**Groundwater flushing of solutes at wetland and hillslope positions during storm events in a small glaciated catchment in western New York, USA**

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**Abstract:**

While the role of groundwater in flushing of solutes has long been recognized, few studies have explicitly studied the within-event changes in groundwater chemistry. We compared the changes in groundwater chemistry during storm events for a wetland and hillslope position in a small (1.5 ha) glaciated, forested catchment in western New York. Flushing responses for dissolved organic carbon (DOC) and nitrogen (DON), nitrate (NO₃) and sulfate (SO₄) in wetland and hillslope groundwaters were also compared against the corresponding responses in stream water. Eight storm events with varying intensity, amount, and antecedent moisture conditions were evaluated. Solute flushing patterns for wetland and hillslope groundwaters differed dramatically. While DOC concentrations in wetland groundwater followed a dilution trend, corresponding values for hillslope groundwater showed a slight increase. Concentrations for NO₃ in wetland groundwater were below detection limits, but hillslope groundwaters displayed high NO₃ concentrations with a pronounced increase during storm events. Flushing responses at all positions were also influenced by the size of the event and the time between events. We attributed the differences in flushing to the differences in hydrologic flow paths and biogeochemical conditions. Flushing of the wetland did appear to influence storm-event stream chemistry but the same could not be said for hillslope groundwaters. This suggests that while a variety of flushing responses may be observed in a catchment, only a subset of these responses affect the discharge chemistry at the catchment outlet. Copyright © 2009 John Wiley & Sons, Ltd.

**KEY WORDS** dissolved organic carbon; nitrogen; wetlands; hillslopes; storm events; flowpaths

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**INTRODUCTION**

In recent years there has been considerable interest in investigating the exports of solutes during storm events and the mechanisms responsible for the mobilization and transport of solutes from watersheds. Understanding the patterns and mechanisms responsible for solute exports are critical to (1) furthering our mechanistic understanding of watershed behaviour and the influence of individual watershed units such as hillslopes, riparian zones, and wetlands; (2) assessing and managing non-point source pollution from watersheds; and (3) determining the impacts of land-use change on watershed hydrology and water quality. Investigating storm-event mechanisms are also especially relevant considering the influence of future climate change on storm-event size, intensity, and frequency. Future climate change predictions for the east coast of United States indicate that the intensity and size of storm events will increase, while the intervening periods between storms will become longer and drier (USGCRP, 2000). These changes will have important implications for the amounts and the rates at which water and solutes are exported from catchments.

One of the mechanisms that has been invoked to explain the storm-event exports of solutes from watersheds has been the ‘flushing’ of solutes from watershed soils (Hornberger et al., 1994; Boyer et al., 1997; Creed and Band, 1998; McHale et al., 2002; Inamdar and Mitchell, 2006; Christopher et al., 2008; Verseveld et al., 2008). However, the term flushing has been used fairly broadly (Burns, 2005) and has encompassed a variety of mechanisms and interpretations, some of which include: transport of solutes with subsurface runoff over an impeding soil layer or bedrock (Hill et al., 1999); rapid delivery of runoff and solutes through macro-pores and other preferential flow paths through the soil profile (Burns et al., 2001; Hill et al., 1999); wash-off of solutes and particulate matter from the vegetative canopy (Hill, 1993) or along the soil surface with saturation- or infiltration-excess overland flow; and the flushing or displacement of solutes with rising groundwaters (GWs), especially in riparian and/or wetland areas (Creed and Band, 1998).

The role of GW flow paths has especially been highlighted for solutes like nitrate (NO₃) and dissolved organic carbon (DOC) (McHale et al., 2002; Schiff et al., 2002; Inamdar et al., 2004). McHale et al. (2002) and
Inamdar et al. (2004) proposed that GW is recharged by NO₃ from dry hillslopes with high nitrification rates (Ohrui et al., 1999) and that this NO₃-rich GW is displaced into the stream at the start of the event. Boyer et al. (1997) reported decreasing DOC concentrations in surficial catchment soils during snowmelt and attributed it to flushing of soil-water DOC by infiltrating melt waters. Boyer et al. (1997) also demonstrated that solute flushing may vary with landscape position with near-stream soils being flushed more rapidly versus those located upslope. Creed and Band (1998) hypothesized that NO₃ was flushed from catchments as GWs rose to the surface and intersected NO₃-rich surficial soils. Hinton et al. (2004) proposed that wetland and riparian forests may differ with respect to solute flushing mechanisms. They suggested that GW flow paths may play a greater role in solute flushing of DOC from riparian areas, while surface mixing of waters may be important for wetlands. Inamdar et al. (2004) and Inamdar and Mitchell (2006) attributed the increase in DOC concentrations during storm events to the flushing of carbon-rich riparian soils by rising GWs.

These studies clearly attest that GW plays an important role in the flushing of solutes from catchments. However, in most studies, the influence of GW for solute flushing has typically been assessed by evaluating stream-water solute concentrations along with GW elevations. Very few studies have explicitly measured the changes in solute concentrations in GW itself during storm events. The few studies that have monitored soil or GW solute concentrations during events have been associated with long-duration snowmelt events (e.g. Boyer et al., 1997). We know of no study that has evaluated the change in GW during rainfall events. Determining how solute concentrations change in soils or GWs within the time period of rainfall events is critical for furthering our understanding of the flushing mechanism. Furthermore, solute flushing by GWs is expected to vary across catchment locations and may not be the same at hillslope, riparian, or wetland locations.

We investigated the within-event patterns of GW chemistry at two contrasting landscape positions—a valley-bottom wetland and at the base of a steep hillslope in a small 1.9 ha catchment. The catchment (S5) is located within the Point Peter Brook watershed (PPBW) which is a glaciated, forested watershed and has been extensively studied (Inamdar et al., 2006; Inamdar and Mitchell, 2006; 2007a, b; 2008a, b). The S5 catchment has a strong topographic contrast where steep hillslopes converge into a mildly sloping wetland in the valley bottom. GW depths in the valley-bottom wetland are close to the soil surface year-round while those on the hillslopes vary considerably during and between storm events. We hypothesized that this difference in topography and surficial geology would likely yield contrasting responses in solute flushing for the two positions. While the focus of this study was primarily on the flushing behaviour of reactive species like DOC, dissolved organic nitrogen (DON), NO₃, and sulfate (SO₄²⁻), additional solutes such as silica (Si), and magnesium (Mg) were also included to help characterize the runoff sources. Specific questions that were addressed in our study included the following.

- What are the temporal patterns of solute flushing in GW during storm events at the wetland and hillslope locations?
- How do the storm-event patterns of GW flushing at the wetland and hillslope locations affect the solute chemistry at the catchment outlet?
- How do the flushing responses vary among solutes at the two positions?

**SITE DESCRIPTION AND METHODS**

*Site description*

This study was conducted in subcatchment S5 (1.9 ha) of the PPBW (Figure 1) which is located in Cattaraugus County and 55 km southeast of Buffalo in New York State, USA (42°26'30"N; −78°55'30"W). Mean annual winter temperature is −3 °C and the mean summer temperature is 21 °C. Annual precipitation averages 1006 mm of which 200–250 mm occurs as snow [20-year average based on the National Atmospheric Deposition Program (NADP) Weather Station at Chautauqua, NY, USA (42°40'08"N, 79°00'30"W). DOI: 10.1002/hyp

![Cross section X-Y showing hillslope profile](image)

Figure 1. Location of Point Peter Brook watershed (PPBW) in New York State, USA (A); instrumentation and attributes of catchment S5 (B); cross-section of catchment along XY showing contributing hillslope and locations of wells at the hillslope (H7 and HS7) and wetland positions (R6 and RS5) (C). The XY axis is displayed in (B). Contour interval in (B) is 2 m. R6 and H7 are logging wells for groundwater elevations, while RS5 and HS7 are sampling wells for groundwater chemistry.
Bedrock geology in the region consists of stratified limestone, dolomite with gypsum, and shale of the Upper Devonian period (Olcott, 1995). The parent material was derived from glacial till (Kent Drift of Woodfordian formed 19 000 year B.P.) (Phillips, 1988). Vegetation on ridgetops and hillslopes is dominated by deciduous trees including sugar maple (Acer saccharum), black maple (Acer nigrum), American beech (Fagus grandiflora), yellow birch (Betula alleghaniensis) with larger proportions of conifers including hemlock (Tsuga canadensis) and white pine (Pinus strobus) in valley bottoms.

Topography of the entire PPBW is fairly distinct with wide ridge tops, steep hillslopes, and narrow valley bottoms. Wetness in the valley-bottom locations vary spatially across the watershed with wetlands at some locations, which are continuously saturated year long while other locations display a seasonal pattern of saturation. Elevations in catchment S5 range between 255 and 304 m above sea level (Figure 1). Hillslopes contributing runoff to the valley-bottom have an average gradient of 23%. Forty nine percent of the catchment area in S5 has a northwest aspect. A low-permeability clay layer that is a part of the till layer underlying the hillslopes generates perched water tables and forces water to move as shallow subsurface flow. At locations where this impeding clay or till layer intersects the surface, GW is released as surface seeps (Figure 1). The valley-bottom riparian and clay layer intersects the surface, GW is released as low subsurface flow. At locations where this impeding clay layer. Well R6 was 14 m upslope of V-notch at S5, while well H7 was 30 m upslope (Figure 1). The difference between soil-surface elevations at R6 and H7 was 2-2 m. All wells were fully screened from a depth of 0-30 m below the soil surface. GW sampling wells (RS5 and HS7) were placed adjacent (beyond a distance of 2 m) to the logging wells (R6 and H7, respectively) and were constructed similarly but were devoted solely to sampling of water chemistry. Wells for sampling of GW chemistry were separated from the GW-elevation logging wells so as to prevent changes in recorded GW elevations during sample recovery. In addition to the GW well, a soil-water lysimeter (LY6–5 cm ID screened PVC pipe inserted diagonally 30 cm from the soil surface and capped at the bottom) was also installed in the valley-bottom wetland. The soil-water lysimeter essentially sampled zero tension soil-water in the wetland.

Water chemistry samples were collected using a combination of manual grab sampling during non-event periods and automated ISCO samplers during storm events. Grab sampling was performed twice a month for stream water at outlet of catchment S5, valley-bottom and hillside GW wells (RS5 and HS7), surface hillslope seeps, and the zero-tension lysimeter (LY6). Grab sampling of GW samples (from RS5 and HS7) was performed using hand-operated pumps. Three ISCO samplers were installed in catchment S5 for storm event sampling—one at the V-notch weir to collect stream-water samples exiting catchment S5 and one each at sampling wells HS7 and RS5 to collect GW from the hillslope and the wetland, respectively. The ISCO sampler tube was lowered half-way down the water column in the GW wells so as to get a representative sample of GW at these locations. The samplers were connected to rainfall gages and were triggered ‘on’ when rainfall exceeded a threshold of 2-5 mm in a 1-h period. Once initiated, the samplers were programmed for ‘non-uniform time’ sampling mode to collect a predetermined number of samples on the rising and falling limbs of the streamflow and GW hydrographs. In addition, following storm events, water samples were also recovered from rainfall and throughfall collectors (Inamdar and Mitchell, 2006). All samples were collected within 24 h of an event in 250-ml Nalgene bottles and samples were filtered with 0.5 μm filters prior to analysis.

Analyses performed on the water samples included DOC on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer and anions (SO₄, NO₃) on a Dionex IC. Mg and Si were determined on a Perkin Elmer ICP-AEC Div 3300 instrument. Total dissolved nitrogen (TDN) was determined using persulfate oxidation (Ameel et al., 1993) followed by colorimetric analysis on an autoanalyzer. Ammonium was also determined on an autoanalyzer.

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using the Berthelot reaction followed by colorimetric analysis. Concentrations of DON were estimated by subtracting NH$_4$ and NO$_3$ from TDN. If the sum of NH$_4$ and NO$_3$ equaled or exceeded the TDN value, DON concentration was recorded as zero (McHale et al., 2000). The overall estimate of analytical uncertainty for the DON analyses was $\pm 5–10\%$. The laboratory is a participant in the United States Geological Survey (USGS) performance evaluation program to ensure data quality. A system of calibration quality control (QC), detection QC, analytical blanks, and replicates is used with every set of samples (Mitchell et al., 2001).

It is important to emphasize that while GW data (elevation and chemistry) for this study is limited to only one set of hillslope (H7 and HS7) and wetland (R6 and RS5) wells, we recognize the importance of spatial variability in GW response, especially in glaciated catchments, and have characterized this variability in our previous work on the PPBW (Inamdar and Mitchell, 2006; 2007a, b). Previous data from multiple GW wells indicated distinct differences between hillslope and valley-bottom positions, and also within riparian and wetland locations in the valley bottom (Inamdar and Mitchell, 2006). However, data from hillslope and wetland wells in catchment S5 (the focus of this study) indicated that the two selected hillslope and wetland well locations were fairly representative of the GW responses for those positions (unpublished data). Since the focus of this study was on high-frequency within-event GW flushing, and since we were constrained by the number of ISCO samplers that were available (one each for the hillslope and the wetland position), only GW data from these two sampled positions were included.

Selection of storm events and hydrologic and solute data

A total of eight storm events were evaluated from June through September 2004. These eight events included: July 7, two events on July 14 (a and b), July 15, 18, and 19, and September 8 and 16. Data from all three ISCO samplers was available for all events except the event of July 15 for which data from the stream ISCO were not collected. Also, stream ISCO data for the long event of September 8 (30 h) were available for only the first half of the event. Total rainfall, peak rainfall, antecedent moisture conditions, streamflow (S5) discharge, and catchment runoff ratio (discharge divided by rainfall for event) were computed to characterize the hydrologic conditions for each event. Antecedent moisture conditions were computed using (1) summation of the precipitation amounts for 7 days prior to the event (antecedent precipitation index — AP$_7$); and (2) average of streamflow at outlet of S5 for 24 h prior to the event.

Our previous observations from PPBW (Inamdar et al., 2006; Inamdar and Mitchell, 2006, 2007b; 2008a) indicated that DOC and DON were derived from surficial sources (throughfall, forest floor, and surficial soils) and thus indicative of surficial flow paths while Mg, SO$_4$, and Si were derived from till and mineral weathering (Inamdar and Mitchell, 2008b) and thus representative of deeper hydrologic flow paths. Other studies in glaciated catchments in the northeast United States (Shanley and Peters, 1993; Hornbeck et al., 1997; Hill et al., 1999) have also reported that Mg and Si are derived primarily from till and deeper mineral soils, and GWs that are in contact with this strata typically have higher concentrations of these solutes. Correlations among the solutes and between solute concentrations, streamflow values, and GW depths were determined using the Spearman Rank test using the SPSS software (SPSS Inc.). Within-event temporal plots of GW depth, streamflow and solute concentrations were analysed for four of the eight storm events included in this study. These four events were selected since the temporal patterns of solutes for these events covered the range of responses across the eight storm events.

Previous model of hydrologic and solute response for the PPBW watershed

A conceptual model describing hydrologic flow paths and transport of DOC and N species has been developed for the PPBW (Inamdar and Mitchell, 2006; 2007a,b). The model was based on previous observations across four catchments in the PPBW — S1 (696 ha), S2 (3-4 ha), S3 (1-6 ha), and catchment S5 (1-6 ha, the focus of this study). The within-event GW flushing data presented here were not used in these previous studies. End member mixing analysis (EMMA) based on silica (Si), magnesium (Mg$^{2+}$), and DOC as tracers identified hillslope GW discharged at seeps (SGW), throughfall (THF), and riparian or wetland water (RW) as the key end members for stream chemistry. We hypothesize two GW systems in PPBW—one that discharged at hillslope seeps and another that recharged the valley-bottom wetlands (Inamdar and Mitchell, 2006). The upwelling of deeper (or regional) GWs resulted in wetlands and variably saturated areas in valley-bottom riparian locations. Local GW discharged at the hillslope seeps which then moved as overland flow over the wetlands and riparian areas on its way to the stream. Thus, while deep GWs in valley bottoms were distinct from seep water, we hypothesized that near-surface soil water in riparian and wetland areas would be some mixture of seep water and deeper valley-bottom GW. Runoff and streamflow generation in PPBW were characterized in three stages (Inamdar and Mitchell, 2007b). During baseflow (stage 1) stream water was primarily a mixture of hillslope seep and riparian or wetland GW. In the early part of the storm event and on the rising limb of the streamflow hydrograph (stage 2), stream water was a mixture of throughfall intercepted on saturated areas (saturation excess runoff), hillslope seep, and riparian water; (3) at peak discharge and on the recession limb of the hydrograph (stage 3) riparian or wetland water contributions reached their maximum as hydraulic gradients associated with subsurface hillslope runoff, and throughfall displaced riparian water to the stream. This model was validated using hydrometric data (Inamdar and
Mitchell, 2007b) and was also able to explain the concentrations of NO$_3$ and other solutes in stream waters (Inamdar and Mitchell, 2006). Stream-water DOC concentrations were primarily derived from throughfall and shallow riparian or wetland water. Hillslope seeps and throughfall had the highest concentrations of NO$_3$ in the catchments and thus were the primary regulators of NO$_3$ in stream waters.

RESULTS

Selected storm events and hydrologic response

The eight storm events that were evaluated for the period of June–September 2004 are indicated in Figure 2 along with the rainfall, wetland (R6), and hillslope (H7) GW depths and streamflow discharge (S5). Hydrologic characteristics associated with the eight events are presented in Table I. Of the eight events, the event of September 8, 2004 (#7 in Table I) produced the largest amount of rainfall (90 mm), was the longest in duration (30 h), and also generated the largest amount of streamflow discharge (33 mm). The event of July 7 resulted in a moderate amount of rainfall (27 mm) but was fairly intense and thus yielded the highest peak discharge value (event 1 in Table I). Three small sequential events occurred during July 14–15 with a gradual wetting-up of the catchment over this 2-day period. These events were again followed by two small sequential events on July 18–19. The three antecedent moisture indices—7-day antecedent precipitation (API$_7$), 24 h streamflow prior to event (24h-S5) and the 7-day antecedent average GW level at H7 (AGI$_7$—H7) provided differing results on the status of moisture conditions in the catchment prior to the events. However, considering all three indices, the event of September 8 had the driest antecedent moisture conditions. Based on API$_7$ and 24hr-S5, conditions were fairly wet prior to the second and third events of July 14–15. While API$_7$ and 24hr-S5 suggested dry antecedent conditions for the event of September 16, the water elevation at the hillslope well H7 was closest to the surface at 0-76 m below ground surface. High evapotranspiration and low rainfall during the period of August 15–24 resulted in streamflow ceasing to flow over the V-notch at S5. Streamflow over the V-notch was initiated again after August 24 and the catchment received large rainfall events following this dry period.

GW depths for the valley-bottom wetland well (R6) and the hillslope well (H7) revealed contrasting patterns over the study period (Figure 2). GW depths in the valley-bottom well were consistently within 0-15 m of the soil surface, even during the extremely dry period of August 15–24 when streamflow discharge at S5 ceased. During storm events, negative values of GW depths were observed in the wetland indicating water ponding above

<table>
<thead>
<tr>
<th>Event #</th>
<th>Date (2004)</th>
<th>Total precipitation (mm)</th>
<th>Precipitation duration (h)</th>
<th>Peak 10-min precipitation intensity (mm)</th>
<th>API$_7$ (mm)</th>
<th>24-h-S5</th>
<th>AGI$_7$—H7 (m)</th>
<th>Total runoff (mm)</th>
<th>Peak runoff (mm/h)</th>
<th>Runoff ratio = total runoff/total precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>July 7</td>
<td>27.4</td>
<td>7.3</td>
<td>4.5</td>
<td>13</td>
<td>0.26</td>
<td>1.07</td>
<td>5.4</td>
<td>4.2</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>July 14a</td>
<td>10.6</td>
<td>1.7</td>
<td>3.8</td>
<td>29</td>
<td>0.25</td>
<td>1.03</td>
<td>2.3</td>
<td>2.0</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>July 14b</td>
<td>7.3</td>
<td>3.3</td>
<td>1.3</td>
<td>37</td>
<td>0.34</td>
<td>1.02</td>
<td>2.8</td>
<td>0.8</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>July 15</td>
<td>10.9</td>
<td>4.1</td>
<td>1.8</td>
<td>20</td>
<td>0.44</td>
<td>1.02</td>
<td>5.2</td>
<td>1.2</td>
<td>0.47</td>
</tr>
<tr>
<td>5</td>
<td>July 18</td>
<td>3.3</td>
<td>0.6</td>
<td>1.5</td>
<td>55</td>
<td>0.32</td>
<td>0.94</td>
<td>1.9</td>
<td>0.9</td>
<td>0.57</td>
</tr>
<tr>
<td>6</td>
<td>July 19</td>
<td>8.9</td>
<td>2.2</td>
<td>3.0</td>
<td>10</td>
<td>0.31</td>
<td>0.91</td>
<td>2.7</td>
<td>1.5</td>
<td>0.30</td>
</tr>
<tr>
<td>7</td>
<td>Sep 8</td>
<td>90</td>
<td>30</td>
<td>2.2</td>
<td>4.6</td>
<td>0.05</td>
<td>1.11</td>
<td>3.3</td>
<td>2.8</td>
<td>0.37</td>
</tr>
<tr>
<td>8</td>
<td>Sep 16</td>
<td>7.9</td>
<td>0.3</td>
<td>4.3</td>
<td>0</td>
<td>0.13</td>
<td>0.76</td>
<td>0.7</td>
<td>1.1</td>
<td>0.09</td>
</tr>
</tbody>
</table>
the wetland soil surface. The consistently high GW in the wetland is in agreement with our previous assertion (Inamdar and Mitchell, 2006; 2007b) that deeper GWs recharged this wetland. In contrast, GW depths at the hillslope well (H7) showed considerable variation over the study period with GW depths fluctuating between 1-1 and 0-5 m from the soil surface. The event of September 8 produced the largest change in hillslope GW depths.

Concentrations in watershed sources for storm and non-storm conditions

Solute concentrations for various watershed sources during non-storm and storm event conditions are presented in Table II. Concentrations were averaged for the study period of June through September, 2004. Following conifer throughfall, DOC concentrations were highest for wetland GWs. Interestingly, DOC concentrations in the soil-water (the top 30 cm in the wetland) were much less than those measured in wetland GW suggesting that near-surface water in the wetland was lower in DOC. Not surprisingly, DOC concentrations in hillslope GW were less than in wetland GW. When baseflow concentrations were compared against the event values, wetland GW indicated a decrease in concentrations during events while the opposite was true for the hillslope GW well. While DOC concentrations in stream water during events were more than twice their non-storm values, they were still lower than the concentrations for wetland GW and conifer throughfall.

Similar to DOC, concentrations for DON were highest in conifer throughfall and wetland GW. Dominant sources of NO$_3$ in the catchment were conifer throughfall, hillslope GW, and hillslope seeps. In contrast to the high NO$_3$ concentrations in hillslope GWs, NO$_3$ concentrations in wetland GW were generally very low or negligible. Average NO$_3$ concentrations in wetland GW did not change much between baseflow and storm-event conditions; however, corresponding value for hillslope GW during events was more than twice the baseflow value. Wetland soil-water NO$_3$ values were only slightly greater than in GW suggesting that the saturated conditions in the wetland produced conditions favourable for denitrification. Nitrate in stream waters had intermediate concentrations and increased from non-storm to storm-event conditions. Silica concentrations in wetland GW were greater than for hillslope GW and seeps. Magnesium concentrations were highest for seep water followed by wetland soil-water and hillslope and wetland GWs, respectively. Similar to Mg, SO$_4$ concentrations were also highest for seeps, soil water, and hillslope GWs, but much lower for wetland GWs where SO$_4$ was likely reduced to sulfides. The intermediate concentrations of DOC, Si,

Table II. Comparison of average solute concentrations for wetland and hillslope groundwaters against other watershed sources. Concentrations were averaged over the period June–September 2004

<table>
<thead>
<tr>
<th>Compartment/ source</th>
<th>$N^a$</th>
<th>DOC (µmol l$^{-1}$)</th>
<th>DON (µmol l$^{-1}$)</th>
<th>NO$_3$$^b$ (µmol l$^{-1}$)</th>
<th>Si (µmol l$^{-1}$)</th>
<th>Mg (µmol, l$^{-1}$)</th>
<th>SO$_4$ (µmol, l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainfall</td>
<td>7</td>
<td>167(72)</td>
<td>10(4)</td>
<td>16(11)</td>
<td>0.9(0.7)</td>
<td>11.5(4.5)</td>
<td>48(27)</td>
</tr>
<tr>
<td>Deciduous throughfall</td>
<td>8</td>
<td>157(74)</td>
<td>13(9)</td>
<td>17(12)</td>
<td>2(0.6)</td>
<td>12(3)</td>
<td>51(23)</td>
</tr>
<tr>
<td>Conifer throughfall</td>
<td>8</td>
<td>972(441)</td>
<td>40(29)</td>
<td>57(51)</td>
<td>3(2)</td>
<td>27(22)</td>
<td>130(62)</td>
</tr>
<tr>
<td>Wetland soil water</td>
<td>7</td>
<td>285(71)</td>
<td>14(3)</td>
<td>5(4)</td>
<td>182(17)</td>
<td>1237(109)</td>
<td>416(283)</td>
</tr>
<tr>
<td>Hillslope seep water</td>
<td>8</td>
<td>99(28)</td>
<td>0.5(3)</td>
<td>31(12)</td>
<td>168(7)</td>
<td>1328(59)</td>
<td>338(44)</td>
</tr>
<tr>
<td>Stream water (S5)—non-event</td>
<td>8</td>
<td>160(31)</td>
<td>3(3)</td>
<td>12(6)</td>
<td>172(10)</td>
<td>1225(40)</td>
<td>362(41)</td>
</tr>
<tr>
<td>Stream water (S5)—event</td>
<td>84</td>
<td>405(100)</td>
<td>25(18)</td>
<td>19(8)</td>
<td>119(27)</td>
<td>810(190)</td>
<td>251(43)</td>
</tr>
<tr>
<td>Wetland groundwater (RS5)—non-event</td>
<td>8</td>
<td>611(89)</td>
<td>23(10)</td>
<td>0(0)</td>
<td>171(18)</td>
<td>882(61)</td>
<td>176(170)</td>
</tr>
<tr>
<td>Wetland groundwater (RS5)—event</td>
<td>84</td>
<td>573(123)</td>
<td>25(7)</td>
<td>0.1(1)</td>
<td>189(12)</td>
<td>898(41)</td>
<td>104(45)</td>
</tr>
<tr>
<td>Hillslope groundwater (HS7)—non-event</td>
<td>8</td>
<td>133(46)</td>
<td>28(32)</td>
<td>22(12)</td>
<td>164(16)</td>
<td>1177(100)</td>
<td>382(61)</td>
</tr>
<tr>
<td>Hillslope groundwater (HS7)—event</td>
<td>84</td>
<td>227(42)</td>
<td>15(10)</td>
<td>52(35)</td>
<td>179(8)</td>
<td>1192(67)</td>
<td>351(42)</td>
</tr>
</tbody>
</table>

Standard deviations are provided within brackets.

$^a$ Number of values averaged.

$^b$ Concentration per charge of the solute—same as µeq l$^{-1}$ (.)
Mg and SO₄ in wetland soil water are in agreement with our hypothesis (Inamdar and Mitchell, 2006) that wetland soil water was some mixture of the wetland GWs and hillslope seep waters, which traversed the wetland surface as saturation overland flow. Both wetland and hillslope GWs revealed a slight increase in average concentrations for Si and Mg from baseflow to storm event conditions, whereas the opposite was true for SO₄.

**Within-event groundwater depths and solute concentrations**

Within-event patterns of rainfall, streamflow discharge, GW depths, and solute concentrations for wetland and hillslope GW and stream water for the four selected events are presented in Figures 3–6. Concentrations of conifer and deciduous throughfall corresponding to the selected events are presented in Table III for comparison with the GW and stream water values. Temporal patterns of GW depths were fairly similar for all the events except the large event of September 8. Wetland GW started rising on the rising limb of the streamflow hydrograph and peaked after the peak in streamflow discharge (Figures 3–6). The change in wetland GW depths during events (Figures 3–6) was fairly small, from 0-08 m below the soil surface to 0-06 m above it (range = 0-14 m). In contrast, hillslope GWs registered a much larger change in GW depths (Figures 3–6) varying from 1-2 to 0-4 m below the soil surface (range = 0-8 m). The rise and peak in hillslope GWs was even more delayed than the wetland GWs and occurred much later on the recession limb of the streamflow hydrograph. The long event of September 8 was an exception where the peaks in hillslope GW depths occurred near the maximum streamflow discharge. Twenty hours prior to the event of September 8, GW depths in the wetland and hillslope positions were very low and at 0-1 and 1-1 m below ground surface, respectively (Figure 2). However, by the end of the event of September 8, the GW depths at both positions recorded the largest increase for the entire study period.

**Wetland groundwater concentrations.** DOC concentrations in the wetland GW decreased sharply as wetland GW depths rose to the surface and were at their minimum when GW depths were closest to the surface (Figures 3–6). Correlation analysis indicated a significant

![Figure 3. Rainfall, streamflow, groundwater depths (below soil surface), and solute concentrations in hillslope, wetland groundwaters, and stream water during the storm event of July 7, 2004. Concentrations of DOC, DON, and Si are in µmol l⁻¹ while others are in µmol, l⁻¹.](imageurl)
positive correlation (Table IV) between wetland GW depths and DOC concentrations. The decreases in DOC concentrations and the concomitant increases in wetland GW depths were most pronounced for the more intense events of July 7 and July 14 (Figures 3 and 4). Except for September 8, initial DOC concentrations were high (700–900 \( \mu \text{mol l}^{-1} \)). The initial DOC concentration for the event of September 8 was low (478 \( \mu \text{mol l}^{-1} \)), likely due to the effect of preceding events with precipitation amounts of 4.3 and 9.1 mm, which diluted GW DOC concentrations. The initial DOC value for the third (July 15) of the three sequential events on July 14–15 was much lower than that for the first event (July 14a) and the decrease in DOC concentrations for the third event was also muted (Figure 4). Other than the event of September 8, DOC concentrations for wetland GW were always greater than for the hillslope GW and the stream water. For the event of September 8, the stream-water DOC concentrations exceeded the wetland GW values.

DON concentrations for wetland GW did not follow the distinct dilution trends observed for DOC. Also, unlike DOC, the DON concentrations of wetland GW were not very different from the hillslope and streamwater values. DON concentrations also displayed considerable variability. Correlation between GW depth and DON concentrations was significant. Nitrate concentrations in wetland GWs were mostly zero or below detection limits across all events.

At PPBW, concentrations of Si, Mg, and SO\(_4\) were highest in GW sources and lowest in surficial sources such as throughfall and rainfall (Table II and Inamdar and Mitchell, 2006). Thus a decrease in concentrations of these solutes in stream or GWs, especially Si and Mg, indicated dilution by surficial water sources (Inamdar and Mitchell, 2006). For wetland GWs, a very slight dilution of Si, Mg, and SO\(_4\) concentrations was observed for the events of July 7, 14–15 and 19. While the concentrations of Si and Mg for the event of September 8 did not reveal a dilution trend, the concentrations of SO\(_4\) did decrease, especially, during the latter half of the event and during streamflow recession (Figure 5).

This asynchrony between SO\(_4\) and Mg and Si suggests

Table III. Concentrations of solutes in conifer and deciduous throughfall for the eight selected storm events

<table>
<thead>
<tr>
<th>Source</th>
<th>Event date</th>
<th>DOC (( \mu \text{mol l}^{-1} ))</th>
<th>DON (( \mu \text{mol l}^{-1} ))</th>
<th>NO(_3) (( \mu \text{mol l}^{-1} ))</th>
<th>Mg (( \mu \text{mol l}^{-1} ))</th>
<th>SO(_4) (( \mu \text{mol l}^{-1} ))</th>
<th>Si (( \mu \text{mol l}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conifer throughfall</td>
<td>July 7</td>
<td>839</td>
<td>62</td>
<td>39</td>
<td>15</td>
<td>103</td>
<td>2-5</td>
</tr>
<tr>
<td></td>
<td>July 14–15</td>
<td>712</td>
<td>30</td>
<td>27</td>
<td>15</td>
<td>84</td>
<td>2-5</td>
</tr>
<tr>
<td></td>
<td>July 19</td>
<td>649</td>
<td>20</td>
<td>31</td>
<td>23</td>
<td>139</td>
<td>3-5</td>
</tr>
<tr>
<td></td>
<td>September 8</td>
<td>677</td>
<td>21</td>
<td>16</td>
<td>11</td>
<td>69</td>
<td>0-7</td>
</tr>
<tr>
<td>Deciduous throughfall</td>
<td>July 7</td>
<td>107</td>
<td>20</td>
<td>17</td>
<td>8.2</td>
<td>52</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>July 14–15</td>
<td>156</td>
<td>17</td>
<td>16</td>
<td>11</td>
<td>43</td>
<td>0-7</td>
</tr>
<tr>
<td></td>
<td>July 19</td>
<td>127</td>
<td>7</td>
<td>24</td>
<td>10</td>
<td>78</td>
<td>1-7</td>
</tr>
<tr>
<td></td>
<td>September 8</td>
<td>58</td>
<td>8</td>
<td>5</td>
<td>9</td>
<td>13</td>
<td>2-5</td>
</tr>
</tbody>
</table>

Table IV. Spearman Rank correlation among groundwater depths and solute concentrations for hillslope and wetland groundwater during the eight selected storm events

<table>
<thead>
<tr>
<th>Source</th>
<th>N(^a)</th>
<th>WT</th>
<th>DOC</th>
<th>DON</th>
<th>NO(_3)</th>
<th>Mg</th>
<th>SO(_4)</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hillslope groundwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WT</td>
<td>83</td>
<td>1.0</td>
<td>-0.638(^c)</td>
<td>0.183</td>
<td>-0.824(^e)</td>
<td>-0.510(^e)</td>
<td>0.527(^c)</td>
<td>-0.403(^c)</td>
</tr>
<tr>
<td>DOC</td>
<td>83</td>
<td>1.0</td>
<td>-0.638(^c)</td>
<td>0.112</td>
<td>-0.739(^c)</td>
<td>0.254(^b)</td>
<td>-0.516(^e)</td>
<td>0.104</td>
</tr>
<tr>
<td>DON</td>
<td>83</td>
<td>0.183</td>
<td>0.112</td>
<td>1.0</td>
<td>-0.072</td>
<td>-0.296(^b)</td>
<td>-0.083</td>
<td>-0.198</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>83</td>
<td>-0.824(^c)</td>
<td>0.739(^c)</td>
<td>-0.072</td>
<td>1.0</td>
<td>0.616(^b)</td>
<td>-0.535(^c)</td>
<td>0.329(^c)</td>
</tr>
<tr>
<td>Mg</td>
<td>83</td>
<td>-0.510(^c)</td>
<td>0.254(^b)</td>
<td>-0.296(^c)</td>
<td>0.616(^c)</td>
<td>1.0</td>
<td>-0.273(^b)</td>
<td>0.641(^c)</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>83</td>
<td>-0.527(^c)</td>
<td>-0.516(^c)</td>
<td>-0.083</td>
<td>-0.535(^c)</td>
<td>-0.273(^b)</td>
<td>1.0</td>
<td>-0.550(^b)</td>
</tr>
<tr>
<td>Si</td>
<td>83</td>
<td>-0.403(^c)</td>
<td>0.104</td>
<td>-0.198</td>
<td>0.329(^c)</td>
<td>0.641(^c)</td>
<td>-0.550(^b)</td>
<td>1.0</td>
</tr>
<tr>
<td>Wetland groundwater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WT</td>
<td>84</td>
<td>1.0</td>
<td>0.512(^c)</td>
<td>0.553(^c)</td>
<td>0.190</td>
<td>-0.131</td>
<td>-0.512(^c)</td>
<td>0.478(^c)</td>
</tr>
<tr>
<td>DOC</td>
<td>84</td>
<td>0.512(^c)</td>
<td>1.0</td>
<td>0.379(^c)</td>
<td>0.189</td>
<td>-0.306(^d)</td>
<td>-0.009</td>
<td>0.632(^c)</td>
</tr>
<tr>
<td>DON</td>
<td>84</td>
<td>0.553(^c)</td>
<td>0.379(^c)</td>
<td>1.0</td>
<td>0.106</td>
<td>-0.516(^c)</td>
<td>-0.494(^b)</td>
<td>0.234(^b)</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>84</td>
<td>0.190</td>
<td>0.189</td>
<td>0.106</td>
<td>1.0</td>
<td>0.028</td>
<td>-0.046</td>
<td>0.092</td>
</tr>
<tr>
<td>Mg</td>
<td>84</td>
<td>-0.131</td>
<td>-0.306(^d)</td>
<td>-0.516(^c)</td>
<td>0.028</td>
<td>1.0</td>
<td>0.339(^c)</td>
<td>-0.026</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>84</td>
<td>-0.512(^c)</td>
<td>-0.009</td>
<td>-0.494(^c)</td>
<td>-0.046</td>
<td>0.339(^c)</td>
<td>1.0</td>
<td>-0.175</td>
</tr>
<tr>
<td>Si</td>
<td>84</td>
<td>0.478(^c)</td>
<td>0.632(^c)</td>
<td>0.234(^b)</td>
<td>0.092</td>
<td>-0.026</td>
<td>-0.175</td>
<td>1.0</td>
</tr>
</tbody>
</table>

\(^{a}\) Number of samples.
\(^{b}\) Correlation is significant at the 0.05 level 2-tailed.
\(^{c}\) Correlation is significant at the 0.01 level 2-tailed.
that dilution was likely not the reason for the continued decrease in SO₄ concentrations through event recession. Unlike Si and Mg, SO₄ is affected by redox conditions such as those found in wetlands (Reddy and DeLaune, 2008). The consistently high GW and very low NO₃ concentrations corroborate the importance of chemical reduction processes in these wetlands. The very wet conditions associated with the event of September 8 may have enhanced the reducing conditions in the wetland leading to dissimilatory SO₄ reduction to sulfide and the consequent drop in SO₄. Correlations between wetland GW depths and solute concentrations were strong and significant for SO₄ (Table IV).

**Hillslope GW concentrations.** In a trend opposite to that observed for wetland GW, DOC concentrations in hillslope GWs increased slightly as hillslope GW depths approached the soil surface. The increase in concentrations was more pronounced for the intense events of July 7 and 14a, muted for the event of July 15, and not apparent for the event of September 8. However, DOC concentrations for the hillslope GWs were much less than the wetland GW values. Even the lowest DOC concentrations in the wetland GW were greater than the highest concentrations for the hillslope GW. Overall, there was a significant and strong correlation between DOC concentrations and GW depths for the hillslope position (Table IV).

DON concentrations for hillslope GWs did not display a consistent pattern and the correlation with GW depths was insignificant. In contrast to the wetland GW, NO₃ concentrations in hillslope GWs were much greater and revealed distinct trends. Nitrate concentrations in hillslope GW increased as GW rose to the surface (depths decreased) and peaked at or after the peak in GW. The correlation between hillslope NO₃ concentrations and GW depths was also strong and significant. Furthermore, NO₃ concentrations in hillslope GW for the event of September 8 were twice (or more) the corresponding values recorded for the other events. Nitrate concentrations for the September 8 event ranged between 80 and 146 µmol l⁻¹ while the values for the other events were between 5 and 70 µmol l⁻¹ (Figure 6). A marked increase in NO₃ concentrations was seen for the event of July 14, which was not replicated for the event of July 15 suggesting a supply limitation or exhaustion of the NO₃ pool in hillslope GWs.
Similar to wetland GWs, concentrations of Si, Mg, and SO\textsubscript{4} in hillslope GWs displayed a very slight dilution during the events of July 7, 14–15, and 19. However, the dilution pattern was not replicated for the event of September 8. On the contrary, Mg concentrations in hillslope GWs increased slightly as GW depths increased. Overall, all three solutes, Mg, Si, and SO\textsubscript{4} were significantly correlated with hillslope GW depths.

*Stream-water solute concentrations.* DOC concentrations in stream water showed a consistent pattern across all events with an increase in concentrations on the rising limb of the hydrograph, a peak in DOC concentration after maximum discharge peak followed by a gradual decrease in concentration. Hence, the peak in stream DOC concentrations occurred at about the same time when wetland GW depths were closest to the surface and wetland DOC concentrations in GW were at their minimum suggesting that a portion of wetland DOC had been transferred to the stream. In terms of magnitude, stream-water DOC concentrations were always less than the wetland values but greater than the hillslope GW DOC concentrations and approached the wetland DOC values during peak concentrations. Among the four events (Figures 3–6), stream-water DOC concentrations recorded a maximum concentration of 794 µmol l\textsuperscript{-1} for the event of September 8, while the concentrations for the other events ranged between 400 and 550 µmol l\textsuperscript{-1}. The peak stream-water DOC concentration for the September 8 event was high enough to exceed the corresponding DOC concentrations for wetland (Figure 6) as well as conifer throughfall (Table III). It should be noted that while stream-water DOC concentrations increased dramatically, wetland GW DOC concentrations recorded their lowest values for the September 8 event. Overall, the correlation between streamflow discharge and DOC concentrations was significant (Table V).

Again, DON concentrations for stream water did not follow the distinct trends observed for DOC and were not correlated with DOC (Table V). Stream-water DON concentrations also did replicate the large increases observed for DOC for the September 8 event. Nitrate concentrations for stream water increased on the rising limb of the hydrograph, peaked at or before the
maximum discharge peak, followed by decreasing concentrations. The increase in NO3 concentrations was however muted for the second of the sequential events of July 14 (Figure 4), suggesting that NO3 resources had been depleted during these events. While the NO3 concentrations for hillslope GW exhibited a large relative increase during the September 8 event, the same level of change was not observed in stream waters. This clearly suggests that NO3 concentrations in stream water were not being influenced by changes in hillslope GW concentrations. Concentrations of NO3 in stream water were significantly correlated with discharge values. In terms of magnitude, the peak NO3 concentrations in stream water were less than the peak values observed for hillslope GWs.

In contrast to GWs, concentrations of Si, Mg, and SO4 in stream waters showed more pronounced dilution patterns suggesting greater contributions of throughfall and rainfall to stream waters during events. During peak discharge, concentrations of all the three solutes were much less than GW values, but approached GW values towards the end of each event (Figures 3–6). Concentrations for all three solutes were significantly correlated with streamflow discharge.

DISCUSSION

What is the temporal pattern of solute flushing in groundwater during storm events at the wetland and hillslope locations?

The wetland and hillslope positions revealed very clear differences in GW flushing of solutes during storm events. We argue that these differences stem from the differences in hydrologic flowpaths and biogeochemical
conditions influencing the solutes at these locations. Temporal changes in GW depths in the wetlands were much less than on the hillslopes. Storm-event DOC concentrations in wetland GW remained high relative to the hillslope, but were diluted as GW approached the surface. Such dilution was not evident for Mg, Si, and SO\(_4\) in wetland suggesting that this dilution of DOC was not due to contributions from throughfall and/or precipitation. The watershed source that was closest to wetland GW was wetland soil water. While the concentrations of DOC in wetland soil water were lower than the corresponding values for GW (Table II), the concentrations of Si, Mg, and SO\(_4\) in soil water were similar to those for GW. Thus, we hypothesize that the dilution in DOC values observed in wetland GW during the events was predominantly due to wetland soil water being displaced into the GW wells. Soil-water contributions would also explain the extremely low concentrations of NO\(_3\) in GWs, which continued to persist through storm events. A decrease in DOC concentrations in wetland GWs during storm events has also been reported by Schiff \textit{et al.} (1998) who attributed it to the dilution of GWs by precipitation and shallow GWs. Similarly, Hinton \textit{et al.} (1998) also suggested that wetland DOC concentrations may decrease during storm events as pre-event water with high DOC is flushed out and replaced with event water with lower DOC content. This DOC flushing response for wetland GWs has been shown to differ from riparian GWs where DOC concentrations continued to increase as GWs rose in fresh, previously untapped DOC pools in upper soil horizons (Hinton \textit{et al.}, 1998).

The GW flushing response at the hillslope location was, however, very different. Not only did the hillslope GW depths show large changes during events but the peak in GW depths occurred much later during the storm events. In contrast to wetland GW, DOC concentrations for hillslope GW increased slightly as the GW depths rose to the surface, followed by a decrease in concentrations later in the event. Within the hillslope, Si, Mg, and SO\(_4\) concentrations in hillslope GWs decreased slightly as hillslope GWs approached the soil surface. The minimum in Si, Mg, and SO\(_4\) concentrations in these GWs occurred when DOC concentrations were close to their maximum. However, the most distinct response for the hillslope GWs was the large increase in NO\(_3\) concentrations during the events. The NO\(_3\) concentrations increased together with DOC concentrations, but highest NO\(_3\) concentrations occurred much later in the event when the Si, Mg, and SO\(_4\) concentrations were also high. This suggests that water event (throughfall or precipitation) was not the source of NO\(_3\). In addition, two unique responses were observed for NO\(_3\) in hillslope GWs—(1) NO\(_3\) concentrations did not display the same level of increase for sequential events, e.g. the event July 15 had lower NO\(_3\) increase compared to the preceding events of July 14; and (2) NO\(_3\) concentrations were nearly doubled for the long and large event of September 8 which occurred after an extended dry period. These two observations suggest NO\(_3\) accumulation on the hillslope and that the level of NO\(_3\) accumulation was affected by the length of time between events.

We hypothesize that the water entering the hillslope well during events was some mixture of hillslope GWs moving down from the upper slopes (over the impeding clay layer) and pre-event soil water held in the unsaturated soil column (just above the saturated soil layer). In addition, contributions of throughfall/rainfall could have also occurred early in the event via preferential flow paths (e.g. macro-pores), but these amounts were likely small. We believe that soil water held in the unsaturated soil column was mobilized during rain events and contributed to the hillslope GW flux. The contribution of unsaturated soil water for hillslope subsurface flux during storm events has previously been highlighted by a number of researchers (Jardine \textit{et al.}, 1990; Luxmoore and Ferrand, 1993; Anderson \textit{et al.}, 1997). The hillslope soil water would likely be similar to the saturated zone GW in terms of Si, Mg, SO\(_4\) concentrations and yet could explain the high NO\(_3\) concentrations observed during the events. The NO\(_3\) was likely derived from mineralization and nitrification of organic N occurring in the unsaturated soil column during the dry periods between events. This accumulated NO\(_3\) was then flushed into the GWs as hillslope soil waters were mobilized and displaced by infiltrating event water. High rates of nitrification on well-drained hillslope soils (Ohrui \textit{et al.}, 1999) and its contribution to GWs has been demonstrated previously (McHale \textit{et al.}, 2002; Schiff \textit{et al.}, 2002). Schiff \textit{et al.} (2002) reported high NO\(_3\) concentrations in hillside GWs and attributed it to the supply of NO\(_3\) by nitrification and steep slope gradients that expedited the movement of this NO\(_3\) to GWs. The supply of NO\(_3\) by nitrification would also explain the depletion of NO\(_3\) for sequential events and the increased concentrations of NO\(_3\) following long dry periods. The soil-water contributions would also explain the slight increases in DOC, since we expect that DOC would indeed be higher for the upper soil layers on the hillslope.

These observations highlight a dramatic difference between flushing responses at the wetland and hillslope positions (illustrated in Figure 7). We believe that topography and biogeochemical conditions at these positions were critical in shaping the flushing responses. The valley-bottom location, flat topography, and contributions from deep GWs resulted in a continuously saturated soil profile in the wetland. The saturated conditions in turn resulted in NO\(_3\) being lost to denitrification and thus a complete absence of a flushing response for NO\(_3\). However, the same saturated conditions facilitated DOC accumulation in wetland GWs and the pronounced flushing response for DOC. The conditions in the wetland were also anaerobic (reducing) enough to lower the concentrations of sulfate (via reduction to sulfide). In contrast, the well-drained soil profile of the hillslope facilitated production of NO\(_3\) and resulted in a distinct flushing response for NO\(_3\). Unlike the wetland, where near-surface water was important for solute flushing, the well-drained...
soil profile resulted in a greater role of inter-flow or subsurface flow for solute flushing. Hinton et al. (1998) have argued that leaching and flushing of DOC at the soil surface would be more important for wetlands while GW flowpaths would play a greater role in relatively well-drained riparian settings. Our observations suggest a similar difference in GW flushing between wetland and hillslope locations.

How do the storm-event patterns of groundwater flushing at the wetland and hillslope locations relate to the solute chemistry in stream waters at the catchment outlet?

Storm-event chemistry at the three locations—stream water at the catchment outlet, hillslope GW, and wetland GW highlight the variety of flushing responses that can be observed within a catchment. In our original model for PPBW (Inamdar and Mitchell, 2006) we had proposed that stream water exiting the catchments was likely a mixture of seep water, throughfall, and riparian or wetland water, with the relative contributions from these end members varying during the course of the event. We had also argued that wetland areas (as in catchment S5) compared with riparian zones would allow for a greater expression of event waters (throughfall/rainfall) that are intercepted on the wetland surface. The depressions in Si, Mg, and SO₄ concentrations for S5 stream water clearly attest to substantial contributions of event water. The peak in stream water DOC concentrations when wetland GW elevations were at their highest (and when wetland GW DOC values were at their lowest) attests to the influence of the wetland on stream-water DOC. We hypothesize that wetland was a source of DOC as wetland GWs rose and it connected hydrologically to the stream network. Following our original model, DOC contributions to the stream were likely some mixture of wetland soil water, GW, and throughfall intercepted on the wetland surface. However, the peak in stream-water DOC concentrations during the event of September 8 was much higher (Figure 5) and even exceeded the wetland GW values. We believe this could have resulted from DOC from additional isolated and disconnected saturated areas which were located in the valley-bottom and hillslope-bench areas (Inamdar and Mitchell, 2006). The large amount of rainfall and the substantial rise in GW elevations during the event of September 8 likely resulted in these relatively isolated saturated areas to become hydrologically connected to the drainage network and provide an additional source of DOC.

A comparison of storm-event chemistry of hillslope GWs and stream water suggests that hillslope GWs likely did not have any immediate influence on stream-water chemistry. While hillslope GWs displayed high NO₃ concentrations late in the event, the same pattern was not observed for the streams. More interestingly, wetland GWs that were immediately downslope of the hillslope had virtually no (non-detect) NO₃ concentrations. This would suggest that if NO₃-rich hill-slope GWs entered the wetland soil profile, NO₃ was lost rapidly via denitrification. Thus, the only way that hillslope GW could influence stream chemistry was if it was released as surface water at seeps where runoff moved over the wetland surface to the stream (Inamdar and Mitchell, 2006). These observations suggest that while a large variety of flushing responses may be observed in a catchment, only a few of these responses are manifested in the runoff chemistry at the catchment outlet.
How do the flushing responses vary among the solutes?

This study also highlighted some very important differences in flushing responses among the various solutes for the three locations. Obviously, these responses were dictated by the reactive nature of the solutes, the biogeochemical conditions, and the hydrologic flow paths responsible for flushing. While DOC displayed consistent and gradual dilution or increase during the events, the same was not observed for DON. DON concentrations also displayed much more variability compared with DOC. Interestingly, these differences in DOC and DON were observed for all three positions with varying redox conditions, flow paths, and solute sources. Similarly, while there was a large increase in stream water DOC for the large event of September 8 (which exceeded the corresponding wetland and hillslope GW values), the same level of increase was not observed for DON. This clearly indicates that there are important differences in the factors and processes controlling the release and transport of these solutes. We have previously (Inamdar and Mitchell, 2007a; Inamdar et al., 2008a) attributed these differences to the differential sources of DOC and DON in the catchment and the likely influence of DON quality (hydrophilic vs hydrophobic fractions; Qualls and Haines, 1991).

Among the six solutes considered in our study, the sequential events had the greatest influence on the flushing responses of DOC and NO₃. Flushing patterns for both DOC and NO₃ suggested depletion in the solute pools with sequential storm events. Between NO₃ and DOC, however the concentrations of NO₃ in hillslope GWs were nearly doubled for the event of September 8, which followed an extended dry period. However, the same level of increase was not observed for DOC. Clearly, this reveals important differences in the mineralization, accumulation, and mobilization of DOC and NO₃. Similarly, while Mg, Si, and SO₄ were derived from the same source (GW), the reactive behaviour of SO₄ resulted in important differences in the patterns of SO₄ with Mg and Si. The decrease in SO₄ during the event of September 8 (Figure 6) was likely due to a reduction of SO₄ to sulfide brought on by enhanced reducing conditions associated with the long rain event. This response can also be characterized as a ‘hot moment’ (McClain et al., 2003) for sulfate which has been defined as a short period of time that can significantly impact the concentration or flux of solutes. Interestingly, the reduction in sulfate during the September 8 event was not replicated at the hillslope position, suggesting that this reduction was confined to the more anaerobic wetland environment.

CONCLUSIONS

This study is the first to characterize the high-frequency flushing of solutes in GWs during storm events. We found that solute flushing responses can not only differ dramatically between the stream and GW but also among GWs at different locations within the catchment. We attributed these differences to the differences in hydrologic flow paths, topography, and the biogeochemical processes influencing the solute concentrations at these locations. Furthermore, while a variety of flushing responses may occur in the catchment, only a subset of those may influence the eventual flushing of solutes in streamflow at the catchment outlet. The influence of the flushing responses of various catchment units (e.g. riparian areas, wetlands, or hillslopes) on streamflow will likely be dictated by the hydrologic connectivity of these units to the stream network. This suggests that simply looking at the flushing behaviour of stream waters may not provide an idea of the range of solute flushing responses in the catchment. Alternatively, if the goal is to only predict the flushing response at the catchment outlet, we need not know the flushing responses for all catchment locations or units. Only catchment locations hydrologically connected to the stream need to be evaluated. This study also highlighted that the availability (e.g. negligible NO₃ in wetlands vs high NO₃ in the well-drained hillslope soils) and the reactive behaviour of the solutes (e.g. the reduction of SO₄ during the long event) may be critical in shaping their flushing response to storm events. Thus, we need to be extremely cautious in extending flushing models across solutes even if they are derived from similar sources and flow paths.

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REFERENCES


