, and represents the potential occurrence of the intersection of saturation throughflow with N near or at the soil surface. If the catch-

ment's source area continually expands during a surface saturating event, the intersection with fresh sources of flushable N results in a comparatively long flushing time represented in extended elevated concentrations of N and a comparatively large rate of N export in the catchment's discharge waters. For the TLW catchments, the broad range in the characteristic flushing times (Table 2, Figure 9) reflects extensive differences in the rates of expansion of the VSA, providing a mechanistic explanation for the inherent variations in the export of N from the catchments.

Support for this conceptual model of the flushing mechanism is provided by recent studies on the export characteristics of DOC [Hornberger *et al.*, 1994; Boyer *et al.*, 1995]. In their examination of the distribution of flushing responses within a catchment, Boyer *et al.* [1995] provided evidence that flushable nutrients entered first from proximal contributing areas but that the area extended to distal contributing areas with time as the VSA expanded to contact the less flushed, nutrient-rich upslope areas, resulting in the extended response of large nutrient concentrations in the discharge waters over the course of the surface saturating event.

This conceptualization of the N flushing mechanism assumes that the flushed N is efficiently exported to the stream. In reality, flushed N may meander from surface or shallow subsurface flowpaths to deep subsurface flowpaths en route to the stream. Possible fates of flushed N include (1) loss to denitrification, (2) loss to biological uptake, and (3) loss to deeper subsurface flowpaths that can be considered "transient" (N reappears in stream months later) or "permanent" (N reappears in stream years later) [Cirimo and McDonnell, 1997].

In temperate forests, the significance of riparian areas as NO_3^- -N removal processes and therefore as barriers to the efficient export of NO_3^- -N to the stream, particularly during the main hydrologically active periods in the spring and autumn, has been well documented [e.g., Groffman and Tiedje, 1989a, b, Groffman *et al.*, 1993; Jordan *et al.*, 1993; Schipper *et al.*, 1993; Pinay *et al.*, 1993, 1995; Cirimo and McDonnell, 1997]. Groffman and Tiedje [1989a] observed that rates of denitrification during brief periods in the spring and autumn exceeded $0.5 \text{ kg N ha d}^{-1}$, with annual N removal to denitrification on an annual basis ranging from $<1 \text{ kg N ha yr}^{-1}$ in well-drained sandy soils to over $40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in poorly drained clay loam soils. Transient [Owens *et al.*, 1991; Burns *et al.*, 1993] and

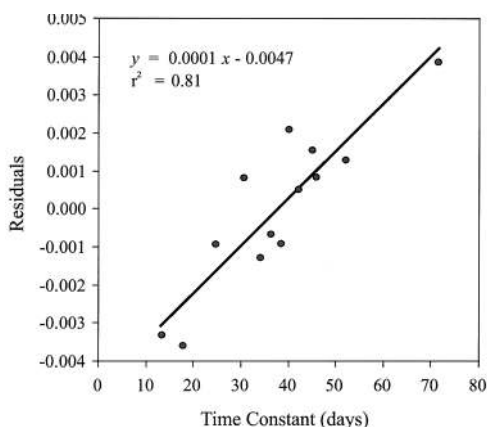


Figure 9. Relationship between the catchment's characteristic time constant and the residuals of the catchment-specific versus catchment-average DIN flux-discharge relationships (refer to Table 1 or Figure 3).

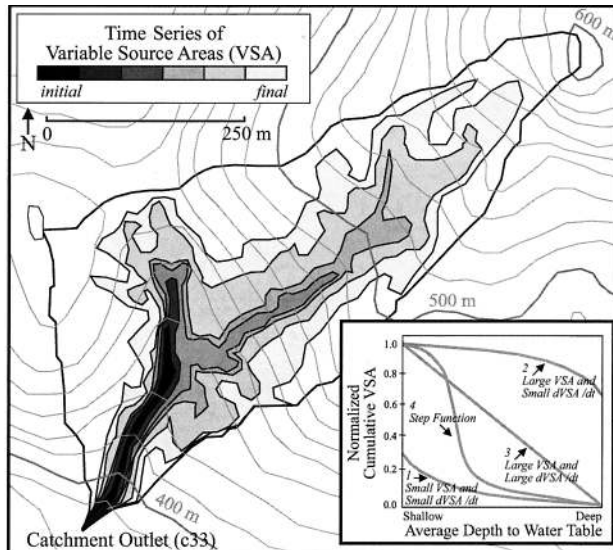


Figure 10. Conceptual diagram of topographic regulation of the catchment's characteristic flushing time. The flushing time is a function of the rate of expansion of the contributing source areas ($dVSA/dt$). The VSA time series is based on the catenary index, $\ln(a/\tan\beta)$, frequency distribution for the catchment. For catchment c33, the black area indicates the VSA at the beginning of the hydrologic event and the progressively lighter gray areas indicates the newly saturated annuli of the saturated areas as the hydrologic event proceeds. The inset graph depicts $dVSA/dt$ for idealized catchments. Curve 1 represents a steep, convex catchment (small VSA, small $dVSA/dt$). Curve 2 represents a gentle, concave catchment dominated by a permanently saturated area (large VSA, small $dVSA/dt$). In both of these idealized catchments, the rate of change in the area of saturation is small. Curve 3 represents a gentle, concave catchment where $dVSA/dt$ is consistent and large. Curve 4 represents a flat, planar catchment where $dVSA/dt$ is inconsistent, with a relatively small $dVSA/dt$ followed by the occasional occurrence of a relatively large $dVSA/dt$.

permanent [Galloway, 1995] losses of N to deeper subsurface flowpaths along bedrock fractures may also be significant [Cirimo and McDonnell, 1997].

However, if the conceptual model is valid, the observed extended response of large concentrations of N in the catchment's discharge waters (Figures 5 and 9) suggests that a significant portion of the flushed N traverses over the saturated areas, avoiding these areas of NO_3^- -N consumption. Recent studies provide insights into how flushed N can bypass potential N denitrifying environments [Cirimo and McDonnell, 1997]. In one example, flushed N could have bypassed denitrifying conditions by flowing over them. In his annual groundwater budget for N for a groundwater discharge swamp located adjacent to a stream in a headwater catchment, Hill [1991] observed that the NO_3^- -N inputs to and outputs from the swamp were equal ($\sim 9.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and that the majority (90%) of the NO_3^- -N input to the swamp was contributed by shallow subsurface flowpaths, emerging along the distal footslope of the swamp, and transported along rivulets over the surface of the swamp to the stream, bypassing the potentially denitrifying conditions of the swamp. In another example, flushed N could have bypassed denitrifying conditions by flowing underneath them [Fitzgerald, 1997]. Therefore, although N removal processes may be important, N bypass mechanisms exist so that N

flushed from the newly saturated annuli of the VSA can be efficiently exported to the stream.

5.3. Is Topography the Key?

Catchment topography may play an important role in determining the inherent variability in the export of NO_3^- -N among the catchments. Topography regulates the N flushing mechanism through its effect on the flushing potential represented in the integration of the time that the rate of change in the VSA, $dVSA/dt$, is positive. On the basis of the VSA concept, the source areas of runoff generation do not develop as a plane over the surface of the catchment but increase gradually in extent in accordance with the complexity of the surface of the catchment [Govindaraju, 1996]. The importance of topography in regulating the expansion and contraction dynamics of the source areas has been recognized in field studies [e.g., Dunne and Black, 1970a, b; Dunne et al., 1975; Anderson and Burt, 1978; Beven, 1978] and modeling studies [Beven and Kirby, 1979; O'Loughlin, 1981, 1986]. These studies conclude that catchment topography will determine the rate of lateral expansion of the source areas within a catchment.

For the export dynamics of NO_3^- -N, the VSA concept is extended to include the introduction of NO_3^- -N in runoff. Catchments with greater lateral expansion of source areas ($>dVSA/dt$) will have longer flushing times and higher rates of NO_3^- -N export while catchments with lesser rates of lateral expansion of source areas ($<dVSA/dt$) will have shorter flushing times and lower rates of NO_3^- -N export. In Figure 10, a conceptual diagram of the effects of a unit increase in the water table (moving from a deep water table to a more shallow water table) on the expansion of source areas in catchments with different topographic properties is presented. In theory, for the extreme cases, catchments dominated by steep, convex slopes would have a consistently low rate of increase of the source area, while catchments with gentle, concave slopes would have a consistently high rate of increase of the source area. These topographic extremes would exhibit differences in the flushing time constants (being the shortest and longest, respectively). In flat, planar slopes, the rate of increase of the source area would be an inconsistent step function. In these slopes, when flushing occurs it would be for very short flushing times, potentially resulting in sharp peaks or pulses of NO_3^- -N export. In reality, the expansion and contraction of source areas will also be influenced by other factors, including geomorphically modified drainage rates (e.g. does the geomorphology facilitate or impede drainage?).

Given the range in the characteristic flushing times of the TLW catchments (Table 2), it is hypothesized that the TLW is comprised of an assemblage of catchments with a significant range in topographic complexity. Compared to the catchment-average response, catchment c33 will show considerable lateral expansion resulting in longer flushing times, while catchments c37 and c50 will show considerably less lateral expansion (and shorter flushing times) over the course of a surface saturating event. The testing of this hypothesis will be the focus of a companion paper, in which relationships between simple indices of the catchments' topographic variability (based on the moments of the catenary index frequency distribution) and the catchment's flushing times will be explored [Creed and Band, 1997].

The catchment's topographic complexity will also regulate the flushing mechanism through its effects on the supply of flushable N. For simplicity, in the preceding discussion, it was assumed that flushable N was available over the entire surface

of the catchment. Previous efforts to characterize the topographic effects on the catchment distribution of the N pool span at least 50 years. These efforts encompass both the spatial distribution of accumulated total N [Aandahl, 1948; Aguilar and Heil, 1988; Huntington et al., 1988; Honeycutt et al., 1990; Giblin et al., 1991; Hairston and Grigal, 1991] and the rates of transformation of the accumulating N, including mineralization and nitrification [Gosz and White, 1986; Zak et al., 1986, 1989; Zak and Pregitzer, 1990; Lensi et al., 1991; Giblin et al., 1991; Zak et al., 1991; Raghubanshi, 1992; Garten, 1993] and denitrification [Bowden, 1986; Groffman and Tiedje, 1989a, b; Lensi et al., 1991; Merrill and Zak, 1992; Groffman et al., 1993a, b; Davidson et al., 1993]. Topographic factors were found to influence the distribution of stored N in the soil of catchments ranging from gentle [Hairston and Grigal, 1991] to moderate [Huntington et al., 1988; Zak et al., 1989; Raghubanshi, 1992; Garten, 1993] to steep [Gosz and White, 1986] relief in tundra, temperate, and tropical biomes. The implication is that the more complex the topography, the more complex the distribution of N-rich versus N-poor areas within the catchment.

In humid, temperate forest catchments, well-drained upland and poorly drained lowland areas may represent NO_3^- -poor areas as the soil conditions may inhibit nitrification (too dry) or promote denitrification (too wet) processes [e.g., Foster, 1989; Foster et al., 1992]. These NO_3^- -poor areas may be N-poor (small stock of N) or N-rich (large stock of N contained in organics or in the B horizon, but this N may exist as DON and may not be flushable). Alternatively, well-drained lowland areas may represent NO_3^- -poor areas due to a greater frequency and/or magnitude of N flushing. In contrast, the dynamic transitional areas characterized as “not-too-dry” and “not-too-wet” may provide conditions that are optimal for the formation of NO_3^- -N-rich areas, through mineralization and nitrification mechanisms, that are self-replenishing when flushing is not active. As saturated throughflow rises into these areas, the NO_3^- -N flushed from these newly saturated annuli would become a significant contributor to the export of NO_3^- -N. The spatiotemporal dynamics of these NO_3^- -rich and -poor areas will be considered in future research.

6. Conclusion

Dissolved inorganic and organic N export from catchments within the Turkey Lakes Watershed in central Ontario is highly variable. Our empirical analysis provided support for a N export mechanism that was common to all of the catchments and that accounted for a significant source of the observed variation in the concentration of NO_3^- -N in discharge waters from the catchments. For NO_3^- -N, N flushing, where N is flushed to surface waters through the intersection of a rising water table with N that has accumulated near or at the surface of the soil, appeared to be an important N export mechanism. A catchment's N flushing response was captured in its flushing time constant; catchments with longer flushing times had higher rates of N-export, while catchments with shorter flushing times had lower rates of N export. In theory, a catchment's N-flushing response is a function of its potential to form variable source areas; with the expansion of source areas, the rising water table taps into the relatively rich sources of NO_3^- -N of the nearly saturated annuli of the source areas and flushes it from the soil to the stream. This implied that among the catchments a significant source of variation in NO_3^- -N export was related to a difference in the potential to form source

areas. In particular, for a given catchment, N flushing may have been regulated not by the source area (A_{VSA}) but by the rate of change of the expanding source area (dA_{VSA}/dt), a rate that would have been regulated by topography. Given the range in the catchments' N-flushing responses, we hypothesized that the Turkey Lakes Watershed contains an assemblage of catchments with a significant range in the potential to form source areas. Specifically, compared to the catchment-average response, catchment c33 is characterized by topography that promotes lateral expansion of source areas resulting in longer flushing times, while catchments c37 and c50 are characterized by topography that inhibits the lateral expansion of source areas resulting in shorter flushing times. The implications of this hypothesis are that for landscapes in which N flushing occurs, an important source of variation in NO_3^- -N export has been identified. For a given landscape, by capturing the topographic properties that regulate variable source area dynamics and therefore flushing dynamics, a means of estimating the potential variation in NO_3^- -N export from catchments is provided. For catchments within a single forest type, topography may be the dominant control on NO_3^- -N export, while for catchments with different forest types, topography may be only one of several controls on NO_3^- -N export. In contrast to NO_3^- -N, variation in the export of DON could not be accounted for by the flushing mechanism, emphasizing the need for further research on catchment controls on DON export.

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L. E. Band, Department of Geography, University of North Carolina, Chapel Hill, NC 27599.

I. F. Creed, Department of Plant Sciences, University of Western Ontario, London, Ontario, Canada N6A 5B7. (icreed@julian.uwo.ca)

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