Dynamics of stream nitrate sources and flow pathways during stormflows on urban, forest and agricultural watersheds in central Pennsylvania, USA

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Abstract:
Understanding the influence of storm events on nitrate (NO3−) dynamics is important for efficiently managing NO3− pollution. In this study, five sites representing a downstream progression of forested uplands underlain by resistant sandstone to karst lowlands with agricultural, urban and mixed land-use was established in Spring Creek, a 201 km2 mixed-land-use watershed in central Pennsylvania, USA. At each site, stream water was monitored during six storm events in 2005 to assess changes in stable isotopes of NO3− (δ15N-NO3− and δ18O-NO3−) and water (δ18O-H2O) from baseflow to peakflow. Peakflow fractions of event NO3− and event water were then computed using two-component mixing models to elucidate NO3− flow pathway differences among the five sites. For the forested upland site, storm size appeared to affect NO3− sources and flow pathways. During small storms (<35 mm rainfall), greater event NO3− fractions than event water fractions indicated the prevalence of atmospheric NO3− source contributions at peakflow. During larger storms (>35 mm rainfall), event NO3− fractions were less than event water fractions at peakflow suggesting that NO3− was flushed from stored sources via shallow subsurface flow pathways. For the urbanized site, wash-off of atmospheric NO3− was an important NO3− source at peakflow, especially during short-duration storms where event water contributions indicated the prevalence of overland flow. In the karst lowlands, very low fractions of event water and even lower fractions of event NO3− at peakflow suggested the dominance of ground water flow pathways during storms. These ground water flow pathways likely flushed stored NO3− sources into the stream, while deep soils in the karst lowlands also may have promoted NO3− assimilation. The results of this study illustrated how NO3− isotopes and δ18O-H2O could be combined to show key differences in water and NO3− delivery between forested uplands, karst valleys and fully urbanized watersheds. Copyright © 2009 John Wiley & Sons, Ltd.

KEY WORDS nitrate sources; hydrologic flow paths; karst hydrology; stable isotopes; land-use; water quality

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INTRODUCTION
Excess nitrogen (N) in streams and rivers has resulted in large-scale eutrophication of coastal waters in the United States (Carpenter et al., 1998; Howarth et al., 2002; Boyer and Howarth, 2008), especially in estuarine systems such as the Chesapeake Bay (Boesch et al., 2001). Although it is widely accepted that much of this N is exported as soluble nitrate (NO3−) during baseflow conditions (Schilling and Zhang, 2004), stormflow periods also are important because the addition of new water sources during storm events may mobilize new and distinctly different sources of NO3− than those at baseflow. Furthermore, other factors such as land-use (Jordan et al., 1997) and geologic differences (Miller et al., 1997) will exert unique influences on the mobilization and subsequent hydrologic transport of NO3− to streams during events. Understanding NO3− sources and flow pathways during baseflow and stormflow periods in watersheds with mixed land-use and geology is of principal interest to those managing NO3− pollution.

In terms of understanding NO3− sources, valuable insight has been gained by using NO3− isotopes (δ15N-NO3− and δ18O-NO3−) (Kendall, 1998; Kendall et al., 2007) to trace NO3− in mixed land-use watersheds (Chang et al., 2002; Rock and Mayer, 2004; Segal-Rozenhaimer et al., 2004; Panno et al., 2006; 2008; Anisfeld et al., 2007; Burns et al., 2009). In general, sources of NO3− derived from sewage and animal manure are typically more enriched in δ15N-NO3− (0 to +25‰) than NO3− originating from atmospheric deposition, fertilizers and microbial nitrification in soils (−10 to +7‰) (Kendall, 1998; Kendall et al., 2007). Values of δ18O-NO3− are typically very positive in atmospheric NO3− (greater than +30‰ using sealed glass tube method—Kendall et al., 2007; greater than +60‰ using denitrifier method—Elliott et al., 2007), which helps to distinguish NO3− in wet and dry deposition from NO3− formed via nitrification in soils (−10 to +15‰) (Kendall, 1998; Kendall et al., 2007).

Measuring changes in NO3− stable isotopes at baseflow and again at peakflow during storms on watersheds with different land-use would help paint a more complete picture of NO3− dynamics in streams. For example, studies by Ging et al. (1996) and Silva et al. (2002) showed
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that $\delta^{15}$N-NO$_3^-$ was a useful tracer of NO$_3^-$ from sewage at baseflow, whereas increases in $\delta^{18}$O-NO$_3^-$ during storms were useful for inferring the importance of atmospheric NO$_3^-$ in direct runoff from impervious surfaces during stormflow in two heavily urbanized watersheds in Austin, Texas. More recent studies by Anisfeld et al. (2007) and Burns et al. (2009) have also suggested that $\delta^{18}$O-NO$_3^-$ may indicate important shifts to atmospheric NO$_3^-$ sources during high flows in urban and suburban watersheds. Similar studies in forested watersheds (Ohte et al., 2004; Sebestyen et al., 2008) have used $\delta^{18}$O-NO$_3^-$ to show the importance of atmospheric NO$_3^-$ in stream water during high flows following snowmelt runoff periods. Although changes in NO$_3^-$ stable isotopes during storm events offer an opportunity to track important shifts in NO$_3^-$ sources, these shifts only yield ancillary information on NO$_3^-$ flow pathways and delivery mechanisms.

In this study, we apply traditional hydrograph separation using $\delta^{18}$O-H$_2$O (Sklash, 1990; Pionke et al., 1993; DeWalle and Pionke, 1994) and extend this idea to NO$_3^-$ stable isotopes to simultaneously calculate and compare event fractions of water and NO$_3^-$ during storm events. We define event NO$_3^-$ as the fraction of new NO$_3^-$ added to the stream at peakflow during an individual storm event. By directly comparing estimated fractions of event water and event NO$_3^-$ for the same storm events, we can ascertain potentially important differences in flow pathways for water and NO$_3^-$ among watersheds with different land-use and geology. For example, we hypothesize that additions of wet NO$_3^-$ deposition and wash-off of dry NO$_3^-$ deposition during storms may result in fractions of event NO$_3^-$ that are greater than fractions of event water. In contrast, assimilative processes and flushing of stored NO$_3^-$ sources that have undergone biogeochemical transformations may result in fractions of event NO$_3^-$ that are less than fractions of event water. Our intent was to combine information on event NO$_3^-$ and event water at peakflow with observed changes in NO$_3^-$ stable isotopes from baseflow to peakflow to shed additional light on NO$_3^-$ flow pathways and delivery mechanisms in mixed land-use watersheds during storms.

MATERIALS AND METHODS

Spring Creek watershed

The Spring Creek watershed is located in central Pennsylvania and is a tributary to the Susquehanna River, which eventually flows into the Chesapeake Bay estuary (Figure 1). Central Pennsylvania has a humid, temperate climate, with mean daily temperatures ranging from $-1^\circ$C during the winter months to $19^\circ$C during the summer months. During 2005, the annual precipitation at State College, Pennsylvania, totalled 1043 mm, which was slightly more than the long-term mean annual precipitation of 970 mm (based on 80 years of data: 1926–2005) (Pennsylvania State Climatologist, 2007). Despite receiving slightly more than the average annual precipitation amount, streamflow at the United States Geological Survey (USGS) gauge in Houserville, Pennsylvania (Gauge# 01546400) (see Figure 1 for location), was approximately 39 cm in 2005, which was slightly less than the long-term mean annual flow of 42 cm based on 21 years of data (1985–2005).

Spring Creek is situated within the Appalachian Section of the Ridge and Valley Physiographic Province, which is characterized by sandstone and shale ridges (elevation ~550–600 m) and wide valleys with karst terrain.
underlain by carbonate geology (elevation ~300–400 m). The complex geology found within the Spring Creek watershed is an important factor that affects the local hydrology. Upland forested watersheds have shallow soils with high infiltration capacities that are underlain by low permeability sandstone and shale bedrock. During storm events, runoff in these upland watersheds is typically generated via subsurface flow pathways that drain laterally downslope along the bedrock surface. This lateral subsurface flow can eventually produce saturation-excess overland flow at the base of hillslopes and in the near-stream zone (Fulton et al., 2005). In contrast, streams that drain the karst valleys are fed by a combination of mountain runoff from the forested ridges and large ground water spring inputs (Fulton et al., 2005; O’Driscoll and DeWalle, 2006). Due to the highly soluble limestone and dolomite bedrock, a significant portion of the carbonate valley aquifer is of the conduit flow type (Fulton et al., 2005), which is characterized by large subsurface drainage pipes of considerable diameter (Shuster and White, 1971; White, 1988). These pipes can store and slowly release significant quantities of ground water during and several days after a storm event (White and Reich, 1970). During dry periods in the late summer and fall months, perched and losing streams are very common in the karst valley (O’Driscoll and DeWalle, 2006), especially in headwater regions.

Spring Creek is a mixed land-use watershed, with forests covering the ridges and a mixture of agriculture, residential and industrial land-use in the valleys. The watershed is undergoing rapid urbanization, with agricultural land-use being replaced by urban and suburban land-use. As a result of the continued development, a variety of significant point and nonpoint sources of NO\textsubscript{3}\textsuperscript{−} pollution exist within the Spring Creek watershed, including one sewage treatment plant (University Area Joint Authority—UAJA) and runoff from agricultural and urban lands. Several miles of Spring Creek are listed on the Federal 303(d) list for impairments due to nutrient pollution from point sources, urban runoff and crop-related agriculture (Pennsylvania Department of Environmental Protection, 2008). Sengle (2002) has shown that the main-stem of Spring Creek typically has NO\textsubscript{3}\textsuperscript{−} concentrations ranging from 10 to 20 mg l\textsuperscript{−1} (2.3–4.5 mg l\textsuperscript{−1} as NO\textsubscript{3}\textsuperscript{−}-N).

Watershed sampling design

The study was designed to take advantage of differences in land-use, geology and potential NO\textsubscript{3}\textsuperscript{−} sources that existed within the upper portion of the Spring Creek watershed. Five watershed sampling sites were selected within the upper Spring Creek watershed (Figure 1), which included three tributary streams with uniquely different land-use (forest, agricultural and urban) as well as two downstream mixed land-use sites located on the main-stem of Spring Creek (Table I). This design allowed us to compare tracer values and NO\textsubscript{3}\textsuperscript{−} sources among watersheds with different land-use and bedrock geology. Study sites were established on the following watersheds: (1) Galbraith Gap Run, a 13 km\textsuperscript{2} forested watershed (95% of land area in forest); (2) Cedar Run, a 45 km\textsuperscript{2} agricultural watershed (66% of land area in row crops and pasture); (3) Thompson Run, an 11 km\textsuperscript{2} urban watershed (80% of land area with at least 30% impervious cover); (4) Spring Creek at Houserville, a 150 km\textsuperscript{2} mixed land-use watershed; and (5) Spring Creek at Rock Road, a 201 km\textsuperscript{2} mixed land-use watershed that is 3-7 km downstream of the site at Houserville (Figure 1) and is influenced by UAJA-treated municipal sewage effluent. The forested watershed is underlain by sandstone and shale bedrock (94%), whereas carbonate bedrock is the dominant geology in the agricultural (88%), urban (100%) and mixed land-use watersheds at Houserville (76%) and Rock Road (81%) (Berg et al., 1980). The addition of the second mixed land-use site at Rock Road allowed us to assess the impacts of sewage discharges on NO\textsubscript{3}\textsuperscript{−} concentrations and stable isotopes in Spring Creek. Treated

Table I. Information on sampling sites, predominant land-use classification, watershed area (km\textsuperscript{2}) and land-use\textsuperscript{a} distribution for each of the sites monitored in the upper Spring Creek watershed

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Site name</th>
<th>Area (km\textsuperscript{2})</th>
<th>Forest (%)</th>
<th>Agriculture (%)</th>
<th>Impervious cover (%)</th>
<th>Other cover (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galbraith Gap Run</td>
<td>Forested watershed</td>
<td>13</td>
<td>78</td>
<td>5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Cedar Run</td>
<td>Agricultural watershed</td>
<td>45</td>
<td>26</td>
<td>0</td>
<td>1</td>
<td>5–30</td>
</tr>
<tr>
<td>Thompson Run</td>
<td>Urban watershed</td>
<td>11</td>
<td>7</td>
<td>0</td>
<td>1</td>
<td>5–30</td>
</tr>
<tr>
<td>Spring Creek at Houserville</td>
<td>Mixed land-use at Houserville</td>
<td>150</td>
<td>34</td>
<td>2</td>
<td>4</td>
<td>31–74</td>
</tr>
<tr>
<td>Spring Creek at Rock Road</td>
<td>Mixed land-use at Rock Road</td>
<td>201</td>
<td>32</td>
<td>1</td>
<td>3</td>
<td>16</td>
</tr>
</tbody>
</table>

Decid., Deciduous Forest; Conif., Coniferous Forest.
\textsuperscript{a} Based on information obtained from 2005 Pennsylvania land-use/land-cover dataset using the Anderson classification system (see: http://www.pasda.psu.edu).
Table II. Information on start and end times, antecedent precipitation (past month), observed precipitation type, precipitation amount and storm characterization for the six storms sampled during 2005

<table>
<thead>
<tr>
<th>Storm number/date</th>
<th>Description</th>
<th>Duration (h)</th>
<th>Antecedent precipitation—past month (mm)</th>
<th>Precipitation characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 23 March 2005</td>
<td>Storm moving along stalled frontal boundary</td>
<td>10</td>
<td>110</td>
<td>Rain/Snow 12.2, 1.0</td>
</tr>
<tr>
<td>2. 28–29 March 2005</td>
<td>Atlantic coastal storm—Nor’easter</td>
<td>32</td>
<td>127</td>
<td>Rain 61.0, 2.0</td>
</tr>
<tr>
<td>3. 5 July 2005</td>
<td>Cold frontal passage—thunderstorm</td>
<td>2</td>
<td>44</td>
<td>Rain 35.4, 18.0</td>
</tr>
<tr>
<td>4. 31 August 2005a</td>
<td>Cold frontal passage—thunderstorm</td>
<td>1</td>
<td>46</td>
<td>Rain 49.0, 49.0</td>
</tr>
<tr>
<td>5. 7 October 2005b</td>
<td>Storm moving along stalled frontal boundary</td>
<td>13</td>
<td>23</td>
<td>Rain 87.0, 6.7</td>
</tr>
<tr>
<td>6. 16 November 2005</td>
<td>Cold frontal passage</td>
<td>5</td>
<td>89</td>
<td>Rain 13.7, 2.7</td>
</tr>
</tbody>
</table>

*a Remnants of Hurricane Katrina.

*b Remnants of Tropical Storm Tammy.

Figure 2. Spring Creek at Houserville hydrograph for 2005 showing the six storm events that were sampled (black stars)

sewage effluent was collected at the UAJA outfall along Spring Creek located about 1.4 km downstream of the Houserville sampling site (Figure 1). Finally, two ground water springs in karst terrain (Figure 1) were sampled once in summer and once again in late fall to characterize the chemistry and stable isotopic composition of shallow ground water.

Stream sampling and precipitation monitoring during storms

All stream sites and the sewage treatment plant effluent were sampled during six storm events of different magnitude, intensity and duration in 2005. This allowed us to characterize a range in hydrological response among the five watersheds. Table II provides information on the individual storm events. For additional details on the origin and evolution of each storm, the reader is referred to Buda (2007). Figure 2 summarizes the hydrologic response to each storm event based on 15-min streamflow rates measured at the USGS gauge on Spring Creek in Houserville, Pennsylvania (Gauge# 01546400).

For each storm event, streams were sampled once during antecedent baseflow and again at or near peakflow. Baseflow samples were typically collected within 24 h of the impending storm and were used to reflect local ground water inputs for each stream site. The sewage treatment plant effluent was only sampled once per storm during baseflow conditions.

Precipitation during each event was sampled using a sequential passive precipitation sampler designed and constructed to collect sufficient volumes of rainwater for NO$_3^-$ stable isotope and inorganic chemical analysis. The sampler was constructed from a polyethylene plastic tarp, approximately 5.7 m$^2$ in area, which funnelled water...
to a series of three 20-1 polypropylene carboys. A new tarp was used for each event that was sampled, and the tarp was washed thrice with deionized water just before the onset of precipitation. Carboys were arranged such that they filled sequentially during storms according to a slightly modified design from that of Kennedy et al. (1979). Approximately 3.6 mm (0.14 inch) of rainfall filled an individual carboy. Once three sequential carboys were filled with rainwater (~10.8 mm of rainfall), three clean carboys were brought in to replace the full ones. This process was repeated during large precipitation events, which enabled within-storm variations of stable isotopes and chemistry to be evaluated. Subsamples or rainwater were collected from individual carboys for inorganic chemistry and δ18O-H2O analysis. Finally, wash-off from the tarp was collected in a carboy after a 3-week long dry period in November 2005 to provide some information on the isotopic composition of dry NO3− deposition.

**Water chemistry and stable isotope analysis**

All stream water and precipitation samples were stored at 4 °C until they could be analysed for inorganic chemistry at the Water Quality Laboratory in the Penn State Institutes of Energy and the Environment (PSIEE). Samples were analysed for pH, specific conductance, nitrate-N (NO3-N) and ammonium-N (NH4-N). All analyses were conducted using standard methods (American Public Health Association, 2005).

Stable isotopes in NO3− (δ15N-NO3− and δ18O-NO3−) were analysed according to the methods outlined by Chang et al. (1999) and Silva et al. (2000). Briefly, anion exchange resins were used to collect dissolved NO3− from all water samples. Silva et al. (2000) showed that anion exchange resins loaded with NO3− can typically be stored for up to 1 year at 4 °C with minimal effects on δ15N-NO3− and δ18O-NO3−. In this study, anion exchange resins loaded with NO3− were stored at 4 °C until they could be shipped to the University of Waterloo Environmental Isotope Laboratory (EIL) for further processing and analysis, usually within 1–2 months of collection. More specific details on the analytical methods used by the University of Waterloo EIL are given in Spoelstra et al. (2004). The results for δ15N-NO3− and δ18O-NO3− are reported in delta notation (δ15N and δ18O in permil units, ‰) versus their respective international reference standards: N2 gas for δ15N-NO3− and Standard Mean Ocean Water (SMOW) for δ18O-NO3−. The analytical error for both isotopes was approximately ±0.2‰ based on duplicate samples (26 duplicates for δ15N-NO3− and 14 duplicates for δ18O-NO3−).

Oxygen-18 in water (δ18O-H2O) was also analysed at the University of Waterloo EIL. Water samples for δ18O-H2O were collected and stored in airtight 20-ml HDPE scintillation bottles before shipment to the EIL at Waterloo. The analysis for δ18O-H2O was conducted using the CO2 equilibration method outlined by Epstein and Mayeda (1953). All results are reported in delta notation (δ18O in permil units, ‰) relative to SMOW. The analytical error for δ18O-H2O isotopes was approximately ±0.1‰ based on 20 duplicate samples.

**Data analysis**

The two-component mixing model (Equation 1) has been commonly used by hydrologists to separate peakflow into its ‘pre-event’ (old) and ‘event’ (new) components using conservative tracers such as δ18O-H2O isotopes (Pionke et al., 1993; DeWalle and Pionke, 1994). The two-component model is summarized below:

\[
\text{Event Fraction} = (\delta_T - \delta_P)/\left(\delta_E - \delta_P\right) \quad (1)
\]

where δT = peakflow isotope or chemical concentration (measured at peak streamflow during the event); δP = pre-event isotope or chemical concentration (measured at baseflow immediately before the event); δE = event isotope or chemical concentration (measured in precipitation).

The two-component model was used to separate pre-event and event water fractions on all five watersheds using δ18O-H2O. 18O-H2O was selected because it is considered a more direct tracer for sources of water than other conservative tracers such as dissolved SiO2 (Wels et al., 1991).

The new approach applied in this study was to use NO3− stable isotopes to partition peakflow NO3− into its ‘pre-event’ and ‘event’ source fractions using Equation (1). δ18O-NO3− was selected as the tracer to perform these calculations because it exhibited better separations between precipitation (event NO3−) and terrestrial NO3− (pre-event NO3−) sources. Comparisons of event water to event NO3− were used to help interpret potential sources and flow pathways of NO3− during storm events.

According to Sklash (1990) and Buttle (1994), users of two-component models in hydrology must assume that (1) δE does not vary while being routed through the watershed, (2) δP remains constant during the storm event, and (3) δP is significantly different from δE. With regard to the first assumption, precipitation represented event water, and therefore δE was measured in precipitation (Table III). During the course of all six storm events, significant variations of δ18O-H2O and NO3− stable isotopes in precipitation were observed (Table III) (Buda and DeWalle, in press). In order to assign an individual isotopic composition for event water and/or event NO3− (δE), a precipitation-weighted mean was calculated for each storm using the incremental mean method proposed by McDonnell (1990). With regard to the second assumption, recent research has shown that δ18O-H2O isotopes in pre-event water (δP) can vary significantly during storm events (Gremillion et al., 2000a). In addition to δ18O-H2O variations, NO3− stable isotopes also may vary in baseflow during storm events. Although variations of δ15N-NO3− and δ18O-NO3− were minimal in
Table III. Summary statistics for relevant physical, chemical and stable isotope data for the five watersheds sampled at baseflow (BF) and peakflow (PF) in upper Spring Creek as well as sewage effluent from UAJA, ground water springs and precipitation

<table>
<thead>
<tr>
<th></th>
<th>Forested BF</th>
<th>Urban BF</th>
<th>Agricultural BF</th>
<th>Mixed LU Houserville BF</th>
<th>Mixed LU Rock Road BF</th>
<th>Sewage effluent</th>
<th>Springs</th>
<th>Precipitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow (mm d⁻¹)</td>
<td>Mean 0.40</td>
<td>2.53</td>
<td>1.81</td>
<td>52.39</td>
<td>0.69</td>
<td>1.40</td>
<td>0.76</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td>Min 0.07</td>
<td>0.27</td>
<td>0.71</td>
<td>9.35</td>
<td>0.33</td>
<td>0.50</td>
<td>0.33</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>Max 1.00</td>
<td>8.31</td>
<td>4.48</td>
<td>124.10</td>
<td>1.42</td>
<td>4.26</td>
<td>1.73</td>
<td>9.30</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>Mean 11.1</td>
<td>11.8</td>
<td>14.6</td>
<td>15.5</td>
<td>12.5</td>
<td>13.4</td>
<td>12.2</td>
<td>13.3</td>
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<tr>
<td></td>
<td>Min 4.5</td>
<td>4.2</td>
<td>10.8</td>
<td>6.2</td>
<td>7.8</td>
<td>6.4</td>
<td>7.1</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Max 17.6</td>
<td>18.4</td>
<td>16.9</td>
<td>23.4</td>
<td>17.5</td>
<td>19.3</td>
<td>18.0</td>
<td>20.8</td>
</tr>
<tr>
<td>EC⁺ (μS cm⁻¹)</td>
<td>Mean 37</td>
<td>52</td>
<td>637</td>
<td>140</td>
<td>488</td>
<td>450</td>
<td>532</td>
<td>363</td>
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<tr>
<td></td>
<td>Min 29</td>
<td>32</td>
<td>594</td>
<td>74</td>
<td>453</td>
<td>399</td>
<td>438</td>
<td>215</td>
</tr>
<tr>
<td></td>
<td>Max 43</td>
<td>86</td>
<td>694</td>
<td>321</td>
<td>518</td>
<td>533</td>
<td>613</td>
<td>527</td>
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<tr>
<td>pH</td>
<td>Mean 7.5</td>
<td>7.6</td>
<td>8.2</td>
<td>8.0</td>
<td>8.3</td>
<td>7.9</td>
<td>7.3</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>Min 6.9</td>
<td>7.0</td>
<td>8.0</td>
<td>7.9</td>
<td>8.2</td>
<td>7.7</td>
<td>6.9</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td>Max 8.6</td>
<td>8.4</td>
<td>8.3</td>
<td>8.5</td>
<td>8.3</td>
<td>8.1</td>
<td>8.3</td>
<td>8.0</td>
</tr>
<tr>
<td>NO₃⁻ (mg l⁻¹)</td>
<td>Mean 0.7</td>
<td>1.6</td>
<td>19.3</td>
<td>2.9</td>
<td>20.9</td>
<td>17.3</td>
<td>15.4</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>Min 0.3</td>
<td>1.1</td>
<td>16.6</td>
<td>1.0</td>
<td>17.1</td>
<td>14.1</td>
<td>11.6</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Max 0.9</td>
<td>2.3</td>
<td>23.0</td>
<td>5.9</td>
<td>28.8</td>
<td>19.9</td>
<td>19.5</td>
<td>14.4</td>
</tr>
<tr>
<td></td>
<td>Min -9.3</td>
<td>-10.3</td>
<td>-9.5</td>
<td>-11.3</td>
<td>-9.3</td>
<td>-9.3</td>
<td>-9.6</td>
<td>-10.1</td>
</tr>
<tr>
<td></td>
<td>Max -8.9</td>
<td>-7.2</td>
<td>-8.5</td>
<td>-4.8</td>
<td>-8.9</td>
<td>-8.2</td>
<td>-8.7</td>
<td>-6.7</td>
</tr>
<tr>
<td>δ¹⁵N-NO₂⁻ (‰)</td>
<td>Mean 1.4</td>
<td>1.3</td>
<td>6.9</td>
<td>2.8</td>
<td>5.1</td>
<td>5.2</td>
<td>5.8</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>Min 0.0</td>
<td>0.3</td>
<td>5.2</td>
<td>-2.5</td>
<td>4.2</td>
<td>4.6</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Max 2.6</td>
<td>2.9</td>
<td>10.4</td>
<td>6.2</td>
<td>7.2</td>
<td>6.0</td>
<td>8.3</td>
<td>5.9</td>
</tr>
<tr>
<td>δ¹⁸O-NO₃⁻ (%)</td>
<td>Mean 4.9</td>
<td>15.9</td>
<td>3.7</td>
<td>30.8</td>
<td>3.7</td>
<td>2.9</td>
<td>3.5</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>Min 0.4</td>
<td>11.3</td>
<td>1.7</td>
<td>11.4</td>
<td>2.3</td>
<td>1.9</td>
<td>1.6</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Max 13.6</td>
<td>22.4</td>
<td>5.8</td>
<td>49.9</td>
<td>7.3</td>
<td>4.0</td>
<td>6.6</td>
<td>7.2</td>
</tr>
</tbody>
</table>

¹EC, electrical conductivity.
Spring Creek during non-storm periods (Buda, 2007), the variations of these isotopes in baseflow (δP) during storm events mostly were unknown. A study by Gremillion et al. (2000b) suggested that isotope variations in baseflow during storms did not adversely affect the results of steady-state two-component hydrograph separations in a Florida river. Therefore, we chose to use the simplified steady-state form of the two-component separation model (Equation 1) to calculate fractions of event water and event NO$_3^-$ in the Spring Creek watershed.

RESULTS AND DISCUSSION

Baseflow conditions

**General trends in NO$_3^-$ concentrations.** Concentrations of NO$_3^-$ in stream water during baseflow conditions varied throughout the Spring Creek watershed, with generally high levels in the mixed land-use, urban and agricultural watersheds (>15 mg l$^{-1}$) and much lower levels in the forested watershed (<1 mg l$^{-1}$) (Table III). The highest baseflow NO$_3^-$ concentrations were measured at the mixed land-use site at Rock Road (mean = 24.1 mg l$^{-1}$, SD = 5.8), which was the most downstream monitoring station used in the study (Figure 1). The high NO$_3^-$ concentrations at Rock Road were influenced in part by a sewage treatment plant that was located approximately 2.3 km upstream, which discharged wastewater with very high NO$_3^-$ (mean = 40.9 mg l$^{-1}$, SD = 8.2). Relatively high baseflow NO$_3^-$ concentrations were also common in the agricultural (mean = 20.9 mg l$^{-1}$, SD = 4.2) and urban (mean = 19.3 mg l$^{-1}$, SD = 2.2) watersheds (Table III). Slightly lower baseflow NO$_3^-$ concentrations were observed at the mixed land-use site in Houserville (mean = 15.4 mg l$^{-1}$, SD = 2.8). In general, baseflow NO$_3^-$ concentrations in all the karst watersheds were similar to those measured in two local ground water springs (mean = 19.8 mg l$^{-1}$, SD = 1.4). Baseflow NO$_3^-$ concentrations at the forested watershed (mean = 0.7 mg l$^{-1}$, SD = 0.3) were by far the lowest of any of the five watersheds monitored during the study (Table III).

**General trends in NO$_3^-$ isotope values and sources.** NO$_3^-$ stable isotope data for all five watersheds at baseflow are given in Figure 3. Although values of δ$^{18}$O-NO$_3^-$ showed very little spread across the five watersheds (Figure 3), values of δ$^{15}$N-NO$_3^-$ varied more substantially owing in part to the influence of different land-use and potential NO$_3^-$ sources affecting each stream. The forested watershed had the lowest δ$^{15}$N-NO$_3^-$ (mean = +1.4‰, SD = 1.0) of all five watersheds. In general, NO$_3^-$ isotope values on the forested watershed plotted within the range of NH$_4^+$ in rainfall and soil N (Figure 3). Values of δ$^{15}$N-NO$_3^-$ in stream water on the agricultural watershed (mean = +5.1‰, SD = 1.1) and mixed land-use site at Houserville (mean = +5.8‰, SD = 1.2) were generally similar at baseflow (Figure 3; Table III). Although the majority of NO$_3^-$ isotope data obtained from the agricultural watershed and the mixed land-use site at Houserville fell in the range of soil N (Figure 3), a few higher values of δ$^{15}$N-NO$_3^-$ (greater than +7‰) suggested a potential influence of animal waste. The highest δ$^{15}$N-NO$_3^-$ measurements in baseflow were recorded at the mixed land-use site at Rock Road (mean = +10.9‰, SD = 1.8) indicating a clear influence of NO$_3^-$ from sewage effluent.
(Figure 3), which discharged into Spring Creek approximately 2.3 km upstream and had a mean $\delta^{15}$N-NO$_3^-$ value of +14.8‰ (SD = 3.2) (Table III; Figure 3). The urban watershed showed considerably more variation in $\delta^{15}$N-NO$_3^-$ (mean = +6.9‰, SD = 2.1) at baseflow than the other four watersheds (Figure 3), suggesting that urban stream water was a mixture of soil N and NO$_3^-$ from animal waste or sewage.

Storm events

$\text{NO}_3^-$ isotopes in wet and dry deposition. In wet deposition, $\delta^{15}$N-NO$_3^-$ (mean = +0-2‰, SD = 3.7) and $\delta^{18}$O-NO$_3^-$ (mean = +44.3‰, SD = 14.6) data generally plotted within the range of previous studies (Figure 3) (Kendall et al., 2007 and references therein), and showed considerable variability within (Buda and DeWalle, in press) and between storm events (Figure 3, Table III). Values of $\delta^{18}$O-NO$_3^-$ in wet deposition that were less than +30‰ (Figure 3) may have been due to the use of the AgNO$_3$ method (Chang et al., 1999; Silva et al., 2000), which has been shown to produce lower $\delta^{18}$O-NO$_3^-$ values than the more recently developed denitrifier method (see Kendall et al., 2007 for a more thorough discussion of this issue). In addition to wet deposition samples, one melted snow sample was collected on 23 March 2005 ($\delta^{15}$N-NO$_3^-$ = -0.6‰; $\delta^{18}$O-NO$_3^-$ = +34.7‰) during a rain-on-snow event (Table II). Of further note is a dry deposition sample collected before a storm in November 2005 ($\delta^{15}$N-NO$_3^-$ = +9.9‰; $\delta^{18}$O-NO$_3^-$ = +68.5‰) that was much more enriched in $\delta^{15}$N-NO$_3^-$ than samples of wet deposition. This trend of higher $\delta^{15}$N-NO$_3^-$ in dry deposition as compared with wet deposition is generally consistent with what has been observed in some previous studies (Elliott et al., in press; Kendall et al., 2007 and references therein).

Forest watershed response to storm events. NO$_3^-$ sources: The forested watershed (Figure 1) exhibited interesting changes in NO$_3^-$ stable isotopes during the six monitored storm events in 2005 (Figure 4). Although changes in $\delta^{15}$N-NO$_3^-$ from baseflow to peakflow were mostly small (±2.1‰), changes in $\delta^{18}$O-NO$_3^-$ were consistently upward (mean increase of +13.7‰ for five storms), with the only exception being a slight decrease (−2.3‰) for the storm that occurred on 7th October (Figure 4). In addition, results from a two-tailed t-test indicated that $\delta^{18}$O-NO$_3^-$ during peakflow (mean = +15.9‰, SD = 4.5) was significantly higher than $\delta^{18}$O-NO$_3^-$ in baseflow (mean = +4.9‰, SD = 4.7) for all six storms ($p$ = 0.002). This indicated that NO$_3^-$ from the atmosphere, which typically had enriched values of $\delta^{18}$O-NO$_3^-$ (Table III), was important during peakflow conditions on the forested watershed.

Changes in $\delta^{15}$N-NO$_3^-$ and $\delta^{18}$O-NO$_3^-$ from baseflow to peakflow during storm events indicated that a mixture of atmospheric NO$_3^-$ and N from soils were the two most important NO$_3^-$ sources added during storm events (Figure 4). If we assume a $\delta^{18}$O-NO$_3^-$ value of +5‰ for microbially produced NO$_3^-$ in forest soils (mean $\delta^{18}$O-NO$_3^-$ from six baseflow samples collected from the forested watershed), then the percent contribution of atmospheric NO$_3^-$ to the forested watershed for all six storm events in 2005 could be estimated using the following two-component mixing equation (Williard et al., 2001):

$$\% \text{ atmospheric NO}_3^- = \left[\frac{\delta^{18}\text{O-NO}_3^-_{\text{peakflow}} - \delta^{18}\text{O-NO}_3^-_{\text{soil}}}{\delta^{18}\text{O-NO}_3^-_{\text{atmosphere}} - \delta^{18}\text{O-NO}_3^-_{\text{soil}}}\right]$$

(2)

The results of these calculations suggested that atmospheric NO$_3^-$ accounted for approximately 33% of the NO$_3^-$ in stream water during peakflow conditions in the forested watershed. These results mostly agreed with recent evidence using $\delta^{18}$O-NO$_3^-$ in other forested watershed studies, which generally have shown that atmospheric (wet + dry deposition) NO$_3^-$ accounts for less

Figure 4. Forested watershed $\delta^{15}$O-NO$_3^-$ versus $\delta^{15}$N-NO$_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO$_3^-$ stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November).

Figure 5. Urban watershed $\delta^{18}$O-NO$_3^-$ versus $\delta^{15}$N-NO$_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO$_3^-$ stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November).
than 30% of the total NO$_3^-$ in stream water during storm events (Williard et al., 2001) and snowmelt runoff episodes (Burns and Kendall, 2002; Campbell et al., 2002; Piatak et al., 2005; Sebestyen et al., 2008). More recent work using $\delta^{18}$O-NO$_3^-$ in a semi-arid watershed showed that atmospheric NO$_3^-$ may account for up to 40% of total NO$_3^-$ exported during storms (Michalski et al., 2004).

Results from the simple two-component models and the plots of NO$_3^-$ stable isotopes in baseflow and peakflow (Figure 4) suggest that the majority of NO$_3^-$ exported during storm events in the forested watershed was from microbial soil nitrification (67% of the NO$_3^-$). The observed NO$_3^-$ isotope values in the peakflow mixture generally support this conclusion (Figure 4). Under ideal conditions (e.g., when soil moisture is low and soils are well aerated), microbial nitrification can produce significant pools of NO$_3^-$ in the mineral soils, which then can be flushed into the stream during storm events (Creed et al., 1996; Christopher et al., 2008) due to the expansion of variable source areas (Creed and Band, 1998). This flushing mechanism appeared to be important on the forested watershed because NO$_3^-$ concentrations consistently increased from baseflow to peakflow for all six storm events in 2005 (Table III) (mean increase = +0.9 mg l$^{-1}$).

NO$_3^-$ flow pathways: Fractions of event NO$_3^-$ and event water at peakflow in the forested, sandstone bedrock watershed appeared to vary for different types of storm events. Hydrograph separations using $\delta^{18}$O-H$_2$O showed a large variation in responses on the forested watershed, with event water fractions ranging from 0.01 (23rd March) to 0.62 (29th March). When event NO$_3^-$ fractions were compared with event water fractions on an event-by-event basis (Table IV), an interesting pattern emerged that appeared to indicate an effect of storm size on flow path responses. In general, small storms (<35 mm rainfall) produced fractions of event NO$_3^-$ that were greater than fractions of event water. In contrast, larger storms (>35 mm rainfall) produced fractions of event NO$_3^-$ that were less than fractions of event water.

During the three largest storm events (29th March, 31st August and 7th October), it appeared that potential increases in $\delta^{18}$O-NO$_3^-$ in stream water from atmospheric NO$_3^-$ inputs with high $\delta^{18}$O-NO$_3^-$ values (greater than +30‰) may have been reduced by significant fluxes of NO$_3^-$ from soil water sources that typically have much lower $\delta^{18}$O-NO$_3^-$ values (less than +13‰) (Mayer et al., 2001; Spoelstra et al., 2007). Soils in the forested sandstone uplands are relatively shallow, compared with soils in the karst valleys, and rapid mobilization of soil NO$_3^-$ in large events is quite possible. Additionally, evidence using $\delta^{18}$O-H$_2$O in Appalachian forested watersheds points to the rapid mobilization of soil water through macropores and other preferential flow pathways as an important source of streamflow during large storm events (Swistock et al., 1989). If this type of flow path was active during the three largest storm events, then high event water contributions and flushing of soil-derived NO$_3^-$ with low $\delta^{18}$O-NO$_3^-$ could represent a plausible explanation for fractions of event NO$_3^-$ that were less than fractions of event water.

During the three smallest storm events (23rd March, 5th July and 16th November), event NO$_3^-$ sources appeared to be more important than pre-event NO$_3^-$ sources from soils as evidenced by fractions of event NO$_3^-$ that were greater than fractions of event water. Two non-competing hypotheses to explain this pattern include the influence of channel precipitation and wash-off of dry-deposited NO$_3^-$ in throughfall, both of which have enriched $\delta^{18}$O-NO$_3^-$ relative to terrestrial NO$_3^-$ sources. A study conducted in a forested Appalachian watershed in central Pennsylvania showed that the percentage of channel precipitation in stormflow was highest during small events, with overall contributions approaching 7% (Crayosky et al., 1999). Thus, significant contributions of channel precipitation could in part explain why fractions of event NO$_3^-$ were greater during

Table IV. Fractions of event NO$_3^-$ and event H$_2$O at peakflow for the five watersheds monitored in upper Spring Creek

<table>
<thead>
<tr>
<th>Storm number/date</th>
<th>Watershed</th>
<th>Event NO$_3^-$</th>
<th>Event H$_2$O</th>
<th>Event NO$_3^-$</th>
<th>Event H$_2$O</th>
<th>Event NO$_3^-$</th>
<th>Event H$_2$O</th>
<th>Event NO$_3^-$</th>
<th>Event H$_2$O</th>
<th>Event NO$_3^-$</th>
<th>Event H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 23 March 2005</td>
<td>Forested</td>
<td>0.50</td>
<td>0.01</td>
<td>1.00</td>
<td>0.91</td>
<td>—</td>
<td>0.09</td>
<td>—</td>
<td>0.25</td>
<td>&lt;0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>2. 28–29 March 2005</td>
<td>Urban</td>
<td>0.19</td>
<td>0.62</td>
<td>0.35</td>
<td>0.97</td>
<td>—</td>
<td>&lt;0.01</td>
<td>0.03</td>
<td>0.46</td>
<td>0.05</td>
<td>0.47</td>
</tr>
<tr>
<td>3. 5 July 2005</td>
<td>Agricultural</td>
<td>1.00</td>
<td>0.05</td>
<td>0.86</td>
<td>0.13</td>
<td>0.06</td>
<td>0.11</td>
<td>0.11</td>
<td>0.18</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>4. 31 August 2005</td>
<td>Mixed LU</td>
<td>0.29</td>
<td>0.43</td>
<td>0.65</td>
<td>—</td>
<td>&lt;0.01</td>
<td>0.17</td>
<td>0.12</td>
<td>0.51</td>
<td>0.08</td>
<td>0.48</td>
</tr>
<tr>
<td>5. 7 October 2005</td>
<td>Houserville</td>
<td>0.23</td>
<td>0.58</td>
<td>0.68</td>
<td>0.68</td>
<td>&lt;0.01</td>
<td>0.21</td>
<td>0.07</td>
<td>0.58</td>
<td>0.06</td>
<td>0.69</td>
</tr>
<tr>
<td>6. 16 November 2005</td>
<td>Rock Road</td>
<td>0.23</td>
<td>0.02</td>
<td>0.83</td>
<td>0.19</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.48</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mean$^a$</td>
<td></td>
<td>0.44</td>
<td>0.23</td>
<td>0.47</td>
<td>0.69</td>
<td>0.02</td>
<td>0.13</td>
<td>0.05</td>
<td>0.41</td>
<td>0.02</td>
<td>0.29</td>
</tr>
<tr>
<td>Standard error$^a$</td>
<td></td>
<td>0.15</td>
<td>0.13</td>
<td>0.16</td>
<td>0.16</td>
<td>0.01</td>
<td>0.04</td>
<td>0.02</td>
<td>0.07</td>
<td>0.02</td>
<td>0.12</td>
</tr>
</tbody>
</table>

$^a$Means and standard errors were only calculated for events where both event NO$_3^-$ and event water could be estimated.
small storms that generated small event water fractions (<0.05).

In addition to channel precipitation, it could be argued that wash-off of NO$_3$\(^-\) in dry deposition from soil and vegetated surfaces was important during small storms. Studies of N deposition in forested watersheds have estimated that dry deposition is a significant pathway of N input, comprising 46% (Lovett and Lindberg, 1993) to 80% (Lindberg et al., 1986) of total N deposition. In the current study, one sample of dry NO$_3$\(^-\) deposition collected in mid-November 2005 had a $\delta^{15}$N(NO$_3$\(^-\)) value of +9.9‰ and a $\delta^{18}$O(NO$_3$\(^-\)) value of +68.5‰. The $\delta^{18}$O(NO$_3$\(^-\)) value measured in dry NO$_3$\(^-\) deposition was similar to that measured in precipitation; however, $\delta^{15}$N(NO$_3$\(^-\)) measured in dry NO$_3$\(^-\) deposition was at least 5‰ greater than $\delta^{15}$N(NO$_3$\(^-\)) measured in precipitation (Figure 3). Comparable differences between $\delta^{15}$N(NO$_3$\(^-\)) measured in dry and wet deposition were observed in a recent study conducted in the Appalachian Plateau region of Ohio, Pennsylvania and New York (Elliott et al., in press). Future studies in forested watersheds may be able to take advantage of the importance of atmospheric NO$_3$\(^-\) used for the forested watershed (Equation 2) to estimate the relative importance of atmospheric NO$_3$\(^-\) during small storms relative to other NO$_3$\(^-\) contributions during storms relative to other NO$_3$\(^-\) source inputs. In this case, we assumed that the average terrestrial $\delta^{18}$O(NO$_3$\(^-\)) value was +4‰ (mean $\delta^{18}$O(NO$_3$\(^-\)) from six baseflow samples collected from the urban watershed; peakflow $\delta^{18}$O(NO$_3$\(^-\)) was +30.8‰ (mean of six storm events) and atmospheric $\delta^{18}$O(NO$_3$\(^-\)) was +44.3‰ (mean of 21 samples). The result of this calculation suggested that the atmosphere contributed as much as 67% of NO$_3$\(^-\) at peakflow on this particular urban watershed.

Indeed, others have also noted the importance of atmospheric NO$_3$\(^-\) in urbanizing watersheds during high flows. For example, Anisfeld et al. (2007) studied two mixed land-use watersheds in Connecticut and Burns et al. (2009) monitored several suburban watersheds in central New York during high stream flow using $\delta^{18}$O(NO$_3$\(^-\)). Results from both studies implied that NO$_3$\(^-\) in atmospheric deposition could contribute upwards of 50% of the NO$_3$\(^-\) in these watersheds. Earlier studies by Ging et al. (1996) and Silva et al. (2002) using $\delta^{18}$O(NO$_3$\(^-\)) in two urbanized watersheds in Austin, Texas, also pointed to the importance of atmospheric NO$_3$\(^-\) in streamflow due to the influence of runoff from impervious surfaces.

Results from the current study point to an even greater contribution of NO$_3$\(^-\) from atmospheric deposition to urban streams than what has previously been reported. Clearly, some portion of this atmospheric NO$_3$\(^-\) is from wet deposition in runoff, and the remainder is from the wash-off of dry deposition that has built-up over time before the storm event. Unfortunately, with only one measurement of the $\delta^{15}$N(NO$_3$\(^-\)) and $\delta^{18}$O(NO$_3$\(^-\)) in dry deposition (Figure 3), it is not possible to estimate the relative importance of wet and dry deposition during individual events, but future work in urban watersheds should focus on characterizing NO$_3$\(^-\) isotopes in both wet and dry deposition to potentially separate out these two important sources of NO$_3$\(^-\) in urban runoff.

**Urban, karst watershed response to storm events. NO$_3$\(^-\) sources:** Changes in $\delta^{18}$O(NO$_3$\(^-\)) and $\delta^{15}$N(NO$_3$\(^-\)) from baseflow to peakflow were significant on the urban watershed (Figure 1) during all six storm events in 2005. Baseflow to peakflow changes in $\delta^{18}$O(NO$_3$\(^-\)) were the most substantial, with consistently upward shifts in the direction of atmospheric NO$_3$\(^-\) ranging in magnitude from +7.3‰ (7th October) to +47.4‰ (31st August) (Figure 5). Indeed, results from a two-tailed t-test indicated that $\delta^{18}$O(NO$_3$\(^-\)) during peakflow (mean = +30.8‰, SD = 14.6) was significantly higher than $\delta^{18}$O(NO$_3$\(^-\)) in baseflow (mean = +3.7‰, SD = 1.7) for all six storms ($p = 0.001$). In addition, $\delta^{15}$N(NO$_3$\(^-\)) decreased from baseflow to peakflow during five storm events (mean decrease = −5.2‰) with the November 16 storm being the only exception (slight increase of +1‰) (Figure 5).

Based on the urban NO$_3$\(^-\) isotope results, it was clear that atmospheric NO$_3$\(^-\) was the most important new source of NO$_3$\(^-\) at peakflow, although additional NO$_3$\(^-\) contributions may have also come from the flushing of detritus stored in storm sewers and on impervious surfaces. We applied the same two-component model used for the forested watershed (Equation 2) to estimate the importance of atmospheric NO$_3$\(^-\) contribution during storms relative to other NO$_3$\(^-\) source inputs. In this case, we assumed that the average terrestrial $\delta^{18}$O(NO$_3$\(^-\)) value was +4‰ (mean $\delta^{18}$O(NO$_3$\(^-\)) from six baseflow samples collected from the urban watershed), peakflow $\delta^{18}$O(NO$_3$\(^-\)) was +30.8‰ (mean of six storm events) and atmospheric $\delta^{18}$O(NO$_3$\(^-\)) was +44.3‰ (mean of 21 samples). The result of this calculation suggested that
roads to flow onto grassy surfaces, infiltrate and shift to shallow subsurface flow pathways. Although a transfer of overland flow to shallow subsurface flow may not have substantially altered the δ18O-H2O signal from precipitation, it may have promoted assimilation of event NO3− as water infiltrated into the soil. Conversion to shallow subsurface flow also may have resulted in the flushing of a mixture of stored NO3− sources that had lower δ18O-NO3− values than atmospheric deposition. Either of these two mechanisms operating independently or in tandem could help to explain why event NO3− fractions were lower than event water fractions during these long-duration storm events.

In contrast to long-duration events, the two most intense storms on 5th July and 31st August would be expected to generate correspondingly high event water and event NO3− fractions due to the fact that both of these events occurred within the span of about 1 h (Table II), thereby limiting any opportunities for infiltration and NO3− storage or assimilation. Despite the fact that changes in δ18O-NO3− from baseflow to peakflow were quite high during these two storms (Figure 5), indicating an important contribution from atmospheric NO3−, we were unable to characterize the event NO3− fractions in these two events due to an inability to sample time variations in very high-intensity events using the resin method of NO3− isotope analysis, which requires large quantities of water. During longer and less intense storms such as the one on 28th–29th March, δ18O-NO3− was shown to be quite variable and changed by as much as 35% during the course of the storm (Buda and DeWalle, in press). If variations of this magnitude also occurred during the more intense storms on 5th July and 31st August, then potentially higher levels of δ18O-NO3− may simply have been missed during both storms. If one of these missed values was associated with a precipitation burst that contributed to the measured peakflow on the urban watershed, this would certainly have affected the calculation of event NO3−. Indeed, the δ18O-NO3− in precipitation from both storms was much less than the δ18O-NO3− measured in peakflow on the urban watershed, which resulted in event NO3− fractions that were much greater than one, a physical impossibility. Clearly, future work using tracers to estimate event fractions of NO3− on urban watersheds should include provisions to more intensively sample precipitation over time. The use of the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002), which requires substantially lower volumes of event water for isotope analysis, may help to resolve this issue.

Non-urban, karst watershed response to storm events. NO3− sources—agricultural watershed: On the agricultural watershed (Figure 1), changes in δ15N-NO3− and δ18O-NO3− from baseflow to peakflow were notably smaller and more variable during storms (Table III) as compared with the forested (Figure 4) and urban (Figure 5) watershed responses. Changes in δ15N-NO3− and δ18O-NO3− during storms typically were less than ±1.5‰. Stable NO3− isotopes measured during storms on the agricultural watershed indicated that NO3− sources probably did not change much with a fairly constant mixture of NO3− from manure/septic system effluent and/or soil-derived sources present before and during storm events.

NO3− sources—mixed land-use watershed at Houseville: Changes in NO3− stable isotopes during storm events at the mixed land-use site at Houserville (Figure 1) were similar in magnitude to those observed on the agricultural watershed. Observed changes in δ15N-NO3− from baseflow to peakflow typically were small (less than ±0.5‰) (Table III). The one exception occurred on 23rd March, when δ15N-NO3− decreased by 2.7‰. This decrease in δ15N-NO3− was potentially due to runoff from melting snow, which had a δ15N-NO3− value of −0.6‰ (Figure 3). Changes in δ18O-NO3− were slightly more significant during storms than changes in δ15N-NO3−, and these changes typically were positive (+1.3‰ to +4.2‰). The largest increase of +4.2‰ occurred on 31st August, which was a high-intensity thunderstorm (48 mm h−1), and therefore this change likely reflected the influence of NO3− from precipitation. Ultimately, the small changes in NO3− isotopes from baseflow to peakflow at the mixed land-use site in Houserville indicated that NO3− sources did not change much during storm events. The source mixture appeared to consist of mostly soil N and manure sources, although a more complex mixture of NO3− sources from upstream forested, agricultural and urban land-use inputs cannot be ruled out because longer transport times and biogeochemical transformation processes may have effectively altered the initial NO3− isotope source signals (Mayer et al., 2002; Burns et al., 2009).

NO3− sources—mixed land-use watershed at Rock Road: The mixed land-use site at Rock Road (Figure 1) generally behaved differently than the upstream site at Houserville during storms, presumably due to the influence of sewage effluent at baseflow (Figure 3). Although changes in δ15N-NO3− were generally minor during storms (+0.1‰ to +2.7‰) (Figure 6), much more substantial changes in δ15N-NO3− were observed during storm events with the predominant movement being towards a lower δ15N-NO3− value in the range of soil N. Essentially, the high δ15N-NO3− at baseflow (Figure 3) caused by the UAJA sewage effluent appeared to be diluted during storms due to the addition of a lower δ15N-NO3− signal from upstream sources and possibly soil N. Sewage effluent contributions to stream flow appear to be easily traced by using δ15N-NO3− isotopes.
and Rock Road (mean = 0.29) as well as the agricultural watershed (mean = 0.13) suggested that pre-event water was typically the predominant water source during most storm events. An exception to this occurred during the most intense storm on 31st August (Table II), where much larger event water fractions were observed on the agricultural (0.17) and mixed land-use watersheds at Houserville (0.51) and Rock Road (0.48). In addition to mostly low event water fractions, mean fractions of event NO$_3^-$ also were low on the mixed land-use watersheds at Houserville (mean = 0.05) and Rock Road (mean = 0.02) as well as the agricultural watershed (mean = 0.02). These results suggested that the water and NO$_3^-$ delivered during storms on the three non-urban karst watersheds followed mostly subsurface ground water flow pathways.

Additionally, fractions of event NO$_3^-$ were generally much less than fractions of event water on all three non-urban karst watersheds, which suggested that flushing of stored NO$_3^-$ and assimilative processes may have been important. With regard to flushing potential, the carbonate aquifers that underlie the valleys in the non-urban karst watersheds promote substantial storage of ground water (Fulton et al., 2005) in pipes and solution cavities (White, 1988). This ground water can be released slowly during storm events (White and Reich, 1970) and can flush of a mixture of stored NO$_3^-$ sources that likely have been subject to biogeochemical processing and transformation. Furthermore, deep soils in the karst valleys also may have promoted storage and assimilation of event NO$_3^-$ through the infiltration of incoming precipitation and nearby sources of surface runoff from impervious surfaces such as roads and parking lots. This process may have been especially important in the two mixed land-use watersheds at Houserville and Rock Road, where impervious cover was more prominent than in the agricultural watershed (Table I), and event NO$_3^-$ fractions were substantially lower than event water fractions for most storm events.

Nitrates-stable isotopes were useful for showing how NO$_3^-$ sources changed from baseflow to peakflow during storm events in the Spring Creek watershed. On the forested, sandstone watershed, NO$_3^-$ predominately was a mixture of event atmospheric and older stored soil sources at peakflow, and the relative importance of these sources appeared to depend on storm size. During small storms (<35 mm rainfall), fractions of event NO$_3^-$ were greater than fractions of event water at peakflow, which suggested that channel precipitation and/or wash-off of dry-deposited NO$_3^-$ from vegetated surfaces represented potentially important NO$_3^-$ sources. During large storms (>35 mm rainfall), fractions of event NO$_3^-$ less than fractions of event water at peakflow suggested that shallow subsurface flow pathways caused by steep terrain and shallow soils with high infiltration capacity over relatively impermeable sandstone and shale bedrock were more important NO$_3^-$ delivery mechanisms to stream water.

On the urban watershed, large changes in $\delta^{15}$N-NO$_3^-$ and $\delta^{18}$O-NO$_3^-$ during storm events clearly showed that atmospheric NO$_3^-$ sources (wet + dry deposition) were predominant during peakflow conditions, and that no other significant urban NO$_3^-$ sources beyond those from the atmosphere were detectable. This was especially true for short-duration, high-intensity type events. In contrast, two long-duration events had event NO$_3^-$ fractions that were less than event water fractions, suggesting that storage and assimilation and/or flushing of stored NO$_3^-$ can be important on the urban watershed, despite contributions of atmospheric NO$_3^-$ in wet and dry deposition.

On the agricultural and mixed land-use karst watersheds, a much different response to storms was observed. Small changes in NO$_3^-$ isotope values from baseflow to peakflow on the agricultural watershed and at the mixed land-use site in Houserville suggested that NO$_3^-$ sources did not change much during storms on these two karst watersheds. Further downstream at the Rock Road mixed land-use site, enriched values of $\delta^{15}$N-NO$_3^-$ served as an excellent tracer for upstream sewage effluent discharges during baseflow conditions, but these values were quickly diluted during storm events due to fluxes of NO$_3^-$ from upstream sources with lower $\delta^{15}$N-NO$_3^-$ signals. In addition to small changes in isotopes during storm events, fractions of event NO$_3^-$ were much less than fractions of event water. This indicated that event effects were potentially muted by the assimilation of event NO$_3^-$ in deeper soils and/or the delivery of stored NO$_3^-$ via subsurface ground water flow pathways. The results of this study illustrate how NO$_3^-$ isotopes and $\delta^{18}$O-H$_2$O can be combined to show major differences in water and NO$_3^-$ delivery mechanisms during storms between forested uplands and karst valleys, and confirm the dominance of overland flow pathways in fully urbanized watersheds during high-intensity storm events.

CONCLUSIONS

Figure 6. Mixed land-use watershed at Rock Road $\delta^{18}$O-NO$_3^-$ versus $\delta^{15}$N-NO$_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO$_3^-$ stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November.)

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