Topographic controls on the chemistry of subsurface stormflow

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Abstract:

Models are needed that describe how topography and other watershed characteristics affect the chemical composition of runoff waters, yet little spatially distributed data exist to develop such models. A topographically driven flushing mechanism for nitrate (NO_3^-) and dissolved organic carbon has been described in recent literature; however, this mechanism has not yet been thoroughly tested. A 24 ha catchment in the Catskill Mountains of New York was clearcut in the winter of 1996–97, resulting in elevated NO_3^- concentrations in soil water, groundwater and streamflow. We sampled shallow subsurface stormflow (SSSF) and streamflow six times during the spring and summer of 1998, 1 year after the harvest. We used a spatially distributed network of piezometers to investigate the relationship between topography and SSSF chemistry. Several indices of topography were computed, including the commonly employed topographic index of Beven and Kirkby (1979; *Hydrological Sciences Bulletin* **24**: 43–69). Topographic index was positively correlated with NO_3^- concentrations in SSSF. The strength of the NO_3^-–topography relationship was best explained by antecedent soil temperature and antecedent precipitation conditions. Results suggest a topographically driven flushing of high NO_3^- shallow soil at the site during storm events. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Predicting the chemical response of streamwater to perturbations such as climate change and forest harvesting requires a quantification of the processes that affect the spatial distribution of solute concentrations in source water throughout the catchment. Unfortunately, these spatial controls are poorly understood (Bonell, 1998). Elevational gradients largely control hydrologic pathways and surface and subsurface soil moisture distributions, especially in steep, headwater catchments (Hewlett and Hibbert, 1963; Dunne and Black, 1970; Beven and Kirkby, 1979; Siebert *et al*., 1997). Thus, topography, together with other factors, plays an important role in determining the age, origin, pathway and chemistry of soil water and shallow groundwater (Robson *et al*., 1992). These linkages between topography and hydrogeochemistry have been explored in several studies (Hornberger *et al*., 1994; Creed *et al*., 1996; Boyer *et al*., 1997), but much remains to be learned.

Much attention has been given to the response of streams to continued nitrogen (N) loading (Stoddard and Murdoch, 1991; Peterjohn *et al*., 1996; Burns, 1998). However, few studies have investigated the relationships between physical watershed characteristics, such as topography, and shallow groundwater and surface water nitrate (NO_3^-) concentrations and mass fluxes (Creed *et al*., 1996). The movement of water through a catchment not only transports N, but can also affect the evolution and biogeochemical transformations of N along subsurface flowpaths. For example, denitrification rates in the Catskill Mountains were highest in

soils that received inputs from groundwater springs (Ashby *et al*., 1998). These groundwater springs in the Catskill Mountains occur at the convex bench–step interface where there is a distinct change in slope (Burns *et al*., 1998).

Streamwater N dynamics have been related to hydrologic response, suggesting that the subsurface flowpath of water is a major factor determining N (Hill *et al*., 1999). Often, dissolved organic carbon (DOC) and nitrate (NO_3^-) exhibit similar concentration–discharge relationships and flushing responses during storm events (Creed *et al*., 1996; Boyer *et al*., 1997). Hinton *et al*. (1998) found the major source area for DOC during stormflow was near stream riparian and wetland areas at two catchments in Ontario, Canada. The proportion of DOC these areas contributed to the stream was dependent upon the depth to the riparian water table. The flowpath and water table depth are, in part, controlled by topography; however, topographic position was not explicitly considered in these previous studies.

Topographic position has been used to explain the flushing of NO_3^- and DOC from soil in different landscape positions (Hornberger *et al*., 1994; Creed *et al*., 1996; Boyer *et al*., 1997). High rates of biological activity cause solutes to accumulate in the forest floor and shallow soil. Because saturated hydraulic conductivity K_{sat} typically decreases with depth in soils (Beven and Kirkby, 1979), a rising water table intersects an increasingly transmissive shallow soil, and flushes solutes from the shallow soil layer laterally towards the stream (Hornberger *et al*., 1994). Topography has been used to identify areas with a high potential for surface saturation (Beven and Kirkby, 1979), and thus a high potential for flushing solutes. For example, topographic position explained differences in the rate of DOC flushing in an alpine catchment in Colorado (Boyer *et al*., 1997). In that study, riparian soils were flushed more quickly than soils upslope, suggesting that a topographically controlled hydrological transport was responsible for the movement of DOC to the stream.

Creed *et al*. (1996) proposed two hydrologic mechanisms to explain stream NO_3^- dynamics at a catchment in central Ontario. They hypothesized a direct flushing process where the water table rises into a more transmissive shallow soil zone and high NO_3^- water is transported laterally downslope towards the stream. A second mechanism was a draining pathway, where high NO_3^- water was recharged vertically to deep groundwater.

Despite the results of these recent studies, little is known about how different catchment locations contribute solutes to streamflow (Peterjohn *et al*., 1999). Is catchment flushing and draining spatially uniform, or are there certain areas of a catchment that contribute a greater proportion of NO_3^- to stream water? Creed *et al*. (1996) suggested that local 'hotspots' of N accumulation may provide disproportionally large contributions to the overall N discharge to the stream. Our study attempts to identify those 'hotspots' in a Catskill Mountain catchment by combining field-based sampling of shallow groundwater with terrain modelling. We focus on NO_3^- and DOC and address the following questions:

(1) Is there a relationship between topography and shallow subsurface stormflow chemistry?
(2) What factors impact the relationship between topography and shallow subsurface stormflow chemistry?

STUDY AREA

The study area is the Dry Creek catchment, a 24 ha subcatchment within the Neversink River basin in the Catskill Mountains of New York, USA (N41°58′, W74°30′). The Neversink Basin has been the site of numerous studies concerning the processes controlling stream chemistry (Murdoch and Stoddard, 1992; Burns, 1998; Burns *et al*., 1998; Murdoch *et al*., 1998, Brown *et al*., 1999). Recent investigations at the Dry Creek catchment have focused on the manner in which forest harvesting affects N cycling (Burns *et al*., 1997). Elevated NO_3^- and DOC concentrations were found in the catchment as a result of a clearcut conducted in the winter of 1996–97. The forest was harvested in winter to minimize the impact to the soils and stream

channel of the catchment. The upper 6 ha of the catchment was located on land owned by New York State, and was not harvested.

Elevations range from 760 m at the catchment outlet to 890 m at the top of the ridge. The topography is dominated by 'bench–step' formations controlled by the horizontal bedding planes of the underlying bedrock. This 'bench and step' topography is expressed more strongly on the east side of Dry Creek than on the west side (Figure 1). Stoddard and Murdoch (1991) present a detailed discussion of the geology and geomorphology of the area.

Two distinct subsurface flow systems exist in the catchment. First, a deep bedrock flow system with a water residence time of less than 2 years. This system maintains baseflow in the stream, and is discharged from springs located throughout the catchment (Burns *et al*., 1998). These springs most often occur at the convex bench–step interface where there is a distinct change in slope. Small wetlands commonly occupy the
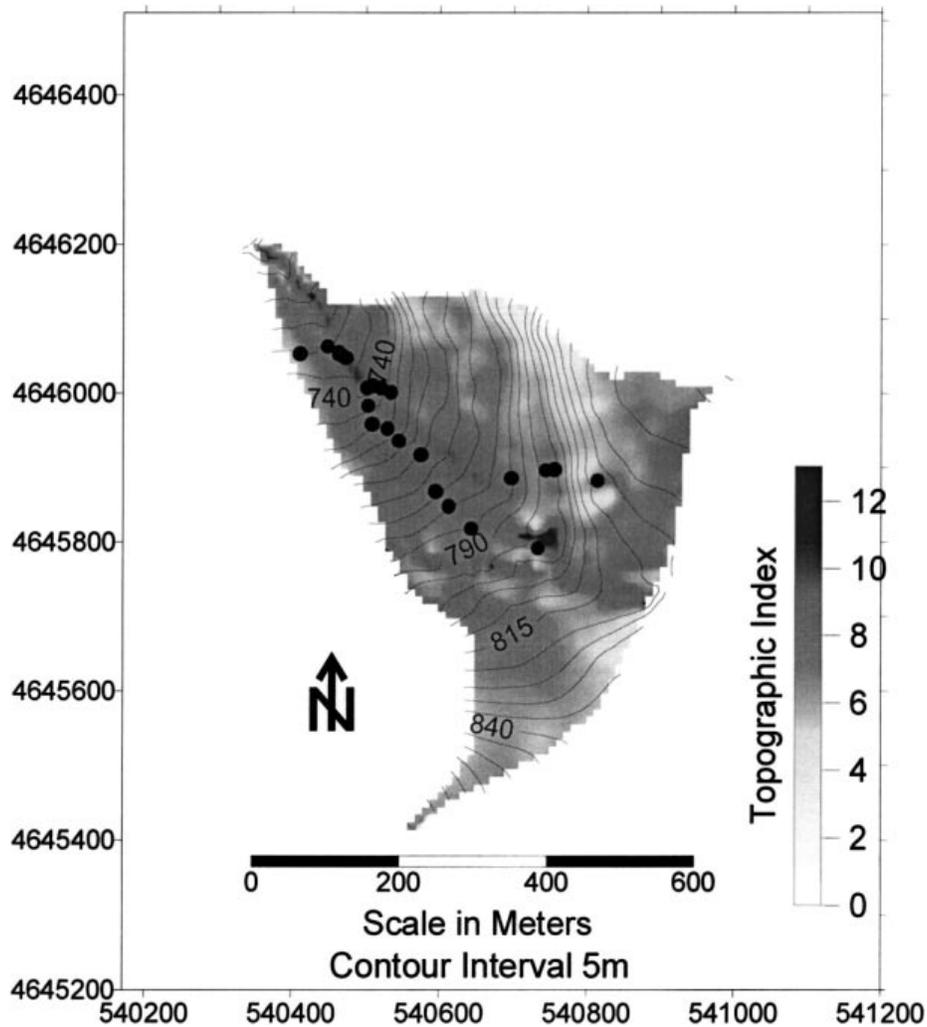

Figure 1. Topographic index map of Dry Creek. Dots represent piezometer locations. Axes are UTM metres

benches where perennial springs discharge. Second, a shallow intermittent flow system above the bedrock–till interface is responsible for the rapid generation of stormflow to the stream (Burns *et al*., 1998; Brown *et al*., 1999). The deep flow system is disconnected from the surface and shallow flow system for much of the hydrologic year (Burns *et al*., 1998). During snowmelt, water recharges the deep flow system through vertical fractures in the sandstone bedrock.

The Dry Creek catchment is drained by a first-order stream with an average annual flow of $4 \, \mathrm{l \, s}^{-1}$ and maximum flow of $113 \, \mathrm{l \, s}^{-1}$ (typically in spring). Summer baseflow in Dry Creek is maintained by discharge from two prominent perennial springs (Burns *et al*., 1998). Soils in the basin are classified as inceptisols in the Arnot–Oquaga–Lackawanna association (Tornes, 1979). The thickness of the soils varies between 0·35 and 1 m, and these soils are excessively to moderately drained, predominantly steep, and medium textured. A fragipan occurs where till is at least 1 m thick. Both soil and till are thicker near the stream and towards the catchment outlet. Catchment soils are underlain by Devonian age coarse sandstone interbedded with shale and siltstone (Way, 1972).

Annual precipitation at the catchment is among the highest in the northeast USA, with mean annual values of 1570 mm at Slide Mountain (elevation 808 m), about 10 km from Dry Creek. Between 20 and 25% of this precipitation falls as snow. Mean annual temperature at Slide Mountain is 3·3 °C (NOAA, 1990).

METHODS

Field

Twenty-one nests of groundwater piezometers (1·9 cm inside diameter PVC pipe) were installed throughout the catchment in the autumn of 1997, encompassing a variety of topographic positions including mid-bench (flat area), mid-slope, shoulder of slope, base of slope, and hollows or depressions (Figure 1). Each nest consisted of a shallow piezometer at between 50 and 70 cm deep, and a deep piezometer installed at a depth between 60 and 100 cm at the till–bedrock interface. Piezometers were installed by driving the piezometer coupled with a steel rod inserted inside, then removing the steel rod. Stream discharge was measured at a V-notch weir with a submersible pressure transducer. Stream samples were taken by hand and also by a stage-activated automatic sampler. Rainfall magnitude and intensity were measured with a weighing rain gauge located at the catchment divide. Soil temperature was monitored by a datalogger every 15 min in the O and B horizons. Soil moisture (via time-domain reflectometry (TDR)) and temperature were measured in the O and B horizons and recorded every 15 min by a datalogger. The calibration of Ledieu *et al*. (1986) was used to determine the volumetric water content of the soil and, therefore, is a relative measurement between points rather than an absolute measurement of volumetric soil water content. Groundwater samples were collected in the field from each piezometer after purging, and each sample was placed in a 500 ml polyethylene bottle. One sample was collected from each piezometer and the stream after each of six storms from March to July 1998.

Catchment topography was mapped with a total station and GPS receiver on approximately a 5 m grid. The portion of the catchment not harvested was not surveyed, and topography for this area was taken from an available 10 m digital elevation model (DEM) compiled by the New York State Department of Environmental Conservation. The combination of the DEM and field survey was tessellated to a 10 m DEM.

Laboratory

All samples were kept chilled at 4 °C until analysed. Samples analysed for DOC were transferred to glass vials with Teflon seals upon returning from the field. Each sample was passed through a 0·7 µm Whatman GF/F filter; samples analysed for NO_3^- were filtered through a 0·4 µm polycarbonate filter and were diluted 10:1 with deionized distilled water. NO_3^- concentrations were determined by ion chromatography and DOC concentrations were determined by persulfate oxidation according to the method described in Lawrence *et al*. (1995).

Modelling

Terrain indices were calculated using the Dry Creek DEM. The standard topographic index (Beven and Kirkby, 1979) was calculated as

$$\text{TI} = \ln\left(\frac{a}{\tan\beta}\right) \qquad (1)$$

where a is the upslope contributing area per unit contour length, and β is the local slope angle. Estimation of the TI was performed using the methodology outlined by Quinn *et al.* (1995). This index incorporates two factors that determine wetness: movement of water due to gravity and the amount of upslope area that contributes lateral flow to a point on the landscape. The result is a theoretical estimation of wetness potential at any point in the catchment (Quinn *et al.*, 1995). The distribution of TI values is presented in Figure 2. Figure 1 shows the spatial distribution of TI across the catchment.

Though local conditions are important, the topography upslope of a specific cell may also impact solute concentrations. It is expected that the concentration of a solute at a point in the catchment is a function of the concentrations of the cells it drains. Two new indices were developed in this study to examine upslope topography. TI1 is the average TI value of all upslope cells, defined as:

$$\text{TI1} = \frac{\sum \text{TI}_i}{n} \qquad (2)$$

where TI_i is the TI value of the ith upslope grid cell, and n is the number of upslope cells. TI2 is a distance-weighted average of all upslope cells, defined as:

$$\text{TI2} = \frac{\sum \dfrac{\text{TI}_i}{d_i}}{\dfrac{1}{d_i}} \qquad (3)$$

where d_i is the horizontal distance from the ith upslope grid cell to the outlet cell.

Analysis

Little difference was seen in the solute concentrations between the deep and shallow piezometers. Therefore, no differentiation is made between these in the analysis. The slope of a linear regression line was calculated
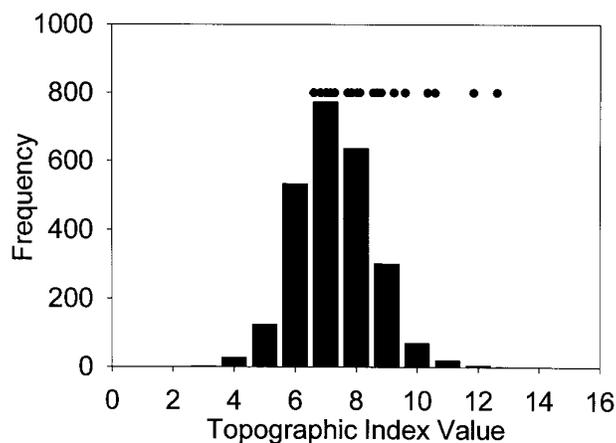

Figure 2. Topographic index distribution of Dry Creek. Dots represent index values of well locations

to determine the strength of the linear relationship between each solute concentration (NO_3^- and DOC) and topographic index (TI, TI1, TI2) according to

$$b = \frac{n\sum xy - \left(\sum x\right)\left(\sum y\right)}{n\sum x^2 - \left(\sum x\right)^2} \tag{4}$$

where n is the number of samples, y is a specific solute concentration, and x is a topographic index value (Devore, 1995). Pearson correlation coefficients were also calculated for each relationship and used as measure of the strength. 95% confidence intervals were calculated for each of the computed indices (Devore, 1995).

The influence of precipitation and temperature on the strength of the chemistry–topographic index relationships was examined. Precipitation was described using three different methods. The first was the sum of all the precipitation that fell in the 5 days prior to sampling, and is denoted as 5 day rain. The second used a 5 day weighted antecedent precipitation index (API) that weights precipitation that fell closer to sampling more heavily than precipitation that fell earlier. The 5 day weighted API is defined as

$$5 \text{ day API} = \frac{\sum \dfrac{p_i}{t_i}}{\sum \dfrac{1}{t_i}} \tag{5}$$

where p_i is the precipitation that fell during the ith hour and t_i is the time from the precipitation to sampling. Precipitation in this index includes that which fell during the storm up until the point of sampling. The third expression of rainfall was the total amount of rain that fell during the storm event, denoted as storm rain. Soil temperature was expressed as the average temperature of the O and B horizons in the 5 days before sampling, and are denoted as temp O and temp B.

RESULTS

Storm, stream, and topography summaries

Storm response. The six storms sampled varied considerably in both rainfall amount, rainfall duration, and antecedent moisture conditions (Table I). Rainfall amounts were between 6·7 mm for the storm sampled on 2 May to 67 mm for the storm on 10 March. Rainfall durations ranged from 8 to 64 h, thus sampling encompassed both short intense events and long events with low intensity. Antecedent moisture conditions, as represented by the 5 day API, ranged from 0·03 on 2 April to 0·94 on 10 March and 1 July. Peak stream discharges ranged from 1·2 l s^{-1} for the 2 May storm to 108 l s^{-1} for the 10 March storm.

Table I. Summary of storm characteristics

Date	Rain amount (mm)	Rain duration (h)	TI range of wells sampled	Time from peak to sample (h)	5 day API (mm h^{-1})	5 day sum (mm)	Temp O (°C)	Temp B (°C)	Peak discharge (l s^{-1})
3-10-98	67·3	34	7·89 to 10·59	12·6	0·94	66·5	−0·16	0·81	108·89
3-20-98	17·8	25	6·62 to 12·62	15·3	0·23	20·2	−0·17	0·59	4·30
4-2-98	19·9	8	6·62 to 12·63	23·5	0·03	24·0	3·47	1·06	17·39
5-2-98	6·7	10	6·62 to 12·63	no distinct peak	0·12	9·7	7·65	5·28	1·20
5-12-98	47·6	64	6·62 to 12·63	48·37	0·53	51·5	10·69	8·47	17·25
7-1-98	66·3	32	6·62 to 12·63	19·17	0·94	83·9	18·26	15·75	14·31

Stream chemical response. A general decrease in stream baseflow NO_3^- concentrations was observed from around 300 μmol l^{-1} at the beginning of the study period to around 250 μmol l^{-1} at the beginning of July (Figure 3). Stream NO_3^- concentrations showed a pattern similar to discharge, with large events producing peaks in NO_3^- concentration of up to 280 μmol l^{-1} followed by a sharp decrease (Figures 3 and 4) for a storm occurring on 14 June 1998. DOC concentrations were also affected by stream discharge, but did not show the general decreasing trend in baseflow observed for NO_3^- (Figure 4).

Chemistry–topographic index relationships

All of the storms, with the exception of the first one sampled on 10 March, show a positive slope and correlation coefficients between NO_3^- concentration of the shallow subsurface stormflow (SSSF) and topography (Figure 5). The reverse trend for the 10 March storm is discussed in the next section. For all but the 10 March storm, slopes ranged from 23·0 to 35·7 for TI, 98·5 to 208·5 for TI1, and 67·1 to 153·5 for TI2. In general, no relationship was observed between DOC and topographic position concentration for the storms sampled.
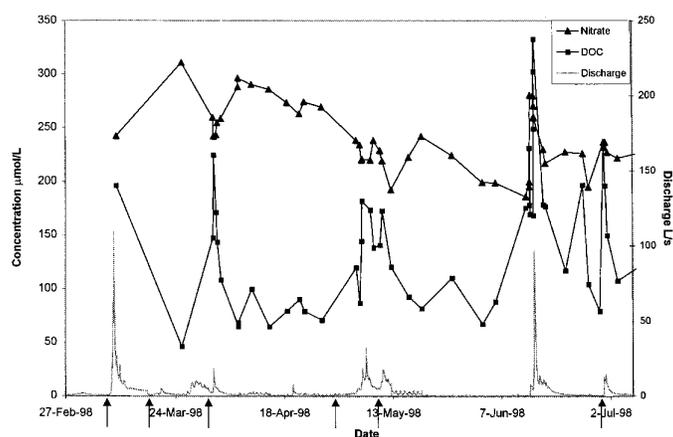

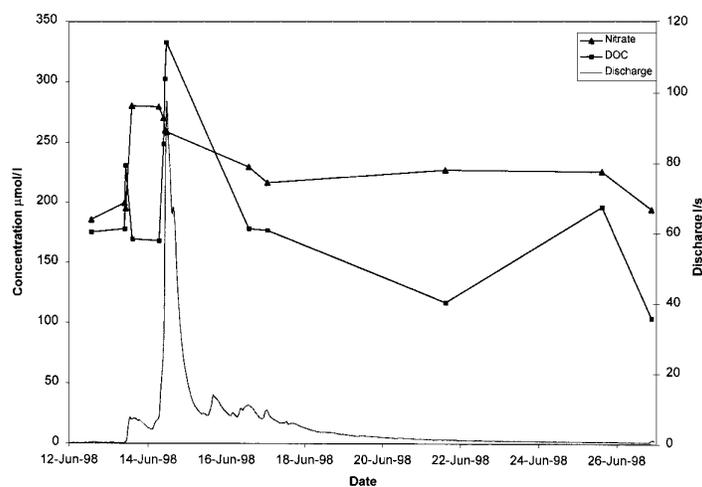Figure 3. Discharge and stream chemistry. Arrows indicate time of sampling

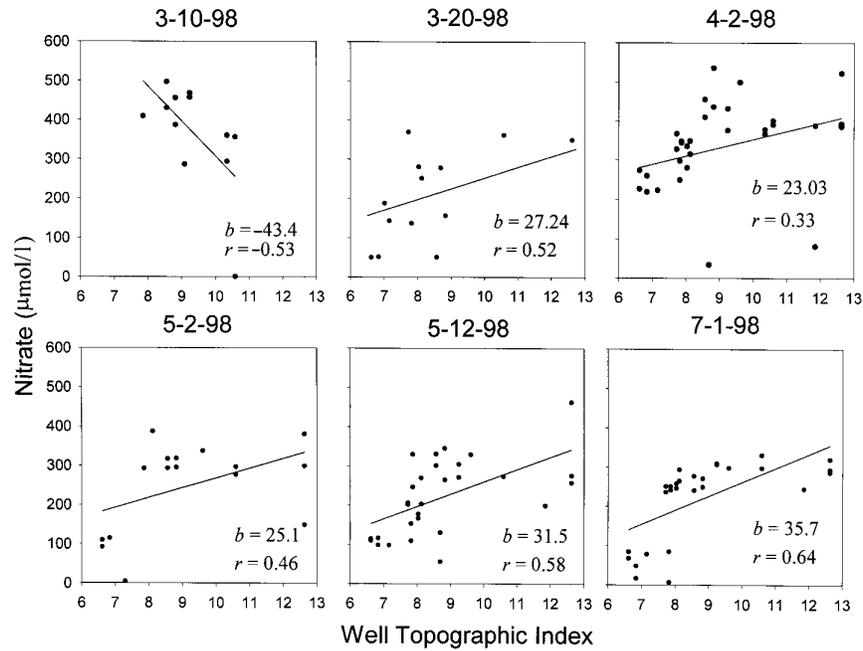Figure 4. Stream discharge and chemistry showing flushing effects of a large storm

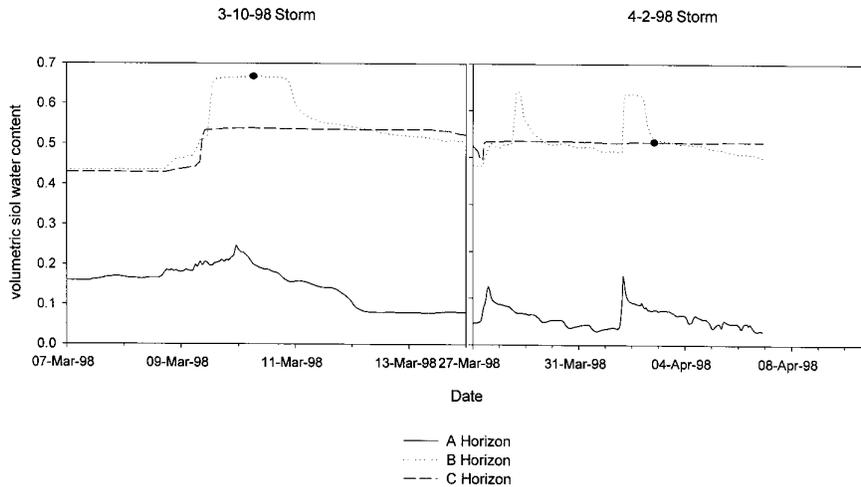Figure 5. Nitrate–TI relationship for all six storms sampled

Figure 6. Soil moisture for 3-10-98 and 4-2-98. Dot indicates time of sample

Uniqueness of the 10 March storm

The first storm sampled on 10 March was fundamentally different than all other storms in the study for at least three reasons. The storm on 10 March was the only rain-on-snow event of the study period, following 2 days of unseasonably warm temperatures. Snowpack water equivalent was between 20 and 30 mm prior to the storm. The soil profile had wetted-up thoroughly, as shown by TDR data in Figure 6, which compares soil

moisture during the 10 March and 2 April storms. The day before sampling, heavy rain fell, further inducing melting of the snow. No other storms sampled in this study caused such a marked rise in stream discharge (peak discharge: $109 \, l \, s^{-1}$; Table I).

Another difference was that only 11 piezometers were sampled during the 10 March storm. The sampled piezometers were located lower in the catchment close to the stream. The range of TI values of the piezometers sampled during this storm was much narrower than for the other storms sampled (Table I). Such sampling limitations may have impacted the results for this storm.

A final issue was the timing of the sampling. For this storm, sampling began within 12 h of the end of rainfall, whereas for all other storms, the sampling began longer after the cessation of rainfall. Thus, for all other storms, sampling occurred during the soil draining phase, whereas for the 10 March storm the sampling occurred near the peak of soil moisture (Figure 6).

Because of the differences in the characteristics of this storm and sampling limitations, this storm is not discussed further.

Point index values

The relationship between the NO_3^- and TI had an average slope of 28·52 and only three storms were statistically significant at a 0·05 level (Table II). For the five storms, the relationship between NO_3^- and topography shows a general trend of increasing strength with time, with a positive relationship throughout the study period. The slope for NO_3^-–TI relationship for the 20 March storm was 27·2, dropped to 23·0 for the 2 April storm, then gradually climbed to 35·7 for the 1 July storm. Interestingly, the Pearson correlation coefficients ρ calculated between NO_3^- and TI for these five storms increased as the slope of the relationship increased (Figure 5).

The relationship between DOC and topography showed no general trend. The DOC–TI relationship had an average slope of −19·8. The slopes were not statistically different from zero for any of the storms sampled.

Upslope index values

There was little difference in the correlation coefficients for the NO_3^-–topographic index relationship between the point and the upslope indices; however, the slopes of these relationships showed large changes (Table II). These slope changes are due to the reduced range of TI1 and TI2 compared with TI. Of the three indices (TI, TI1, TI2), TI1 showed the greatest change in solute concentration with change in topography.

Slopes of the regression line between DOC and topography were not statistically significant for any of the five storms for all of the indices examined.

Controls on strength of the chemistry–topographic indices relationship

The slope of the relationship between the topographic indices and chemistry varied between storms. Of interest was whether antecedent conditions impacted the slope of this relationship. Five potential controls on the slope of the relationship between chemistry and topographic indices were investigated: 5 day rain, 5 day API, storm rain, temp O, and temp B. These controls were discussed in the section entitled Analysis.

Table II. Slopes and Pearson correlation coefficients between topography and chemistry for all five storms. Topographic indices were calculated as described in text. The value in parentheses is the number of the five storms for which slopes were statistically different from zero at a 5% level

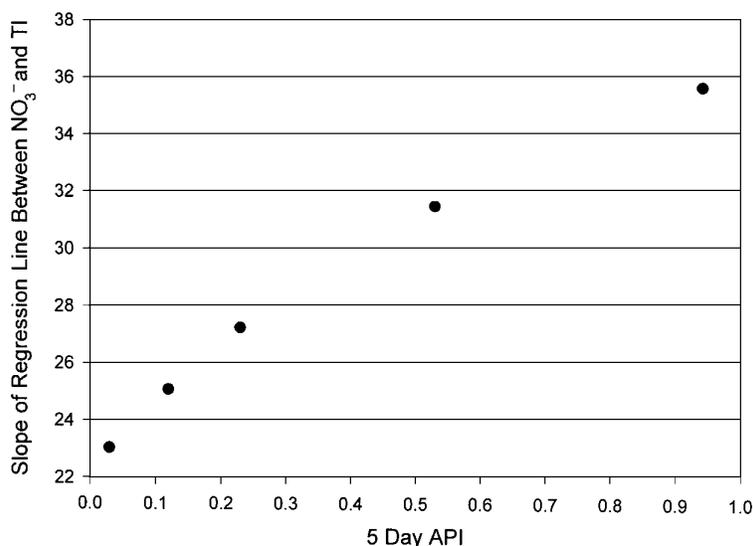|	TI		TI1		TI2	
	Mean slope	Mean r	Mean slope	Mean r	Mean slope	Mean r
NO_3^-	28·52 (3)	0·46	156·01 (4)	0·56	112·05 (4)	0·54
DOC	−19·08 (0)	−0·25	36·23 (0)	0·03	−43·52 (0)	−0·21

Figure 7. The NO_3^- concentration–TI slope as a function of the 5 day API for the five storms analysed

To investigate the relationship between the five antecedent conditions (controls) and the chemistry–topographic indices relationships, the slope and Pearson correlation for each storm were analysed. As the 5 day API increases (conditions get wetter) the slope of the relationship between NO_3^- and TI increases (Figure 7). Figure 8 presents the results for NO_3^- (DOC was neglected because all DOC–topographic indices slopes were insignificant).

Nitrate. Variation in the slope of the NO_3^-–TI relationship is well explained by all of the five potential controls tested. The highest correlation coefficient is the 5 day API and the NO_3^-–TI relationship, with a correlation coefficient of 0·99.

Across all five potential controls, the best estimator of the strength of the NO_3^-–TI relationship is the B-horizon temperature, with an average correlation coefficient of 0·84 (Figure 8). The O-horizon temperature followed, with an average correlation coefficient of 0·83. The 5 day API had an average correlation coefficient of 0·70, and the 5 day rain had an average value of 0·63. It should be noted that not all the controls had significant correlation coefficients for each topographic index.

DISCUSSION

Is there a relationship between topography and shallow subsurface stormflow chemistry?

Nitrate. In general, as the value of an index of topography increases, NO_3^- concentrations in the SSSF increase, indicating that wetter areas of the catchment have higher SSSF NO_3^- values than drier locations. This finding is consistent with the work of Creed *et al.* (1996), who suggested that 'hotspots' within the catchment, such as areas of high topographic index value, may export more NO_3^- to the stream than other catchment positions. They hypothesized that lowland areas within the Turkey Lakes catchments were capable of producing high concentrations of NO_3^- through enhanced nitrification. Additionally, results from a lysimeter experiment, in which soil moisture conditions were varied at a Japanese catchment, indicate that the highest NO_3^- concentrations were found in wet soils typical of lower hillslopes (Ohte *et al.*, 1997).
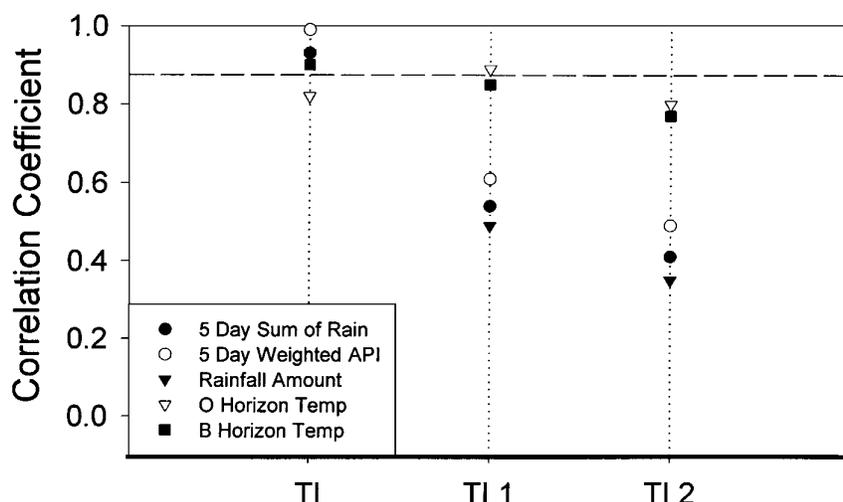
Figure 8. Correlation coefficients for the controls on the strength of the topography–chemistry relationship. Dashed horizontal lines represent confidence intervals at the 5% level

The flushing theory discussed previously (Hornberger *et al.*, 1994) provides a conceptual model that is consistent with both the topography–NO_3^- concentration relationships and the pattern of change in NO_3^- concentration in stream water at the Dry Creek catchment. For example, during a large storm in mid-June 1998, stream NO_3^- concentration peaked slightly before stream discharge, then dropped to below pre-storm levels (Figure 4). The flushing theory of Hornberger *et al.* (1994) predicts that the water table should rise during storm events or snowmelt into a more transmissive shallow soil layer with high levels of solute as the wedge of saturation moves upslope from the near stream zone. The abundant solute in the shallow soil would then be quickly flushed laterally downslope to the stream, indicated by the peak in solute concentration before peak discharge. After the initial stream pulse, stream concentration decreases through dilution by increased discharge. The Dry Creek catchment response is broadly consistent with this flushing theory, though the complex topography (benches, steps, and springs) may contribute to local sources of elevated NO_3^-.

The results of this study indicate that wetter areas of the catchment have higher NO_3^- concentrations. Ashby *et al.* (1998) showed that wetter sites at Dry Creek had the highest rates of denitrification potential due to a high NO_3^- source, leading to potentially lower NO_3^- concentrations. Although denitrification potential rates were higher in a relative sense, they may not be high enough to compensate for the large supply of water with high NO_3^- concentrations. Thus the topographic mechanism of water delivery overwhelms any denitrification effects in the clearcut Dry Creek catchment.

The upslope indices (TI1 and TI2) were expected to be more highly correlated with NO_3^- than the point index (TI), because the upslope indices were calculated on the assumption that conditions at a point are a function of conditions and processes of the area draining to that point. The distance-weighted average index (TI2) also incorporates the assumption that cells farther from the piezometer will have less influence than cells close to the piezometer. One reason for the poor performance of these indices may be the decrease in the range of the topographic data (TI had a range of 6·62 to 12·65, whereas TI2 had a range of 6·42 to 7·94). Thus these upslope indices may have smoothed microscale processes.

DOC. The relationship between DOC and the topographic indices was not significant for any of the five storms. The clearcut and residual slash that was heterogeneously distributed at the site may have provided a discontinuous source of DOC and masked the TI–DOC relationship. Data on the relationship between DOC and timber harvest is highly equivocal. At Hubbard Brook, there was no change in DOC concentrations after

the forest was cut (Hobbie and Likens, 1973). At the Coweeta Hydrological Laboratory in North Carolina, a 28% decrease in stream DOC was seen after harvest (Meyer and Tate, 1983). Moore (1989) found no relationship between DOC and discharge at the clearcut Maimai catchments in New Zealand, and instead found that the amount of slash and organic debris left in or near the stream channel appeared to be a major factor controlling stream DOC concentrations. Similar to the Maimai catchments, in the present study the slash and organic debris left after the cut may be masking a topography–DOC relationship. At Dry Creek, stream baseflow DOC concentrations were elevated from pre-cut conditions. Brown (1996) found that the average baseflow DOC concentration at Dry Creek before the cut was 75·9 μmol l^{-1} in 1995, whereas for the period of this study the average DOC baseflow concentration was 87·1 μmol l^{-1}. At Dry Creek, it appears the influence of slash has overwhelmed the natural processes controlling DOC concentrations, and topographic influences on the spatial distribution of DOC are insignificant. The lack of a relationship between the catchment topography and DOC concentrations and the strong relationship between NO_3^- and the topographic indices indicates the differing processes controlling formation and movement of these two solutes. This shows the danger in assuming similarities between DOC and NO_3^- simply due to of the flushing behaviour exhibited by both solutes.

What factors influence the relationship between topography and SSSF chemistry?

Nitrate. In general, the slope of the regression line between NO_3^- and the topographic indices was highly correlated to each of the three precipitation controls and the two temperature controls. This reflects two of the main processes affecting NO_3^- in forested catchments: formation and movement. Because N-mineralization and nitrification are biologically mediated processes, they are accelerated by increasing temperature, as shown by Murdoch *et al.* (1998) for a catchment 2 km from Dry Creek. This results in increased NO_3^- formation as soil temperature increases. As more NO_3^- is produced in the catchment, more is available to be flushed and moved downslope to areas of high index value. Thus, as the temperature of the soil increased, the strength of the relationship between NO_3^- and the topographic indices increased.

Antecedent precipitation was also a significant control on the strength of the relationship between NO_3^- and the topographic indices. As antecedent wetness increased, the strength of the relationship between NO_3^- and the indices increased, indicating a hydrologic connectivity in the catchment. Creed and Band (1998) found that for catchments with a high degree of variable source area (VSA) expansion, a larger amount of NO_3^- was exported to the stream. Their rationale was that the expanding VSA was linked hydrologically to the stream, resulting in elevated stream NO_3^-. As water moves towards the stream during drier conditions, it eventually reinfiltrates from rapid flowpaths into the deeper system, draining to deep groundwater instead of to the stream. The 5 day API is more highly correlated with the slope of the NO_3^-–TI relationship than the 5 day rain or storm rain. This is because the 5 day API gives more weight to the rainfall occurring closer in time to sampling, which is more indicative of moisture conditions during sampling. In addition, wetter conditions would create a higher water table; thus, one would expect more flushing of NO_3^- from shallow subsurface soils and a greater flux of high NO_3^- waters to areas of high index value. When the catchment is drier, the hydrologic connectivity throughout the catchment may not exist.

CONCLUSION

The results of this study indicate a strong positive relationship between NO_3^- concentration and topographic indices in SSSF. It is hypothesized that a rising water table flushes the shallow soil, and water with high NO_3^- moves vertically to depth and then moves laterally downslope to areas of high index values. The relationship between NO_3^- concentration and TI is highly variable. This high variability is well explained by two factors: soil temperature and antecedent precipitation. Increased soil temperature increases NO_3^- production, which resulted in greater NO_3^- availability to move down slope to areas of high index values. Antecedent moisture conditions potentially control the extent of hydrologic connectivity in the catchment, and thus the ability for

high NO_3^- water to be transported to the stream. When the catchment was wet, water moved rapidly from upland locations to high index locations lower in the catchment. When the catchment was dry, hydrologic connectivity was limited and the water movement was therefore hindered.

DOC was not correlated with any of the topographic indices calculated for Dry Creek because of the high spatial variability of slash and organic debris left after the harvest of the catchment. The DOC signal from the slash may have overwhelmed any DOC–topography relationship at this site.

The influence of the clearcut conducted in this catchment must be considered when analysing the results of this study. The cut resulted in elevated levels of NO_3^- throughout the catchment. In addition, the vegetative component of the catchment had been removed. These two factors created a unique opportunity to examine the processes controlling NO_3^- formation and movement while somewhat 'uncoupled' from the rest of the N cycle. It is, as yet, unclear how these results will apply to catchments with an intact forest. However, this study serves to identify some basic relationships to enable us to understand further the topographic controls on the chemistry of subsurface stormflow.

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