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Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA

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Abstract:

Nitrate and dissolved organic carbon (DOC) concentrations during a summer storm for a forested catchment in the Adirondack Mountains displayed a clear separation in trajectories and timing of maximum values. Nitrate concentrations peaked early on the rising limb of the hydrograph, whereas DOC concentrations gradually increased through the rising limb with maximum concentrations following the discharge peak. Solute data from precipitation, throughfall, soilwater, and ground/till water indicated till water and near-surface soil waters as the controlling end members for stream NO_3^- and DOC concentrations respectively. Streamflow concentrations of major base cations (Ca^{2+} and Mg^{2+}), which were assumed to represent water originating from deep flow paths, matched the NO_3^- trajectory. These data suggest that streamflow NO_3^- concentrations are derived from till groundwater and that DOC is derived from near-surface soil waters. We attributed the early expression of NO_3^- to the displacement of till waters by infiltrating precipitation. In contrast, we hypothesized that the delayed DOC concentrations occurred with surface and near-surface runoff from near-stream wetlands/peatlands and isolated saturated areas that became connected only under conditions of maximum water content in the catchment. Copyright © 2004 John Wiley & Sons, Ltd.

KEY WORDS nitrogen; carbon; hydrologic flow paths; flushing; variable source areas

INTRODUCTION

There has recently been considerable interest in determining the mechanisms responsible for the exports of dissolved organic carbon (DOC) and NO_3^- from forested watersheds (Hornberger *et al.*, 1994; Boyer *et al.*, 1997; Burns *et al.*, 1998; Creed and Band, 1998; Hill *et al.*, 1999; McHale *et al.*, 2002). Understanding the mechanisms of episodic acidification (Wigington *et al.*, 1996), evaluating the biological impacts of changes in DOC and NO_3^- concentrations, and the need for providing models that link hydrological and chemical processes have driven this interest. In upland forested catchments of the Colorado Rocky Mountains, stream DOC concentrations were found to peak on the rising limb of the snowmelt hydrograph, prior to peak discharge, followed by a rapid decrease in concentrations as snowmelt continued (Hornberger *et al.*, 1994; Boyer *et al.*, 1997). This temporal pattern in DOC concentrations was attributed to the flushing of the near-surface soil DOC pool by the rising water table (Hornberger *et al.*, 1994). Creed and Band (1998) found a similar trajectory in NO_3^- concentrations during snowmelt discharge from glaciated catchments in the Canadian Shield and attributed this pattern to the flushing of NO_3^- from near-surface soil layers. Although Boyer *et al.* (1997) confirmed the accumulation of DOC in surface layers via field measurements (a key condition for flushing), no such direct evidence was provided by Creed and Band (1998) for the origin of NO_3^-.

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In contrast to the flushing of DOC and NO_3^- from near-surface layers, Hill *et al.* (1999) and McHale *et al.* (2002) did not find any evidence of NO_3^- flushing. Hill *et al.* (1999) identified throughfall as the principal contributor to stream NO_3^-. McHale *et al.* (2002) found that groundwater springs that discharged deep till groundwater controlled the stream NO_3^- chemistry at the same study site being employed in the current investigation. McHale *et al.* (2002) also observed NO_3^- peaks on the rising limb of the stream discharge hydrographs for some summer/autumn storm events, but, unlike Creed and Band (1998), they attributed the early NO_3^- concentrations to the rapid displacement of till water by infiltrating precipitation.

Welsch *et al.* (2001) investigated the role of topography in the Catskills Mountains of New York on subsurface water chemistry and observed staggered NO_3^- and DOC peaks during a summer storm event - with a NO_3^- peak on the rising limb and a delayed DOC peak, which followed the maximum discharge (Welsch *et al.*, 2001: figure 4). Following Creed and Band's (1998) rationale, Welsch *et al.* (2001) speculated that NO_3^- was flushed from the catchment, but they did not present any direct evidence to support this conclusion. Brown *et al.* (1998), working in the same Catskill catchments as Welsch *et al.* (2001), reported summer DOC peaks that occurred after the peak in discharge and DOC concentrations which were greater on the recession limb than those on the hydrograph rising limb. Brown *et al.* (1998) were not able to explain the lag in DOC concentrations, but they attributed the high DOC concentrations to contributions from O-horizon soil waters. In a forested catchment in Germany, Hangen *et al.* (2001) also found delayed DOC contributions that occurred after maximum discharge. Hangen *et al.* (2001) hypothesized that the delay in DOC expression was due to the time lag associated with the onset of stemflow, which displaced DOC-rich waters from the topsoil to the stream via macropores.

These studies together suggest that the temporal expression of NO_3^- and DOC may vary with seasonal conditions especially related to antecedent moisture conditions and the intensity and duration of storm events. The flow paths taken by the solutes and/or the contributing sources appear to be the key determinants in the eventual expression of the solutes in streamflow. Our interest in this study was to focus on the temporal patterns of DOC and NO_3^- associated with summer storm events. Data from a 135 ha glaciated forested catchment located in Adirondack Mountains in New York was used in this study. DOC and NO_3^- concentration peaks from two precipitation events that constituted the remnants of the Floyd tropical storm of September 1999 showed a clear temporal separation. The highest NO_3^- concentrations occurred early on the rising limb on the discharge hydrograph, with the highest DOC concentrations following maximum discharge. These distinct patterns in NO_3^- and DOC concentrations raised three key questions: (1) Are NO_3^- and DOC exported along different flow paths during the summer events? (2) Why is the DOC peak delayed? (3) Can an integrated event model be developed that can explain the disparate NO_3^- and DOC signatures? We addressed these questions by evaluating the spatial and temporal patterns of solutes as a function of different sources in the catchment.

METHODS

Site description

The 135 ha Archer Creek catchment (Figure 1) is the main inlet to Arbutus Lake, located in Huntington Forest (HF) within Adirondack Park, NY (43° 59′N, 74° 14′W). The climate of HF is cool, moist, and continental. HF has a mean annual temperature of 4·4 °C, and the average annual precipitation is 1010 mm based on records from the period 1950–80 (Shepard *et al.*, 1989). The bedrock consists of Precambrian rock, which is mainly granitic gneiss with some gabbro-amphibolite (Fisher, 1957). The surficial geology is dominated by glacial till. Glacial till in the Adirondacks has a high sand ($\sim$75%) and low clay ($<$10%) content, with cobbles and boulders often being very abundant. Upland mineral soils are coarse, loamy, mixed frigid, Typic Haplorthods in the Becket–Mundell association, and are typically less than 1 m thick (Somers, 1986). Greenwood mucky peats are found in valley-bottom wetlands and range from 1 to 5 m in thickness (Somers, 1986; McHale *et al.*, 2002). The watershed is characterized by low drainage density (1·68 km km^{-2}), mean slope of 11%, and a total relief of 225 m (McHale *et al*., 2002). Vegetation consists of northern hardwoods (72%), mixed hardwood–conifer (18%), and conifer (10%). Overstory in the upper slopes is dominated by *Fagus grandifolia* (American beech) and *Acer saccharum* (sugar maple). Overstory vegetation at lower elevations is characterized by *Tsuga canadensis* (eastern hemlock), *Pinus rubens* (red spruce), *Alnus rubrum* (alder), and scattered individuals of *Abies balsamea* (balsam fir). Conifers dominate in riparian zones and at higher elevations.

Runoff contribution to the main stem of Archer Creek occurs from two tributaries draining the northwest and northeast portions of the catchment (Figure 1). Both contributing streams originate as groundwater springs (S1 and S2 in Figure 1). Groundwater springs also occur in numerous locations within the Archer Creek catchment. Most of these groundwater springs emanate from deep in the till (McHale *et al*., 2002). Surface saturation in Archer Creek occurs in the wetland/peatland areas that predominate in the lower half of the catchment, and in numerous isolated patches where the mineral soil is thin (McHale, 1999; McHale *et al*., 2002).

Instrumentation and data collection

Four components of stormflow were sampled during the Floyd event of September 1999, i.e. streamflow, throughfall, soilwater, and ground/till water. Stream discharge at the outlet of Archer Creek (Figure 1) was gauged at an H-flume equipped with an automated stage logging and sample collection system (McHale *et al*., 2000; Bischoff *et al*., 2001). Precipitation amounts and chemistry data were available from a National Atmospheric Deposition Program (NADP) and National Trend Network (NTN) site located 1·5 km from the watershed outlet. Throughfall chemistry was sampled using throughfall collectors located on an instrumented hillslope in the lower portion of the catchment (Figure 1). Soil water was collected using porous-cup tension

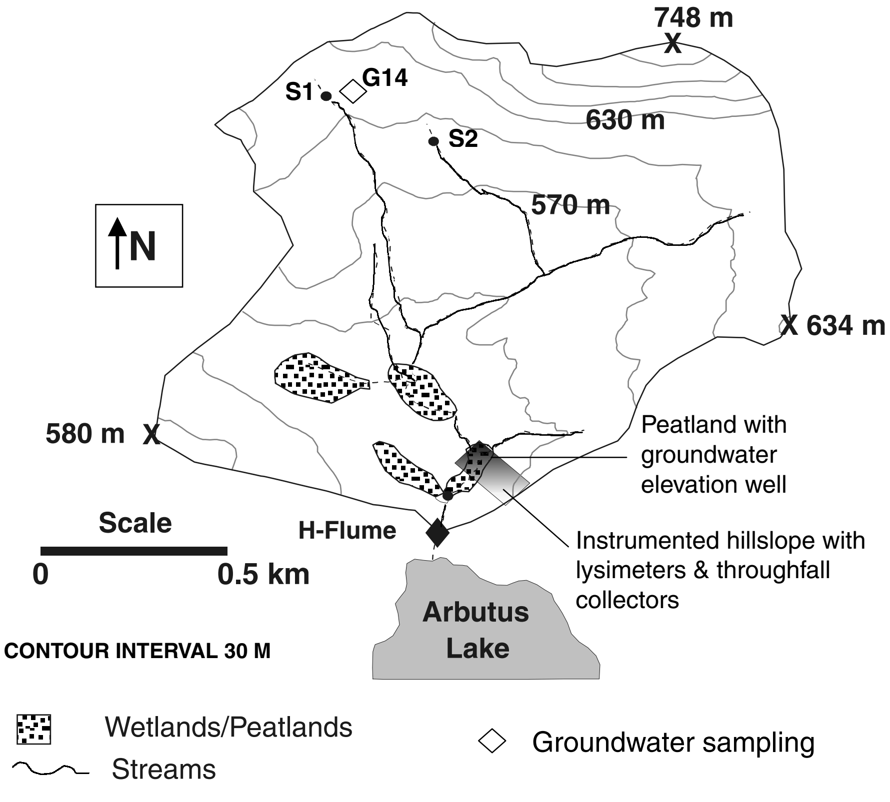

Figure 1. The Archer Creek catchment and instrumentation (revised from McHale *et al*. (2002))

lysimeters at depths of 15 and 50 cm. Three transects of 10 pairs of lysimeters each were located alongside the throughfall collectors on the instrumented hillslope (Figure 1). Ground/till water was sampled from a groundwater well (G14) located adjacent to groundwater spring S1 in the upper portion of the catchment (Figure 1). A complete description of the instrumentation is provided in McHale *et al.* (2002).

Throughfall, lysimeters, groundwater well, and stream samples collected for the events were analysed for Ca^{2+}, Mg^{2+}, $NO_3{}^-$, and DOC. Procedures and methods used for laboratory analysis of these solutes have been described previously (McHale *et al.*, 2000; Bischoff *et al.*, 2001; Mitchell *et al.*, 2001).

SURFACE SATURATION IN NEAR-STREAM WETLAND/PEATLAND AREAS

Groundwater elevations in near-stream wetlands/peatlands (Figure 1, well located 5 m from the channel edge) were monitored by McHale (1999) through 1995–96. We present these data since it is critical to our model describing evolution of solute signatures during the storm events. The focus here was on the temporal response of groundwater elevations in near-stream peatlands vis-à-vis streamflow discharge. Groundwater elevations from two storm events—a late fall event (11–13 November 1995) and a summer event (15–16 July 1996)—along with stream discharge and precipitation are shown in Figure 2. Groundwater elevations during both events indicate surface saturation and water ponding in the peatlands. Importantly, these water levels showed that: (a) surface saturation in the peatlands occurred after the precipitation peak and during the latter portion of the hydrograph rising limb; (b) the temporal pattern of saturation build-up followed the trend in the discharge hydrograph more than the pattern of the rainfall hyetograph; (c) surface saturation and ponding was at its maximum at (for the November 1995 event) or immediately after (for the July 96 event)

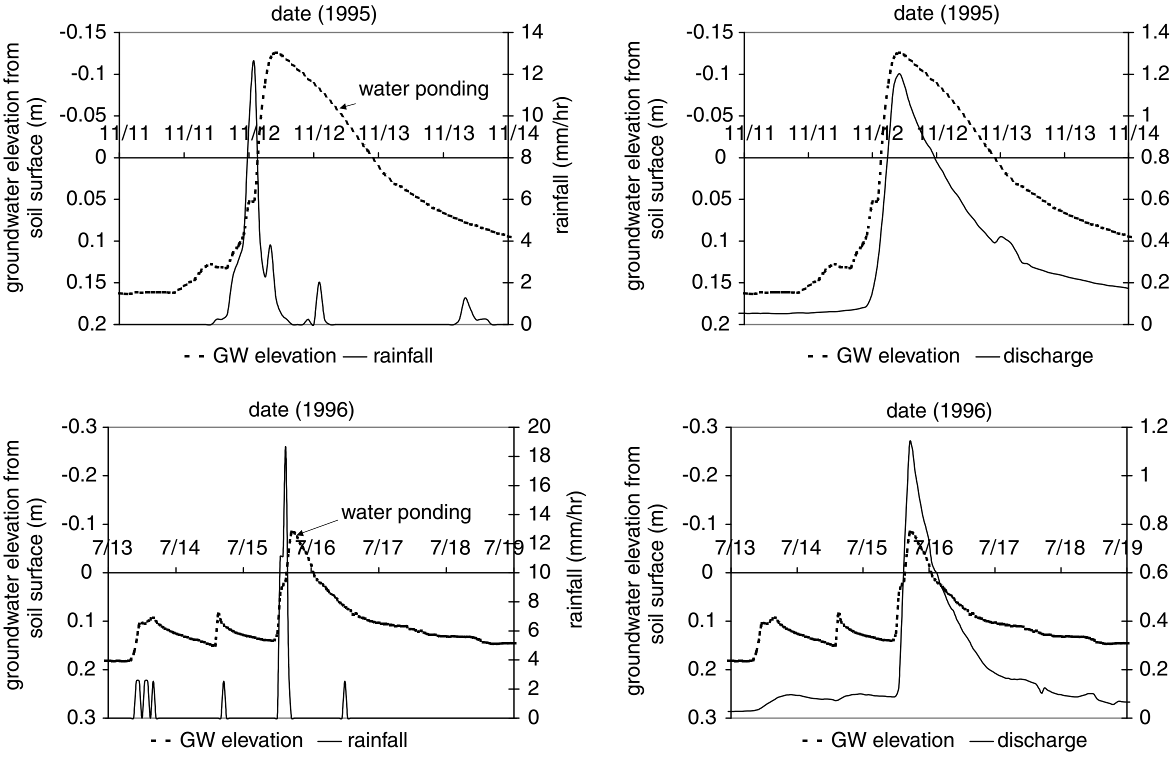

Figure 2. Peatland groundwater elevations with precipitation and streamflow discharge for 11–13 November 1995 and 15–16 July 1996 storm events (modified from McHale (1999))

peak discharge; and (d) surface saturation was maintained even after precipitation cessation. We attribute the slight delay in the maximum groundwater elevations for the July 1996 event (compared with the November 1995 event) to drier conditions in the catchment prior to the July event. Soil moisture conditions in the catchment are typically higher in the fall than in the summer (McHale, 1999; McHale *et al.*, 2002).

It is obvious from these observations that saturation in peatland/wetland areas is not dictated by incident precipitation alone. The importance of surface seeps located at the base of hillslope hollows and at the hillslope–peatland interface in contributing to surface waters has previously been reported for this catchment (McHale, 1999). We believe that groundwater in the near-stream peatland and wetland area is recharged by return flow and subsurface water from contributing hillslopes, which is released as surface seeps just above the peatlands. This return flow and subsurface flux from contributing hillslopes is most likely responsible for the continued saturation of the peatlands even after precipitation cessation and through hydrograph recession.

RESULTS

Concentration of solutes prior to Floyd storm events

The concentrations of solutes measured in precipitation, throughfall, soil water at 15 and 50 cm depths and ground/till water are presented in Table I. The concentrations of the dominant base cations (Mg^{2+} and Ca^{2+}) displayed a progressive increase in concentrations with soil depth, with maximum values recorded for ground/till water. Similar concentration profiles with soil depth have previously been reported for these solutes at the Sleepers River catchment in Vermont (Kendall *et al.*, 1999; McGlynn *et al.*, 1999). This vertical stratification in these concentrations has led to the use of these base cations to infer the hydrologic flow paths, with high Mg^{2+} and Ca^{2+} concentrations assumed to represent water originating from deep flow paths (Mulholland *et al.*, 1990; Bazemore *et al.*, 1994; Brown *et al.*, 1998; Kendall *et al.*, 1999)

Although NO_3^- concentrations in precipitation were greater than those recorded in throughfall and soil water, ground/till water had the highest NO_3^- values. The low values of NO_3^- in soil water were likely the consequence of the high biotic demand during the summer growing period. In contrast to base cations and NO_3^-, DOC concentrations were highest in near-surface layers and decreased progressively with soil depth (Table I). Elevated DOC concentrations in near-surface soil have previously been reported (Boyer *et al.*, 1995, 1997; Brown *et al.*, 1998; Kendall *et al.*, 1999). The high concentrations measured in near-surface soil suggest that, during periods of overland and near-surface flow, near-surface horizons could be a significant source of DOC to streams.

Temporal evolution of solutes concentrations during the Floyd storm events

The remnants of the Floyd storm comprised three individual events that deposited a total of 166 mm of precipitation in the period 16–24 September (Figure 3a). These events equalled 16% of the total precipitation

Table I. Mean concentration of solutes from various catchment sources for the Floyd storm events (16–24 September). Standard deviations given in parentheses; n: number of samples

Solute	Precipitation (NADP data)	Through fall ($n = 15$)	Lysimeter		Ground/till water	Average streamflow (events 1 & 3; $n = 21$)
			15 cm ($n = 9$)	50 cm ($n = 12$)		
Mg^{2+} (μeq l^{-1})	<0·2	18.0 (12.2)	40.8 (19.1)	43.3 (11.5)	135.6 (2.6), $n = 2$	65.1 (7.0)
Ca^{2+} (μeq l^{-1})	1·0	37.6 (21.9)	91.9 (46.1)	91.8 (27.9)	431.5 (24.6), $n = 2$	257.3 (27.5)
NO_3^- (μeq l^{-1})	6·5	1.1 (0.9)	1.8 (0.8)	4.6 (6.9)	23.3 (10.2), $n = 4$	12.9 (7.4)
DOC (μmol l^{-1})	—	715.2 (591.2)	4463.1 (1620.2)	1536.1 (1097.2)	170.3 (45.4), $n = 2$	1147.7 (287.0)

inputs for 1999. The events of 16–17 September and 22 September produced the most marked changes in discharge. Prior to the arrival of these events, high evapotranspiration losses and unusually low antecedent precipitation had produced extremely dry soil conditions, leading to very low discharge in the stream draining the catchment.

Solute concentration data were available for the two larger precipitation events and are plotted along with stream discharge in Figure 3. Increased discharge was initiated approximately 10 h after the initiation of the first (16–17 September) precipitation event. On the hydrograph rising limb of 16 September, Ca^{2+} and Mg^{2+}

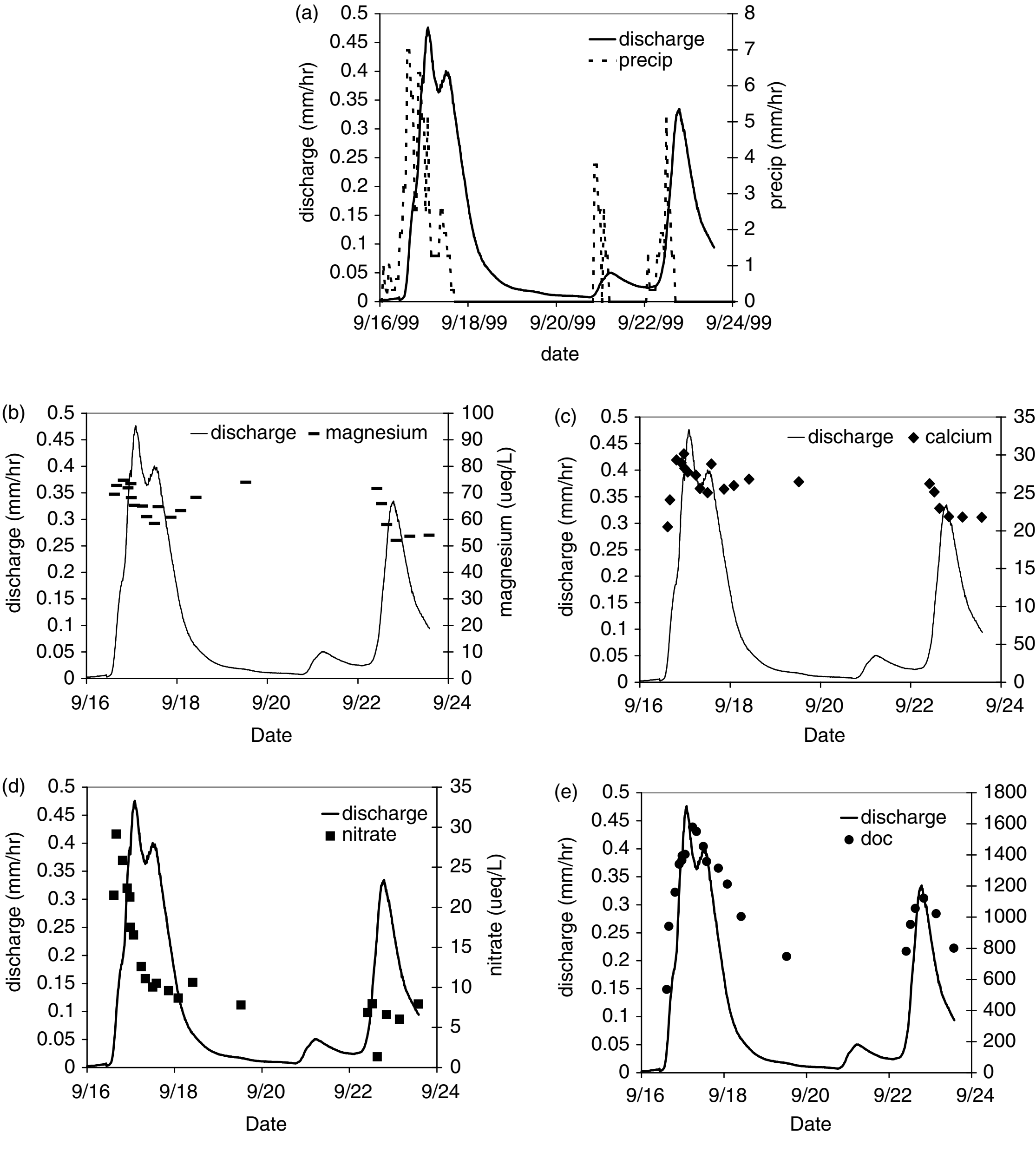

Figure 3. Precipitation, streamflow, and solute concentrations for the Floyd storm events

concentrations showed a small yet distinct increase in concentrations, with both solutes reaching peak values 7 h after discharge began to increase (Figure 3b and c). After reaching maximum concentrations, both Ca^{2+} and Mg^{2+} concentrations decreased through the storm. The pattern of $NO_3{}^-$ concentrations also displayed an initial increase, similar to that observed for Ca^{2+} and Mg^{2+}, followed by decreasing concentrations (Figure 3d).

The temporal pattern of DOC concentrations differed from the other solutes. DOC concentrations increased steadily during the hydrograph rising limb and reached a maximum 3 h after the discharge peak followed by a gradual decrease in concentrations through the hydrograph recession (Figure 3e). The temporal pattern of DOC during the third event (22 September) was similar to that observed during the first storm event. Although $NO_3{}^-$ concentrations during the event of 22 September suggest a slight early rise, the clear pattern of initial rise observed for Ca^{2+}, Mg^{2+}, and $NO_3{}^-$ during the first storm event was not replicated for the third storm event.

DISCUSSION

Are $NO_3{}^-$ *and DOC exported via different flow paths during summer events?*

The differences in the temporal patterns of $NO_3{}^-$ and DOC concentrations, including the timing of the peak concentrations, imply different flow paths. The parallel trends in $NO_3{}^-$ and base cations Ca^{2+} and Mg^{2+} suggest that $NO_3{}^-$ export occurred via deep flow paths. The high concentrations of $NO_3{}^-$ in ground/till water and the low values observed in surface soil layers support this hypothesis. The range of $NO_3{}^-$ concentrations observed in catchment streamflow (1·3–29·1 μeq l^{-1}) rules out precipitation (6·5 μeq l^{-1}), throughfall (1·1 ± 0·9 μeq l^{-1}) and near-surface waters (1·8 ± 0·8–4·6 ± 6·9 μeq l^{-1}) as the controlling end members, and implicates ground/till water (23·3 ± 10·2 μeq l^{-1}) as the only remaining end member with sufficiently high concentrations. Earlier, McHale *et al.* (2002), using hydrometric and chemical data, also reached a similar conclusion in analyses of events from previous years.

We attribute the initial increase in Mg^{2+}, Ca^{2+}, and $NO_3{}^-$ concentrations during the event of 16–17 September to 'till-water displacement'. We believe that the rise in solute concentrations was associated with the rapid displacement of till water by infiltrating precipitation. We hypothesize that the till water was released at groundwater springs located at channel heads (e.g. S1 and S2) and was rapidly delivered via the stream network to the catchment outlet. It is very likely that the dry antecedent period led to the accumulation of the solutes at the soil–till interface, and the arrival of the Floyd storms allowed for these solutes to be displaced with till water. We have observed similar $NO_3{}^-$ 'spikes' for summer/autumn storm events that have followed dry periods (Inamdar, unpublished data). Recently, Iqbal (2002) reached a similar conclusion when he attributed the elevated $NO_3{}^-$ flux on the hydrograph rising limb to the displacement of the groundwater from aquifer storage in response to the fluid pressure generated by vertical recharge from precipitation. The lower $NO_3{}^-$ concentrations for the 22 September event following the event of 16–17 September (Figure 3) suggest depletion of the soil solution nitrate pool with consequent storm events.

In contrast to $NO_3{}^-$ being sustained by deep ground waters, we believe that the exports of DOC occur with near-surface soil runoff and/or overland flow generated during the storm event. Near-surface soil waters appear to be the only source with sufficiently high concentrations (Table I) to match the concentrations of DOC observed in streamflow (14·4–1579·1 μmol l^{-1}). We attribute the steady rise in DOC concentrations to the flushing of surface horizons in near-stream peatlands and other pockets of surface saturation (areas with thin soil cover) in the catchment.

Why is the DOC peak delayed?

We attribute the delay in DOC peak to two likely causes: (1) the delay in surface saturation of near-stream wetlands/peatlands; and (2) the disconnected nature of surface saturated areas in our catchment. Surface ponding in the near-stream peatlands was delayed and reached a maximum either coincident or immediately after the peak in discharge (Figure 2). The maximum areal extent of surface saturation very likely allowed for DOC to be flushed from previously unconnected, distal, wetland areas, resulting in high DOC concentrations. Increase in flushable nutrient concentrations with the expansion of saturated variable source areas has previously been reported by Boyer *et al.* (1995).

In addition to the near-stream wetlands/peatlands, surface saturation in the Archer Creek catchment has been observed in numerous isolated patches where soil depths are shallow. Many of these patches are located below hillslope hollows, or in depressions along the bench–step topography in the upper areas of the catchment (McHale, 1999). Many of these isolated patches of saturation are either hydrologically disconnected from the stream network or connected only briefly during periods of high saturation. Moreover, surface or near-surface runoff generated from these areas is not immediately routed to receiving streams but moves slowly as near-surface flow through the organic surface mat, often infiltrating and reappearing as seeps. This pattern of water mixing in the catchment provides ample opportunity for saturation excess runoff to interact with the DOC-rich near-surface soil layers. We hypothesize that the delayed DOC peak observed in our catchment results from the disconnected nature of saturated areas in the catchment (potential sources for DOC) and the delay associated with the movement of water from these isolated patches to the catchment outlet. This hypothesis is consistent with our observations on the role of these saturated areas in the mixing and evolution of event and pre-event waters in the catchment (Inamdar *et al.*, submitted). The importance of connectivity of saturated areas in catchments in affecting solute mixing from various water sources has been suggested by other investigators (e.g. Bazemore *et al.*, 1994; Creed and Band, 1997).

A conceptual model for export of NO_3^- *and DOC*

Integrating the hypotheses presented above, we present a conceptual model for the evolution of NO_3^- and DOC for summer/autumn storms. We classify the model in four stages, representing varying levels of water and solute contributions from deep and near-surface flow paths and hydrologic connectivity of near-stream wetlands/peatlands and other surface-saturated patches (Figure 4):

- *Stage 1. Early portion of the rising limb of hydrograph.* Discharge is dominated by pre-event water from till and soil reservoirs. The sharp rise of the hydrograph during this period suggests that pre-event water is likely being displaced via rapid flow paths or discontinuities along the soil–till interface. High NO_3^- concentrations in till water contribute to the high NO_3^- concentrations in streams. Nitrate concentrations at the catchment outlet are a composite of the high till-water concentrations and low values in precipitation intercepted directly by the stream channel. For storm events after a prolonged dry period, an initial rise in NO_3^- occurs (corresponding to the 'till-water displacement' hypothesis), otherwise NO_3^- concentrations follow a gradual decrease through this stage due to dilution by infiltrating precipitation water with relatively low NO_3^- concentrations. DOC contributions are minimal, since near-surface flow or event-water contributions are negligible.
- *Stage 2. Latter portion of the rising limb.* Nitrate concentrations continue to drop as more precipitation with low NO_3^- concentrations mixes with NO_3^--enriched ground/till water. As soil moisture increases, surface saturation occurs in isolated patches, hillslope hollows, and near-stream wetlands. DOC contributions occur from direct channel interception, wetlands/peatlands, and surface-saturated areas connected to the drainage network.
- *Stage 3. Peak discharge.* Saturation excess runoff contributions from hydrologically connected wetland/peatland and saturated areas are at their maximum, and runoff contributions also occur from some discrete saturated areas with sufficient surface water to sustain rivulets that connect the stream network. Some surface runoff from the remaining disconnected patches of surface saturation is lost to infiltration and/or moves laterally as near-surface flow through the organic surface mat, reappearing as seeps in areas with shallow soils. The DOC peak is associated with the peak in near-surface flow contributions. Nitrate concentrations continue to drop and reach their lowest levels.

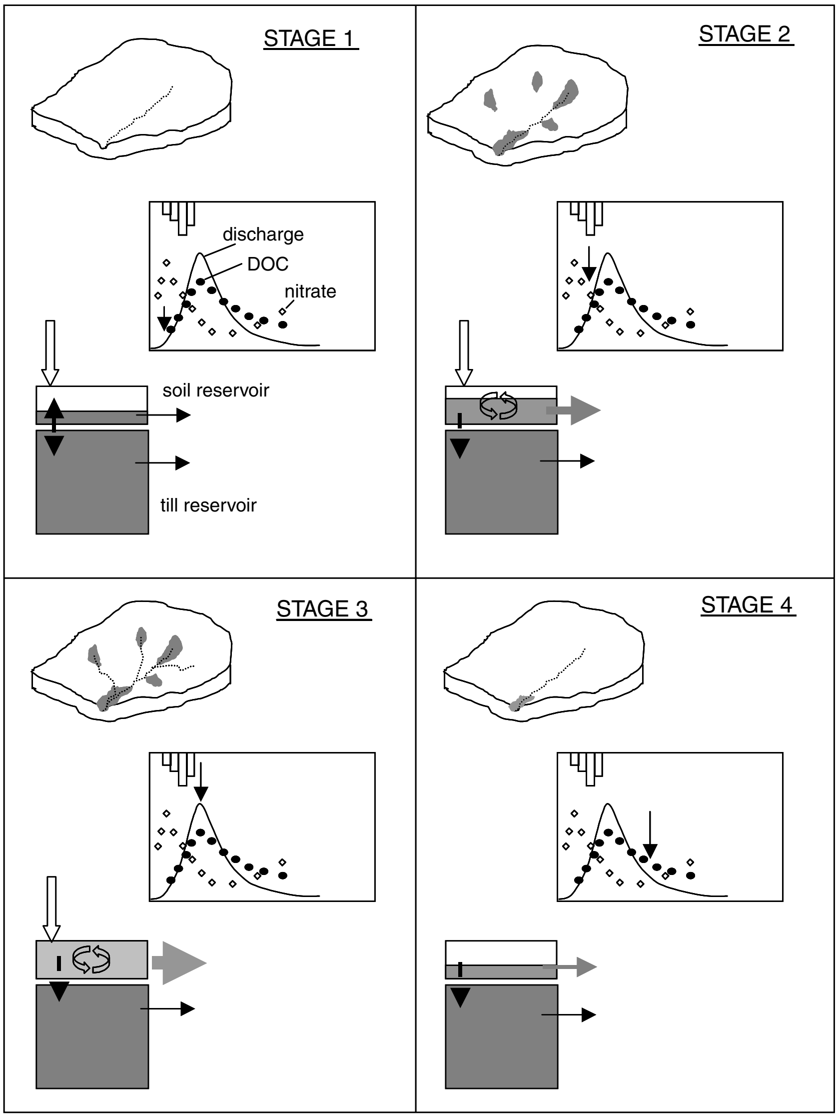

Figure 4. Conceptual model for NO_3^- and DOC evolution considering water and solute contributions from deep and near-surface flow paths and spatial connectedness of saturated areas. Note: arrow on the hydrograph (inset) indicates position of the stage during the event

- *Stage 4. Hydrograph recession*. Patches of surface saturation have receded. Stream discharge is sustained by a mix of previously infiltrated saturation excess that reappears as seeps, water from the recharged soil reservoir, and ground/till water. As the event recedes, the near-surface flow contributions continue to drop with proportional increase in deeper ground/till water, resulting in a gradual increase in NO_3^- concentrations and a simultaneous decrease in DOC.

CONCLUSIONS

A distinct separation of NO_3^- and DOC signatures during summer storm events was observed in this study. We have argued that the opposing trajectories of the signatures and the staggered nature of the peaks represent the export of these solutes along different flow paths: NO_3^- with deep ground/till water flow versus DOC along near-surface flow paths. We suggest an implicit linkage describing the temporal evolution of NO_3^- and DOC in streamflow by using solute concentrations measured in potential catchment sources. Efforts are currently under way to test these linkages explicitly in the Archer Creek catchment using detailed hydrometric data, and isotopes of carbon, nitrogen and oxygen.

It is obvious from this study that detailed storm event sampling allowed us to decipher the unique temporal patterns of NO_3^- and DOC signatures during summer storm events. This realization underscores the need for detailed event data if we are to identify the event-scale mechanisms responsible for solute export correctly. Although daily scale sampling might be appropriate for long-duration events, such as spring snowmelt (e.g. Creed and Band, 1998), it is highly unlikely that the same sampling frequency will be adequate to capture variations in solute signatures for summer or autumn storm events.

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