



Storm event exports of dissolved organic nitrogen (DON) across multiple catchments in a glaciated forested watershed

Shreeram P. Inamdar¹ and Myron J. Mitchell²

Received 14 September 2006; accepted 26 January 2007; published 4 May 2007.

[1] Storm event patterns of dissolved organic nitrogen (DON) were studied for multiple events across four catchments (1.6–696 ha) in a forested, glaciated watershed in western New York State. Highest concentrations of DON in the watershed were recorded for litter leachate followed by throughfall. Storm event concentrations of DON consistently peaked at or before peak discharge while dissolved organic carbon (DOC) concentrations peaked on the hydrograph recession limbs. Concentrations of DON in stream water were derived from throughfall and litter layer while the DOC expression was attributed to throughfall, litter, and the flushing of the mineral soil by a rising water table. Temporal patterns of ammonium (NH_4^+) concentrations during events consistently matched those of DON indicating similar sources and flow paths. A previously validated end-member mixing analysis (EMMA) for NO_3^- failed to predict the DON concentrations observed in streamflow. DON concentrations and DON as % of total dissolved nitrogen (TDN) differed considerably between baseflow (% DON: 6 to 19%) and storm events (% DON: 6 to 64%). DON concentrations and % DON of TDN increased with catchment size and amount of saturated/wetland areas. A wetland catchment that consistently yielded high storm-event DOC concentrations produced variable amounts of DON, indicating a decoupling of DOC and DON dynamics in the wetland. Our study suggests that storm events and watershed characteristics, especially the proportion of saturated and wetland areas, may have a greater influence on DON exports than atmospheric N deposition.

Citation: Inamdar, S. P., and M. J. Mitchell (2007), Storm event exports of dissolved organic nitrogen (DON) across multiple catchments in a glaciated forested watershed, *J. Geophys. Res.*, 112, G02014, doi:10.1029/2006JG000309.

1. Introduction

[2] Inorganic forms of nitrogen (N), especially nitrate (NO_3^-), have received considerable attention over the past few decades resulting in an improved understanding of the sources, flow paths, and transport mechanisms responsible for the export of inorganic N from watersheds [Burns *et al.*, 1998; Creed and Band, 1998; Hill, 1993; Inamdar and Mitchell, 2006; McHale *et al.*, 2002; Schiff *et al.*, 2002]. This focus on inorganic N has been motivated by concerns of elevated atmospheric deposition of nitrogen (N), N saturation and acidification of forest ecosystems, overapplication of N fertilizers in agricultural and urban landscapes, and the consequent eutrophication of surface waters [Aber *et al.*, 1989; Driscoll *et al.*, 2003; Howarth *et al.*, 1996; Wigington *et al.*, 1990]. Similar progress is also being made regarding our understanding of dissolved organic carbon (DOC) [Hinton *et al.*, 1998; Hornberger *et al.*, 1994;

Inamdar and Mitchell, 2006; McGlynn and McDonnell, 2003]. In contrast, less attention has been paid to the organic forms of N, especially dissolved organic N (DON). Recent studies suggest that contributions of DON can be significant [Campbell *et al.*, 2000; McHale *et al.*, 2000; Willett *et al.*, 2004] and in some ecosystems constitute a major portion of the total N solute export [Hedin *et al.*, 1995; Perakis and Hedin, 2002].

[3] Research on NO_3^- and DOC has shown that sources and flow paths for these solutes may vary and shift with storm events and seasons [Boyer *et al.*, 1997; Burns *et al.*, 1998; Hill, 1993; Hornberger *et al.*, 1994; Inamdar and Mitchell, 2006]. Similar investigations on DON have been few and inconclusive. Although DON concentrations have been observed to be high in throughfall, higher concentrations have been recorded in the forest floor or the litter layer [Aitkenhead-Peterson *et al.*, 2003; Currie *et al.*, 1996; Qualls and Haines, 1991; Yavitt and Fahey, 1985]. The few studies on within-event patterns of DON have produced mixed results. Hagedorn *et al.* [2000] found that concentrations for both DOC and DON peaked on the recession limb suggesting similar transport and release mechanisms for the two solutes. In contrast, Buffam *et al.* [2001] reported DOC and DON peaks on the rising limb of the hydrograph but were unable to conclusively identify the source and transport mechanisms. Others have suggested

¹Bioresources Engineering, University of Delaware, Newark, Delaware, USA.

²Faculty of Environment and Forest Biology, College of Environmental Science and Forestry, State University of New York, Syracuse, New York, USA.

that although DOC and DON exports from watersheds were correlated they were likely influenced by different sources and transport mechanisms [McDowell, 2003; Michalzik and Matzner, 1999; Willett *et al.*, 2004]. Williams *et al.* [2001] did not find any correlation between DOC and DON concentrations and also concluded that different transport mechanisms were responsible for DON.

[4] Watershed features such as topography, wetlands, riparian zones, and groundwater seeps have been found to have a strong influence on the expression of NO_3^- and DOC [Creed and Band, 1998; Hinton *et al.*, 1998; Inamdar and Mitchell, 2006; McGlynn and McDonnell, 2003; Schiff *et al.*, 2002]. Again, limited information is available on how these features influence DON exports. Pellerin *et al.* [2004] found that in the northeastern U.S. the % of wetlands in the watershed explained 56% of the variability in DON. McHale *et al.* [2000] examined DON export across multiple landscape positions within a single watershed in the Adirondacks and found that within-lake processes and not wetlands had the greatest impact on DON. Lovett *et al.* [2000] did not find any specific catchment characteristics that could explain the concentrations of DON in 39 watersheds in the Catskills Mountains of New York State.

[5] These results clearly show that there are significant gaps in our understanding of DON. Similar concerns have also been voiced recently by McDowell [2003]. Especially important is the need to understand the sources and flow paths responsible for the export of DON during storm events and how they differ from or match those of inorganic N species and DOC. Furthermore, investigations need to be performed across multiple catchments with varying topographic attributes so that the influence of these attributes on DON can be discerned.

[6] We explored the storm event exports of DON for the Point Peter Brook watershed (PPBW) located in the glaciated, forest region of Western New York. Investigations were performed for four subcatchments (1.6–696 ha) with varying topography and the extent of surface-saturated areas. Topographic attributes and wetness index [Hjerdt *et al.*, 2004] for the catchments have been developed from a 2 m DEM [Inamdar and Mitchell, 2006]. End-member mixing analysis (EMMA) for PPBW identified throughfall (THF), groundwater discharged at hillslope seeps (SGW) and riparian water (RW) as the three controlling members for stream chemistry [Inamdar and Mitchell, 2006] (also S. P. Inamdar and M. J. Mitchell, Contributions of riparian and hillslope waters to storm runoff across multiple catchments and storm events in a glaciated forested watershed, manuscript submitted to *Journal of Hydrology*, 2006) (hereinafter referred to as Inamdar and Mitchell, submitted manuscript, 2006). Sources and flow paths responsible for the export of NO_3^- and DOC have also been identified [Inamdar and Mitchell, 2006]. Nitrate in PPBW was influenced by the contributions from SGW and THF while DOC was more affected by contributions from THF and RW [Inamdar and Mitchell, 2006]. Storm event analysis for our current study showed that the temporal pattern of DON concentrations differed from those for NO_3^- and DOC but matched the pattern of ammonium (NH_4^+) concentrations. These findings suggest that sources and flow paths for DON and NH_4^+ were similar but distinct from those for NO_3^- and DOC. Specific questions that were addressed in this study

include the following. (1) What are the sources of DON in the watershed and can they explain the storm-event DON concentration patterns? (2) How do the storm-event patterns of DON differ from those of DOC, NH_4^+ , and NO_3^- and what does this indicate about the flow paths and transport mechanisms for DON? (3) How do DON exports vary among catchments of varying size and wetness?

2. Site Description and Methods

2.1. Site Description

[7] Our study was conducted in the PPBW (Figure 1), located in Cattaraugus County and 55 km southeast of Buffalo in New York State ($42^\circ 26' 30''\text{N}$; $-78^\circ 55' 30''\text{W}$). 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 Weather Station at Chautauqua, New York; 35 km southwest of PPBW; National Atmospheric Deposition Program (NADP) online weather site, last accessed 2006, <http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=NY10> (hereinafter referred to as NADP site, 2006). Atmospheric N deposition in the region is fairly high (annual average for the Chautauqua NADP station for 2003–2004 was $573 \text{ mol N ha}^{-1}$; NADP site, 2006).

[8] The parent material was derived from glacial till (Kent Drift of Woodfordian formed 19,000 yr B.P.) [Phillips, 1988]. Vegetation on ridgetops and hillslopes was 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 watershed is fairly distinct with wide ridgetops, steep hillslopes, and narrow valley bottoms. Slope gradients in the watershed range from 0 to 69%, with a mean gradient of 14%. Elevation ranges from 252 to 430 m above mean sea level. A low-permeability clay layer that generates perched water tables and forces water to move as shallow subsurface flow on the steep hillslopes underlies the soils. The depth to the clay/till measured using soil cores varies from 1.2–1.7 m in the valley-bottom locations, 0.3–0.5 m along the side slopes and 0.6 m at the ridgetops.

[9] The catchments that were studied (S1, S2, S3, and S5) are shown in Figure 1. Outlet for S1 (696 ha) was located on the main drainage of PPBW with S2 (3.4 ha) and S3 (1.6 ha) nested within S1. The width of the stream at S1 (third-order drainage) was 3.4 m. Catchment S3 drained a hillslope hollow with streamflow originating from two perennial seeps S3a and S3b that discharged at the channel head (Figure 1). The width of the stream at S3 (first-order tributary) was 0.40 m. Outlet S2 was located in a valley-bottom riparian area downstream of S3 and the width of the stream at S2 (first-order tributary) was 0.38 m. Catchment S5 (1.9 ha) located outside and downstream of S1 enclosed a valley-bottom riparian wetland. Runoff to S5 also originated from a seep (S8) located more than two thirds of the distance along the contributing hillslopes along the northeastern edge (Figure 1). The width of the stream at S5 (first-order tributary) was 0.45 m.

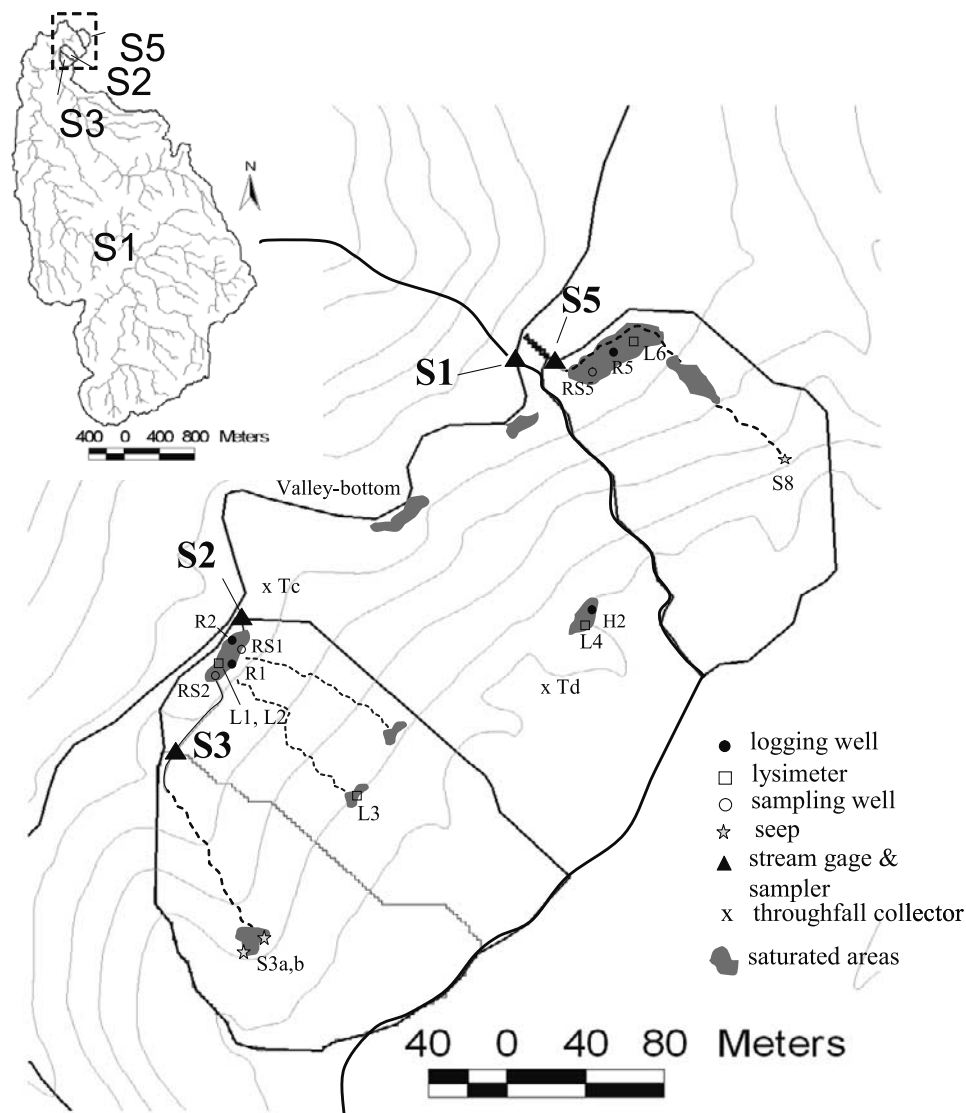


Figure 1. Point Peter Brook watershed and study catchments (inset) and the sampling locations in the selected portion of the watershed.

[10] Watershed boundaries, slope gradients, aspect, and spatial extent of hillslope and valley-bottom saturated areas for the catchments were determined using a combination of field surveys and GIS-based analysis [Inamdar and Mitchell, 2006]. The spatial distribution of wetness was characterized by the downslope wetness index (DWI) of Hjerdt *et al.* [2004] and is presented graphically by Inamdar and Mitchell [2006]. The dominant slope aspect for all three small subcatchments was northwest, whereas 17% of the hillslopes for S1 were oriented to the west (Table 1). Field-surveyed surface-saturated areas were highest for S5 at 5.9% of the catchment area followed by S2 (2.0%) and S3 (0.8%). The valley-bottom wetland in S5 constituted 4.7% with 1.2% of the saturated areas on hillslopes. Organic matter concentrations of the wetland soil were ~70%. Soil thickness in the S5 wetland was 1 m or less (above gravel/loose unconsolidated material) and lower than that observed for the riparian area at S2. The valley-bottom riparian area in S2 accounted for only 0.7% of the saturated area with the remaining saturation (1.3%) in discrete pockets

on hillslope benches (Figure 1). The organic matter content of surficial (0–20 cm) soils in the riparian area at S2 was between 3 and 11%. Organic matter concentrations of surficial soils in these isolated saturated areas ranged from 3 to 70%. Soil thickness in the riparian area ranged from 1.5 to 2 m above loose gravel or unconsolidated material. Saturated areas in S3 were limited to the channel head (0.8%).

[11] The field-surveyed saturated area % values for the small catchments were compared against wetness thresholds derived from the DWI map [Inamdar and Mitchell, 2006]. A DWI value of 10 produced the best fits between field-surveyed % saturated areas. A threshold value of 10 indicated a DWI area of 4.3% for S5 that was similar to the valley-bottom wetland area of 4.7% (Table 1). For S2 the DWI value was 0.9%, which was again similar to the field measured value of 0.7%. Using a threshold of 10, the extent of surface saturation for S1 was computed to be 2.1%. Although the value of 2.1% for S1 likely represents the valley-bottom saturated areas and does not include the more dynamic hillslope-bench saturated areas, this

Table 1. Watershed Characteristics and Topographic Attributes for the Four Subcatchments

Attribute	Subcatchments			
	S1	S2	S3	S5
Area, ha	696	3.4	1.6	1.9
Relief, m	254–430	255–307	260–307	255–304
Mean catchment gradient	14.1	14.3	15.0	14.9
Stream order and width, m	3rd, 3.4	1st, 0.38	1st, 0.4	1st, 0.45
<i>Field-Surveyed Saturated Area in % and m² in Parentheses</i>				
Total	-	2.0 (675)	0.8 (129)	5.9 (1122)
Valley bottom	-	0.7 (231)	0	4.7 (896)
Hillslope	-	1.3 (444)	0.8 (129)	1.2 (226)
<i>Downslope Wetness Index (DWI) Moments</i>				
Mean	5.12	5.39	5.28	5.67
Variance	1.98	1.34	1.36	2.60
Skew	1.61	0.90	0.91	1.44
Percent catchment area with DWI >10	2.1	0.9	0.7	4.3

value provides a useful estimate for comparison against the other catchments.

2.2. Watershed Monitoring and Sampling

[12] Precipitation in PPBW was recorded using a tipping-bucket rain gage located 400 m downstream from S1. Streamflow discharge measurements at S1 were initiated in November 2002, at S2 and S3 in May 2003 and at S5 in April 2004. Streamflow stage was recorded every 15 min using a pressure transducer with a recorder (Global Water Inc.). At S1, a stage-discharge relationship was developed for the stream channel. Parshall flumes were installed on streams at S2 and S3 and a V notch weir was installed at the stream channel at S5. Groundwater elevations were recorded using pressure transducers (Global Water Inc.) nested within logging wells that were constructed of 5 cm (ID) PVC tubing. The logging wells were constructed by coring to the depth at which an impeding clay or loose/unconsolidated gravel or till was intersected. Two logging wells R1 and R5 were located in the valley-bottom riparian and wetland areas of S2 and S5 respectively (Figure 1). One hillslope well (H2) was positioned in a saturated area on the hillslope bench.

[13] Water chemistry was monitored by grab sampling and automatic sampling using ISCO samplers. Grab sampling was performed twice a month for: valley-bottom and hillslope groundwater wells, surface seeps, and lysimeters located in valley-bottom and hillslope-bench saturated areas. Groundwater sampling wells were constructed of 5 cm (ID) PVC tubing and were cored to the depth at which an impeding clay or gravel layer was intersected (between 1.5 and 3 m). The wells were screened from 30 cm below the soil surface to the bottom. Three groundwater-sampling wells (RS1, RS2, and RS5) were established in riparian and wetland valley-bottom locations (Figure 1). Seep samples were collected from surface seeps at S3a and S3b (Figure 1) in the catchment S3. Starting in spring 2005, samples were also collected downstream of the seep S8 located in catchment S5. Zero-tension lysimeters were constructed of 5 cm (ID) PVC tubing and were inserted at a 45-degree angle to a depth of 30 cm from the soil surface. The lysimeters were installed to collect soil water from the A horizon. Lysimeters were installed in valley-bottom riparian

and wetland areas (L1, L2, and L6) and hillslope-bench saturated areas (L3 and L4) (Figure 1). Sample water was obtained from the groundwater wells and lysimeters using a hand-operated suction pump. In summer 2005, litter layer (O horizon) samplers were installed at two separate sites to collect litter leachate associated with storm events. The litter sampler was a 1 m² plastic tray with raised edges (3 cm) with a hole and plastic tube that connected to a 500 mL plastic bottle. The tray was inserted at the junction of the O and A horizon and was positioned such that water drained into the receiving bottle. Although only five samples (three rainfall events) were collected from the driest period of the year (August–September 2005), this data was included to provide some estimate of the DON contributions from litter leachate. Both litter samplers were placed on hillslopes.

[14] Storm event sampling for the four catchments was performed using a limited number of ISCO samplers over 2003–2005. For S1 and S2, storm-event sampling was initiated from May 2003. Availability of a third sampler in September 2003 allowed us to sample S3. Sampling at S5 was initiated after 19 April 2004 by moving the sampler from S1 to S5. Sampling for S1 was resumed again in 2005 by moving the sampler from S3. The automated ISCO sampler was triggered for event sampling when the rainfall rate exceeded a threshold of 2.8 mm within a 2-hour period. The sampler was programmed on the “variable time” mode so as to sample more frequently on the hydrograph rising limb than on the recession limb. Composite precipitation samples were collected in a collector placed in the open; throughfall samples were collected from two collectors, one placed under a coniferous canopy (Tc) and one placed under a deciduous canopy (Td) (Figure 1). Precipitation and throughfall collectors were 3.8 L plastic containers connected to funnels, which had a plastic mesh on the mouth to prevent entry of debris. All samples were collected within 24 hours of an event in 250 mL Nalgene bottles.

[15] All samples were filtered with 0.5 μ m filters prior to analysis. Analyses performed on the samples included: DOC on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer and anions (NO₃⁻) on a Dionex IC. Total dissolved N (TDN) was determined using persulfate oxidation [Ameel *et al.*, 1993] followed by colorimetric analysis on an autoanalyzer. Ammonia was also determined on an autoanalyzer 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 $\pm 5\text{--}10\%$. The laboratory is a participant in the United States Geological Survey (USGS) performance evaluation program to ensure data quality. A system of calibration QC, detection QC, analytical blanks and replicates is used with every set of samples [Mitchell *et al.*, 2001].

2.3. Selection of Storm Events

[16] Multiple storm events were monitored for S1, S2, S3, and S5 over the period May 2003 through August 2005. Because of budget, equipment and personnel restrictions not all catchments were sampled simultaneously for all events. Events that are evaluated in this study include: 27 July and 9 August 2003 (summer events); 12 April, 20 May and 27 May 2004 (spring events); and 16 June and 30 August 2005 (summer events). These events were selected since: (1) they showed clear and distinct temporal patterns in the solutes; (2) were representative of the events for those seasons; and (3) had the most complete data set across the catchments. Of these, three events, 27 July and 9 August 2003 and 20 May 2004 were selected to display detailed temporal patterns of the solutes within events.

2.4. Isotopic ($\delta^{18}\text{O}$) Data for Event of 27 July 2005

[17] Supplemental funds allowed us to sample and analyze selected events in the summer of 2005 for ^{18}O . We present data from a single event of 27 July 2005 that was collected for S1. While chemical tracers such as Si and DOC provide insight on the water flow paths, $\delta^{18}\text{O}$ values can potentially provide quantitative information about water sources [Buttle, 1994]. Lower $\delta^{18}\text{O}$ values indicate contributions of “event” water while higher values indicate “pre-event” water. Although a definitive hydrograph separation into event and pre-event water components [Buttle, 1994] was not possible because of inadequate separation between precipitation and stream $\delta^{18}\text{O}$ values, the temporal pattern of $\delta^{18}\text{O}$ values provides some estimate on the timing and relative contributions of event water. The ^{18}O analysis was performed at the Cornell Stable Isotope Laboratory, Ithaca, New York, using a mass spectrometer and reported in ‰ relative to VSMOW.

2.5. Event Computations and Statistics

[18] The start of the event was defined when a perceptible rise in discharge was observed after precipitation or the occurrence of first ISCO sample, whichever occurred earlier. The end of events was defined by the first occurrence of when discharge returned to the pre-event values or when a subsequent event began. Discharge per unit area or specific discharge (mm) was the total volumetric flow for the event divided by the catchment area. Antecedent moisture conditions for each storm were computed by: (1) summation of the precipitation amounts for seven days prior to the event (antecedent precipitation index, API_7); and (2) average of groundwater elevations (antecedent groundwater index, AGI_7) for seven days prior to the event. AGI_7 values were computed using the riparian well R1, hillslope-bench well

H2, and wetland well R5. Groundwater elevations at H2 varied over a larger range of values compared to wells R1 and R5 and thus provided a more dynamic picture of the changes in catchment wetness.

[19] The differences in DON concentrations between various watershed compartments were evaluated using the nonparametric Kruskal-Wallis test since the concentrations were not normally distributed. Thereafter the Mann-Whitney U-test was performed to determine the differences between the mean values for two compartments. Correlations between DON, throughfall amounts, NH_4^+ , and DOC concentrations were evaluated using the nonparametric Spearman rank (ρ) statistic. All statistical analyses were performed using SPSS (SPSS, Inc.).

2.6. Previous Determinations of Runoff Sources Determined From EMMA and a Model for Runoff Response

[20] Spatial sources of runoff in the PPBW were identified by Inamdar and Mitchell [2006] using silica (Si), magnesium (Mg), and dissolved organic carbon (DOC) as tracers in an EMMA model [Burns *et al.*, 2001; Christopherson and Hooper, 1992]. The EMMA model was evaluated by comparing the model-predicted concentrations for Mg^{2+} , Si, DOC, NO_3^- , Ca^{2+} , and SO_4^{2-} against observed stream concentrations assuming conservative mixing.

[21] EMMA identified groundwater discharged at seeps (SGW), throughfall (THF), and riparian water (RW) as the end-members for stream chemistry. SGW contributions were high prior to the event and declined through the hydrograph rising limb. THF amounts increased on the rising limb and peaked in the vicinity of the discharge peak. RW contributions also increased slowly through the rising limb but reached a maximum after the discharge peak on the recession limb. The delayed rise in valley-bottom riparian groundwater levels supported the late expression of RW [Inamdar and Mitchell, 2006, Figure 6].

[22] A three-stage model explaining the role of topography in runoff generation and the temporal expression of the three end-members has been developed for PPBW [Inamdar and Mitchell, 2006; Inamdar and Mitchell, submitted manuscript, 2006]. The three stages of runoff generation were as follows. (1) Prior to storm events and during baseflow conditions, streamflow was composed of SGW and RW. (2) In the early part of the storm and on the rising limb of the hydrograph, THF was intercepted on saturated areas and contributed to streamflow as saturation overland flow. (3) During hydrograph recession, hydraulic gradients associated with subsurface hillslope runoff displaced RW into the stream.

2.7. Previous Model for NO_3^- and DOC Exports From PPBW

[23] Inamdar and Mitchell [2006] also developed a conceptual model explaining the storm event exports of NO_3^- and DOC from PPBW. Across the watershed compartments, highest concentrations of NO_3^- were measured in SGW and occasionally in THF (spring events only). The expression of NO_3^- in stream water was dictated by the combined contribution of NO_3^- from SGW and THF. High concentrations of NO_3^- in THF produced a pronounced rise and maximum on the hydrograph rising limb while low concentrations of

Table 2. Comparison of Mean DON Concentrations With NH_4^+ , NO_3^- , and DOC Values Across Watershed Compartments and Stream Locations^a

Compartment	N ^b	Data Period	DON, $\mu\text{molN L}^{-1}$	NH_4^+ , $\mu\text{molN L}^{-1}$	NO_3^- , $\mu\text{molN L}^{-1}$	DOC, $\mu\text{molC L}^{-1}$	%DON	DOC:DON
<i>Watershed Compartments</i>								
Rainfall	38	May 2003 to June 2004	8 (12)	18 (24)	26 (23)	259 (207)	15	32
Snow	9	Jan 2003 to March 2004	17 (21)	15 (14)	48 (42)	207 (395)	21	12
Conifer throughfall (THFC)	39	April 2003 to June 2004	29 (19)	17 (21)	46 (72)	1182 (616)	32	41
Deciduous throughfall (THFD)	36	April 2003 to June 2004	16 (14)	30 (46)	36 (25)	358 (203)	20	22
Litter leachate	5	Aug 2005 to Sep 2005	57 (22)	63 (24)	27 (27)	6035 (5658)	39	106
Topsoil water (average of lysimeters L1-6)	34	Dec 2003 to June 2004	15 (21)	14 (28)	2.1 (3.4)	653 (919)	48	44
Seep groundwater (SGW)	41	March 2003 to June 2004	3 (6)	2 (1.6)	58 (30)	44 (19)	5	15
Riparian water (average of wells RS1 and RS2)	55	Jan 2003 to June 2004	13 (14)	12 (10)	4 (6)	251 (66)	45	19
Wetland water (well RS5)	8	April 2004 to Oct 2004	21 (5)	20 (18)	0 (0)	491 (128)	51	23
<i>Catchment Baseflow</i>								
S1	56	Jan 2003 to June 2004	7.6 (16)	4.1 (12)	28 (7)	177 (63)	19	23
S2	49	Jan 2003 to June 2004	3.1 (7)	2.2 (2)	51 (13)	67 (25)	6	22
S3	46	Jan 2003 to June 2004	3.8 (9)	1.9 (1)	54 (16)	57 (13)	6	15
S5	11	April 2004 to Oct 2004	3.7 (2)	5.2 (3)	14 (8)	156 (28)	16	42

^aStandard deviations are provided in parentheses.

^bNumber of samples.

NO_3^- in THF lowered the concentrations in streams as NO_3^- rich SGW was diluted by THF. Highest DOC concentrations among the watershed compartments were found in THF and RW. Thus DOC concentrations in streamflow reached a maximum when the combined DOC contributions from THF and RW sources were highest. DOC concentrations increased gradually during events, with a peak on the recession limb.

3. Results

3.1. Concentrations of DON in Watershed Compartments and Baseflow

[24] Concentrations of DON increased as precipitation traversed the forest canopy (Table 2). Mean concentrations of DON in conifer (THFC) and deciduous (THFD) throughfall ($16\text{--}29 \mu\text{mol N L}^{-1}$) were nearly 4 and 2 times greater, respectively, than in precipitation ($8 \mu\text{mol N L}^{-1}$). Highest concentrations for DON in the watershed were recorded in litter leachate ($57 \mu\text{mol N L}^{-1}$) with subsequent decrease as water moved through the mineral soil. Concentrations for DON were lowest in seep groundwater (SGW). DON concentrations in valley-bottom groundwater were much greater at the wetland well (RS5) compared to the riparian wells (average of RS1 and RS2).

[25] When DON as a percent of the TDN is considered, highest % values were observed for valley-bottom riparian/wetland waters and topsoil water followed by litter leachate (Table 2). The high percentage of DON in the wetland water

was due to low dissolved inorganic N (DIN) values rather than high DON concentrations. Similar to DON, concentrations of NH_4^+ were also generally high in throughfall, litter leachate, and valley-bottom riparian and wetland water. NH_4^+ was much higher, however, in deciduous versus conifer THF. DOC concentrations were highest for litter leachate followed by throughfall, riparian and wetland water. In contrast to DON, NO_3^- concentrations were highest for SGW followed by throughfall. It is important to note here that two new THF samplers (one each under conifer and deciduous canopies) were installed in PPBW in summer of 2005 and provided similar patterns in concentrations as reported in Table 2 for the old samplers.

[26] A Kruskal-Wallis test on DON concentrations indicated a significant difference between the watershed compartments ($p < 0.001$). Correlations between the solutes were determined by combining the results from all watershed compartments. Spearman correlation tests indicated no correlation between DON and NH_4^+ ($\rho = 0.084$; $p = 0.184$), but a significant correlation between DON and DOC ($\rho = 0.521$; $p = 0.01$) for the watershed compartments.

[27] Mean DON concentration during baseflow for S1 was significantly ($p < 0.001$) greater than for the smaller S2, S3, and S5 catchments (Table 2), while no significant difference was observed between DON values for S2, S3, and S5 ($p > 0.1$). Baseflow stream DON concentrations were lower than all watershed compartments except SGW. The percent of DON for S1 and S5 (19 and 16%, respectively) was more than twice the values for S2 and S3. DIN

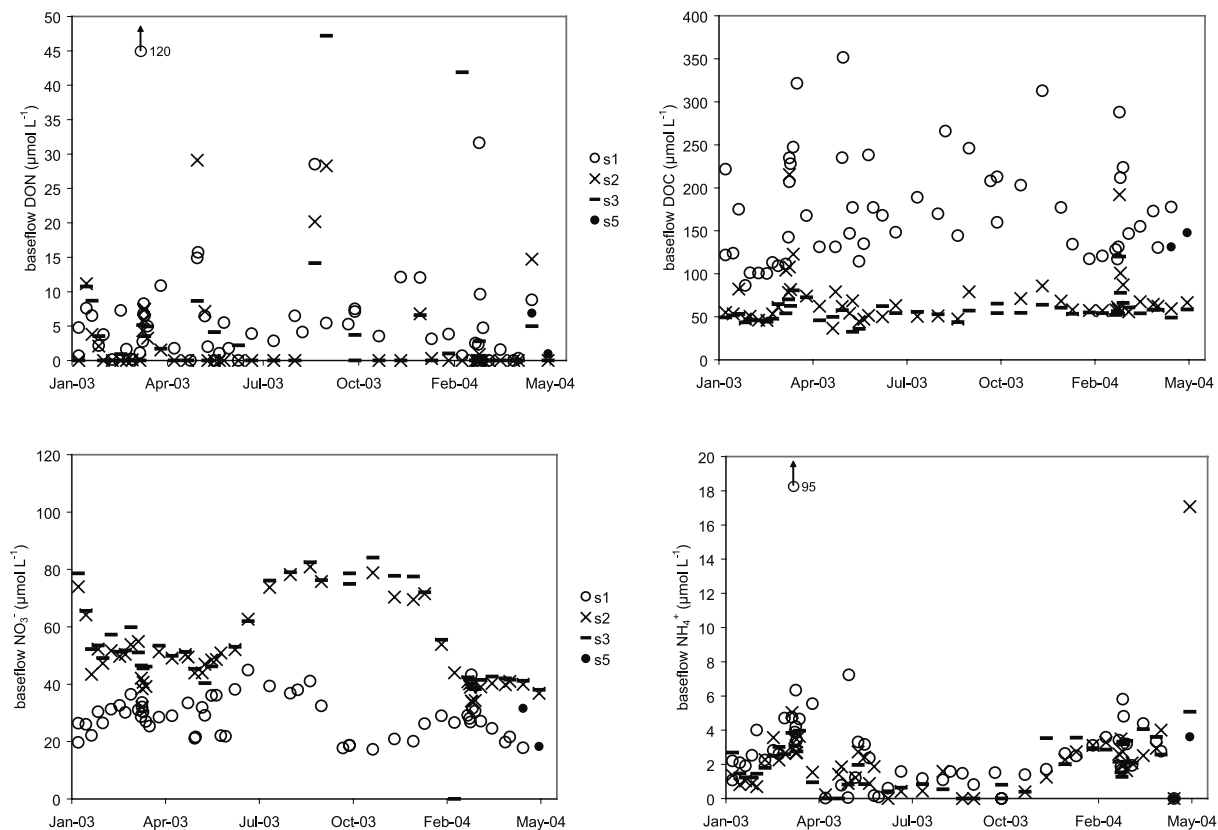


Figure 2. Comparison of baseflow DON concentrations with NH_4^+ , NO_3^- ($\mu\text{mol N L}^{-1}$), and DOC ($\mu\text{mol C L}^{-1}$) for catchments S1, S2, S3, and S5 over the period 1 January 2003 to 30 June 2004.

(especially nitrate) constituted a major % of baseflow TDN across all catchments. The DOC:DON ratio in stream discharge at baseflow was highest for the wetland catchment S5. There was no correlation between stream DON and NH_4^+ concentrations during baseflow ($\rho = -0.18$; $p = 0.012$), but a significant correlation was observed between DON and DOC ($\rho = 0.455$; $p < 0.001$) concentrations.

[28] Baseflow DON and DOC concentrations did not reveal any seasonal variations (Figure 2). However, baseflow DOC concentrations for catchments S1 and S5 were much greater than the values for S2 and S3 (Figure 2). In contrast to DON, there were some seasonal trends in baseflow NO_3^- and NH_4^+ concentrations. Nitrate concentrations for streams S2 and S3 were high in winter and during the low base flow period in summer. The trend in baseflow NO_3^- concentrations for the largest catchment S1 was not as distinct as that for S2 and S5. Baseflow NH_4^+ concentrations across all catchments were similar and peaked around late winter and early spring (February–March).

3.2. Within-Event Patterns of the Solutes

[29] The within-event concentrations of DON, NH_4^+ , NO_3^- and DOC for two summer events (27 July and 9 August) and a spring event (20 May) are presented in Figures 3–5 along with plots of EMMA-derived end-member contributions. For both the summer storms (27 July and 9 August) DON concentrations increased with discharge reaching a maximum either just before or at peak discharge subsequently then subsequently. Event DON concentrations in

streams were markedly greater than baseflow DON values (Table 2). Ammonium concentrations followed a pattern very similar to DON with a peak in concentrations prior to the discharge peak. The temporal patterns of DOC and NO_3^- , however, were markedly different. The peak in DOC concentrations occurred always after the peak in DON values and often on the recession limb of the hydrograph. For NO_3^- patterns highest concentrations were found at the start of the event, with minima close to peak discharge, followed by increasing concentrations with decreasing discharge. Of the three end-members (THF, SGW, and RW), the contributions from THF most closely matched the temporal pattern of DON values.

[30] For the event of 20 May (Figure 5), concentrations of DON from S2 and S3 were highest at or before the discharge peak while the highest concentration for S5 was slightly delayed and occurred later on the recession limb. The pattern of NH_4^+ concentrations for this event was again similar to DON. DOC concentrations peaked later than DON for catchments S2 and S3 but coincided with the DON peak for S5. However, unlike the summer events, NO_3^- did not follow a dilution trajectory but followed a pattern similar to that of DON and NH_4^+ with an increase and subsequent highest concentration on the rising limb, followed by a decrease. The increase in NO_3^- concentrations on the hydrograph rising limb was most pronounced for catchment S5. Other spring events (not presented here) also followed a temporal pattern of solute concentrations similar to that for the 20 May event. Similar to the summer events,

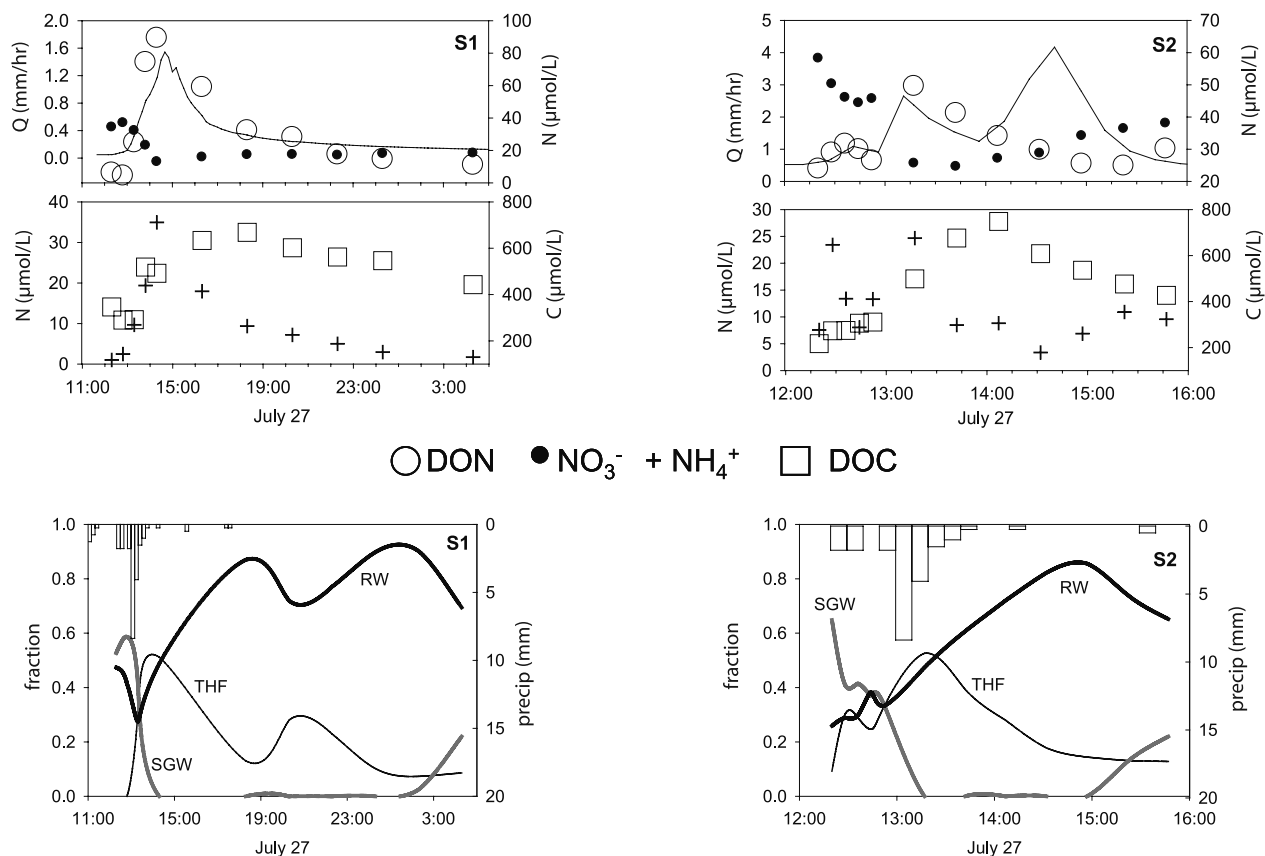


Figure 3. (top) Discharge (Q mm hr⁻¹) and concentrations of NH_4^+ , NO_3^- , DON ($\mu\text{mol N L}^{-1}$), and DOC ($\mu\text{mol C L}^{-1}$) and (bottom) precipitation (mm) and fractional contributions of end-members (throughfall [THF], seep groundwater [SGW], and riparian water [RW]) for the event of 27 July 2003. Catchment IDs are provided in top right corner of each plot.

the temporal pattern of EMMA-predicted THF contributions again closely followed the concentration pattern of DON.

[31] DON concentrations were significantly correlated with THF contributions across all events for catchments S1 and S2 (Table 3). Strong (i.e., high values of ρ) and significant ($p < 0.05$) correlations between DON and NH_4^+ were observed for S1 (27 July, 9 August), S2 (20 May) and S5 (20 May). Significant correlation between DON and DOC concentrations was observed only for the event of 9 August. In addition to the difference in timing of the DON and DOC concentrations, there was considerable difference in the relative change of these concentrations through the storm events. Across all events and catchments the % change in DON (from concentration at start of event to peak value) in DON versus DOC was much greater for the former solute (Table 3). Clearly, storm events had a greater influence on DON than DOC.

3.3. Solute Concentrations Versus $\delta^{18}\text{O}$ Values for 27 July 2005

[32] The event of 27 July 2005 was generated by two sequential rain events of 9.9 and 9.1 mm and a bimodal discharge curve was recorded at S1 (Figure 6). The downward deflections in $\delta^{18}\text{O}$ values indicate increasing contributions from event water since precipitation has lower $\delta^{18}\text{O}$ values than stream water [Buttle, 1994]. The first minimum

in $\delta^{18}\text{O}$ values occurred at the first discharge peak with an increase in $\delta^{18}\text{O}$ values followed by a larger depression of $\delta^{18}\text{O}$ values due to the second rain event (Figure 6). This pattern in $\delta^{18}\text{O}$ values suggests that event water contributions are at their maximum at or just before the discharge peak, similar to the THF contributions determined using EMMA. Concentrations of DON and NH_4^+ increased with increasing event water contributions, reached a peak when event water was maximum (for the first event), and then decreased as event water receded. DON and NH_4^+ values, however, showed no response in the second event suggesting that the sources of DON and NH_4^+ were depleted as the storm progressed. Concentrations for NO_3^- decreased with increasing discharge with a minimum coinciding with the minimum $\delta^{18}\text{O}$ followed by increasing concentrations. DOC concentrations reached a peak as event water contributions receded. The temporal patterns of DON, DOC, NH_4^+ , and NO_3^- for this summer 2005 event were similar to the patterns observed for the events of summer 2003 (Figures 3 and 4).

3.4. Observed Versus EMMA-Predicted Storm Event Concentrations

[33] To evaluate if EMMA-derived end-members (especially THF) could explain the stream DON concentrations we compared the EMMA-predicted DON concentrations

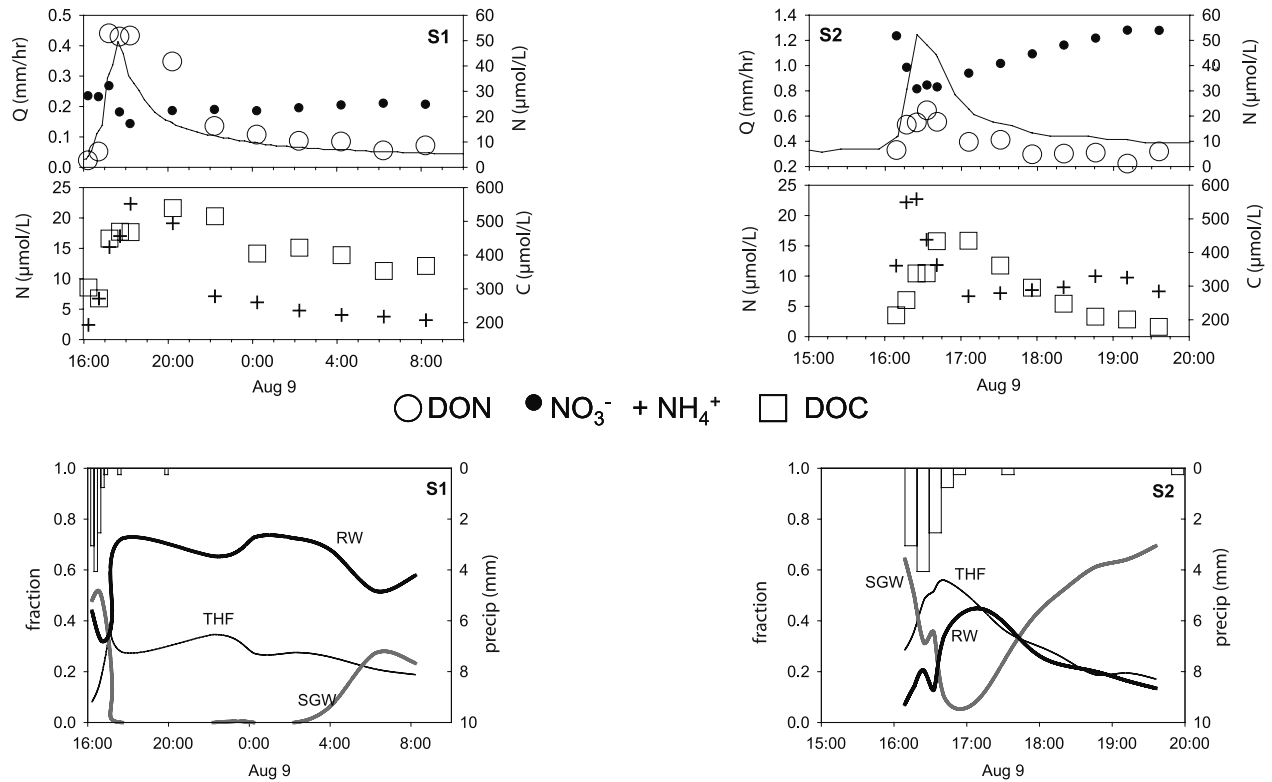


Figure 4. (top) Discharge (Q in mm hr^{-1}) and concentrations of NH_4^+ , NO_3^- , DON ($\mu\text{mol N L}^{-1}$), and DOC ($\mu\text{mol C L}^{-1}$) and (bottom) precipitation (mm) and fractional contributions of end-members (throughfall [THF], seep groundwater [SGW], and riparian water [RW]) for the event of 9 August 2003. Catchment IDs are provided in top right corner of each plot.

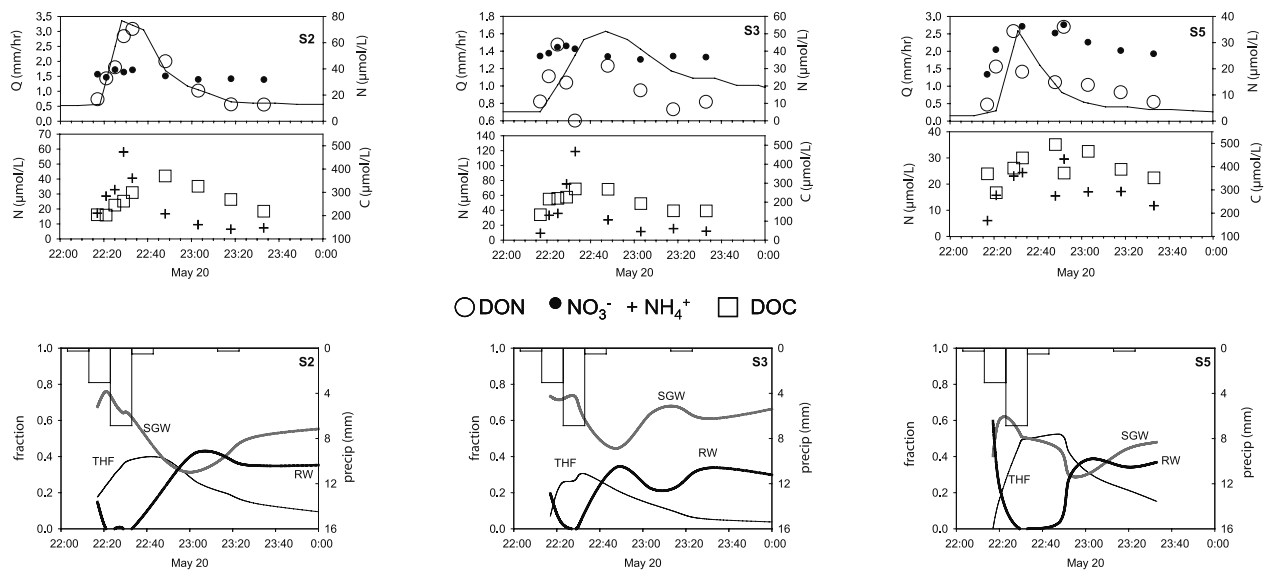


Figure 5. (top) Discharge (Q in mm hr^{-1}) and concentrations of NH_4^+ , NO_3^- , DON ($\mu\text{mol N L}^{-1}$), and DOC ($\mu\text{mol C L}^{-1}$) and (bottom) precipitation (mm) and fractional contributions of end-members (throughfall [THF], seep groundwater [SGW], and riparian water [RW]) for the event of 20 May 2004. Catchment IDs are provided in top right corner of each plot.

Table 3. Spearman Correlation (ρ) Between DON, NH_4^+ , and DOC Concentrations, and Throughfall Amounts for the Three Selected Events^a

Catchments	Parameters	Events		
		27 July 2003	9 August 2003	20 May 2004
S1	number of data points	11	12	
	DON versus NH_4^+	0.94 (<0.01)	0.84 (<0.01)	
	DON versus DOC	0.54 (0.09)	0.85 (<0.01)	
	DON versus THF amounts	0.88 (<0.01)	0.94 (<0.01)	
	% change in DON	1820	1910	
	% change in DOC	131	99	
S2	number of data points	12	12	10
	DON versus NH_4^+	0.34 (0.29)	0.52 (0.08)	0.88 (<0.01)
	DON versus DOC	0.45 (0.14)	0.64 (0.02)	0.55 (0.09)
	DON versus THF amounts	0.83 (<0.01)	0.82 (<0.01)	0.94 (<0.01)
	% change in DON	643	247	1270
	% change in DOC	246	104	147
S3	number of data points			10
	DON versus NH_4^+			0.21 (0.55)
	DON versus DOC			0.31 (0.38)
	DON versus THF amounts			0.30 (0.40)
	% change in DON			418
	% change in DOC			130
S5	number of data points			9
	DON versus NH_4^+			0.77 (0.01)
	DON versus DOC			0.12 (0.76)
	DON versus THF amounts			0.60 (0.08)
	% change in DON			477
	% change in DOC			72

^aThe p values are provided within parentheses.

against the observed values for the events of 9 August 2003 and 20 May 2004 (Figure 7). Our previous work [Inamdar and Mitchell, 2006] showed that EMMA was able to predict the concentrations of NO_3^- associated with storm events [Inamdar and Mitchell, 2006, Figure 5]. The concentrations of DON used for the end-members for the comparisons in Figure 7 are presented in Table 4. Despite the good match for NO_3^- , observed DON concentrations were considerably greater than those predicted by EMMA for all catchments (Figure 7). For example, for catchment S2 during the event of 20 May 2004, observed DON concentrations were as high as $70 \mu\text{mol N L}^{-1}$ while EMMA-predicted values did not exceed $20 \mu\text{mol N L}^{-1}$. Such differences were also seen for other events (data not presented), with EMMA predictions of DON consistently underestimating the observed concentrations.

3.5. Flow-Weighted Mean DON Concentrations and Flux Across the Catchments for the Selected Events

[34] The seven selected events represented a range in precipitation amount (11 to 66 mm) and antecedent soil moisture conditions (API_7 0.2 to 83 mm) (Table 5). The largest amount of rainfall (66 mm) was associated with the event of 30 August 2005 (remnants of Hurricane Katrina) which occurred when antecedent soil moisture conditions in the catchments were very low or dry ($\text{API}_7 = 1.8$ mm; AGI_7 for H2 = 134 mm). The event of 27 July 2003 was the most intense and resulted in the peak discharges from S1 and S2 (1.5 and 4.2 mm hr^{-1} , respectively) that were the highest for the year 2003. The summer event of 9 August 2003 and the

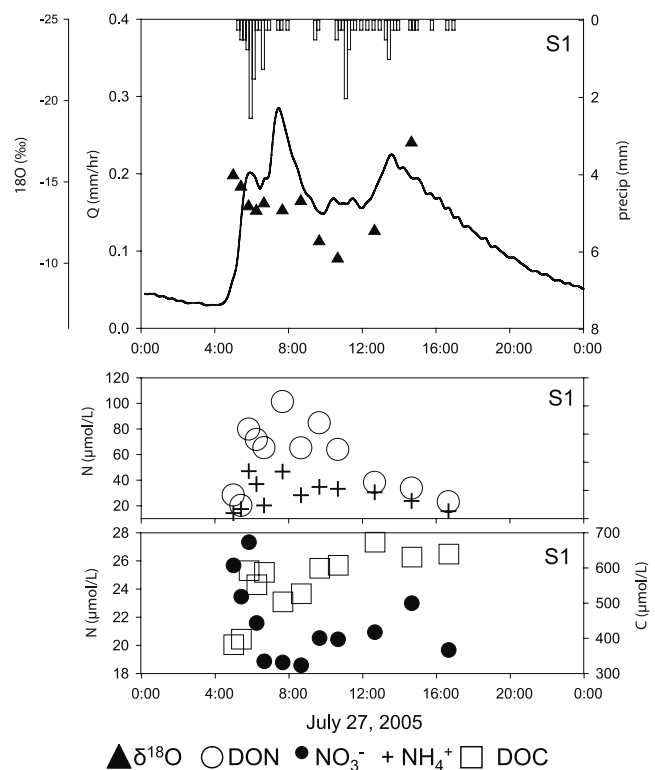


Figure 6. (top) Precipitation (mm), discharge (mm hr^{-1}) and $\delta^{18}\text{O}$ (‰) values; (middle) DON and NH_4^+ ; and (bottom) NO_3^- and DOC for the event of 27 July 2005.

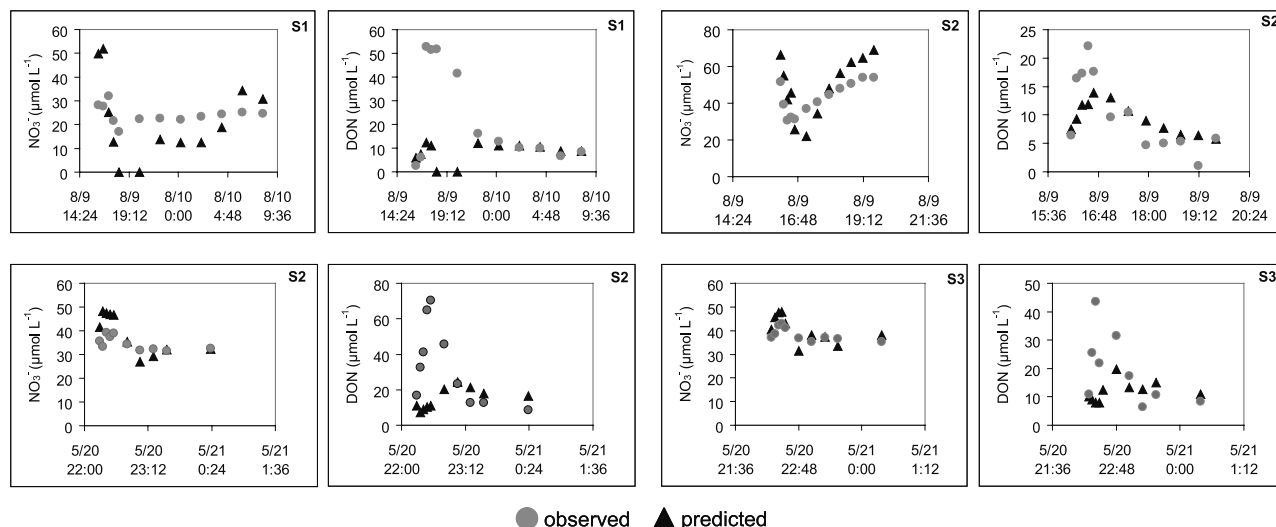


Figure 7. Comparison of EMMA-predicted (triangle) and observed (solid circle) concentrations ($\mu\text{mol N L}^{-1}$) for NO_3^- and DON for the events of (top) 9 August 2003 (catchments S1 and S2) and (bottom) 20 May 2004 (catchments S2 and S3).

spring events of 12 April and 20 May 2004 were moderate in size and occurred under fairly wet antecedent soil moisture conditions. Antecedent moisture conditions ($\text{API}_7 = 83$) were wettest during the event of 27 May 2004 when water level at well H2 was 4 cm above the soil surface (Table 5). Discharge rate (mm) for individual storms was highest for the headwater catchment and decreased with increasing catchment area (Table 5).

[35] For five of the seven events for which S1 data was available, DON concentrations for S1 were greater than those recorded for the smaller catchments (S2, S3, and S5) (Figure 8). Among the nested catchments (S1, S2, and S3) DON concentrations increased with increasing catchment size and saturated area (e.g., events of 27 July, 9 August, and 12 April). The percent of DON as a portion of TDN was also highest for the largest catchment S1 and ranged between 46–64% (Figure 8). In comparison to the nested catchments, concentrations and % DON from the wetland catchment S5 showed considerable variability. DON concentrations for S5 were greater than S2 for the event of 30 August 2005, as much as S1 for the event of 16 June 2005, but lower than S2 for the spring events of 20 and 27 May 2004. The hollow catchment S3 with the least extent of saturated area yielded the lowest DON concentrations and % DON values.

[36] In comparison to DON, the differences in mean DOC concentrations among the catchments were less (Figure 8). For example, for the event of 27 July the DOC concentrations were 540 and 517 $\mu\text{mol C L}^{-1}$ for S1 and S2, respectively, while the corresponding DON values were 47 and 18 $\mu\text{mol N L}^{-1}$. DOC concentrations increased with increasing catchment size for the nested catchments. Unlike DON, DOC concentrations from the wetland catchment S5 consistently exceeded the values from the other two smaller catchments (S2 and S3) for all sampled events.

[37] Other than the event of 30 August 2006, N inputs from precipitation were primarily of inorganic form with total values ranging between 3.7 to 10.5 mol N ha^{-1} (Figure 9). Nitrogen exports for the catchments were

highest for the largest event of 30 August 2006. DON flux increased with catchment size across the nested catchments. Catchment S5 displayed a mixed pattern with low DON fluxes during the spring 2004 events but very high exports for the events of summer 2006. The flux of NH_4^+ generally followed a pattern similar to DON among the catchments. However, in contrast to NH_4^+ and DON, exports of NO_3^- were elevated for the headwater catchments and decreased with increasing catchment and saturated area extent. When precipitation inputs of total N were compared with corresponding values of catchment exports, there was a net retention of N across all events except the two largest events of 27 July 2003 and August 2006 (Figure 9). Other than the events of 27 July 2003 and 16 June 2006 the difference in %N retention among the catchments was not substantial.

4. Discussion

4.1. What are the Sources of DON in the Watershed?

[38] For PPBW, highest concentrations of DON were recorded for litter leachate (57 $\mu\text{mol N L}^{-1}$) and conifer throughfall (30 $\mu\text{mol N L}^{-1}$). Previous studies have also already shown that litter layer and throughfall are important sources of DON with litter DON concentrations often exceeding the throughfall [Currie *et al.*, 1996; Goller *et al.*, 2006; Hagedorn *et al.*, 2000, 2001; Michalzik *et al.*, 2001; Qualls and Haines, 1991; Yavitt and Fahey, 1985].

Table 4. Concentrations of DON for End-Members Used for EMMA Model Predictions (Figure 7) for the Events of 9 August 2003 and 20 May 2004^a

Events	End-Members		
	THF	SGW	RW
9 August 2003	20	2	8
20 May 2004	28	0.25	39

^aConcentrations of DON are in $\mu\text{mol N L}^{-1}$.

Table 5. Hydrologic Parameters for the Seven Selected Storm Events Across the Four Catchments

Parameter	Events							
	2003		2004			2005		
	27 July	9 Aug	12 April	20 May	27 May	16 June	30 Aug	
Rain, mm	24	11	16	11	11	20	66	
Peak 10-min rain intensity, mm	8.4	3.0	2.3	6.9	3.8	4.8	2.5	
API ₇ , mm	47	31	0.2	23	83	6.6	1.8	
AGI ₇ -H2, cm	12	2	2	12	-4	51	134	
AGI ₇ -R1, cm	23	27	27	19	12	23	37	
AGI ₇ -R5, cm				4	4	6	12	
			<i>Catchment S1</i>					
Discharge, mm	6.6	1.8	3.1	1.2	2.8	0.9	8.6	
Runoff ratio	0.27	0.16	0.19	0.11	0.26	0.05	0.13	
Peak discharge, mm hr ⁻¹	1.5	0.4	0.3	0.3	0.26	0.12	1.1	
			<i>Catchment S2</i>					
Discharge, mm	6.9	3.0	5.9	2.0	3.4	3.1	22	
Runoff ratio	0.29	0.27	0.37	0.18	0.32	0.15	0.35	
Peak discharge, mm hr ⁻¹	4.2	1.2	1.7	3.4	1.7	1.3	2.3	
			<i>Catchment S3</i>					
Discharge, mm			7.8	3.2	3.5			
Runoff ratio			0.49	0.28	0.33			
Peak discharge, mm hr ⁻¹			1.7	1.6	1.5			
			<i>Catchment S5</i>					
Discharge, mm				1.9	3.2	8.9	24	
Runoff ratio				0.17	0.30	0.44	0.36	
Peak discharge, mm hr ⁻¹				2.6	1.0	1.7	3.15	

Michalzik *et al.* [2001] review of DON found ranges of 18–79 $\mu\text{mol N L}^{-1}$ for throughfall; 29–175 $\mu\text{mol N L}^{-1}$ for forest floor; and 14–79 $\mu\text{mol N L}^{-1}$ for mineral soil horizons. Concentrations of DON measured for PPBW fell within the lower half of these values. Our observations show that DON concentrations in conifer throughfall were nearly twice the values for deciduous canopy (Table 2). Contrasting results have been reported in literature regarding the influence of conifer and deciduous canopies. Some studies have reported higher DOC and DON concentrations for conifer forests [Currie *et al.*, 1996] while others have found no significant difference [Matzner, 1988].

[39] Concentrations of DON and DOC at PPBW were slightly higher in wetland versus riparian locations (Table 2). High DON concentrations in wet anaerobic soils have also been reported by Hagedorn *et al.* [2001] who attributed the elevated DON concentrations to low sorption onto mineral surfaces. Laboratory and microcosm experiments have shown that anaerobic conditions in wetlands can depress the adsorption and/or decomposition processes resulting in increased solubility of DOC and DON [Kalbitz *et al.*, 2000]. Higher organic matter contents of wetland soils reduce the number of sites available for adsorption of DOC or DON [Vance and David, 1992; Moore *et al.*, 1992] resulting in an increase in the soluble fraction of dissolved organic matter (DOM). In addition, reductive dissolution of Fe and Al oxides under anaerobic conditions can lead to release of DOM that was previously adsorbed on the oxides [Tipping, 1981].

[40] DON and DOC concentrations in catchment baseflow did not reveal any seasonality (Figure 2). Similarly, no seasonality was observed for DON and DOC concentrations in watershed compartments (data not plotted). Absence of

seasonality in DON exports have also been reported in many previous studies [Bernal *et al.*, 2005; Campbell *et al.*, 2000; McHale *et al.*, 2000; Willett *et al.*, 2004]. Others however, have reported elevated DON exports during summer and fall [Arheimer *et al.*, 1996; Hagedorn *et al.*, 2001]. Hagedorn *et al.* [2001] attributed the high summer and fall DON exports to elevated decomposer activity and availability of fresh leaf litter during these periods. In contrast, seasonality was apparent for NO_3^- and NH_4^+ in catchment streamflow (Figure 2), very likely associated with a reduced biological/vegetative demand during the dormant (winter) period. These differences suggest that biotic factors that influenced the concentrations of inorganic N species were not affecting the release of DON from the watershed.

4.2. Can the Sources of DON Explain the Temporal Patterns During Storm Events?

[41] THF, SGW, and RW were identified as the controlling end-members for storm runoff in PPBW and these end-members were able to successfully reproduce the storm event concentrations of NO_3^- , SO_4 , and Ca [Inamdar and Mitchell, 2006, Figure 5]. The close correspondence in temporal patterns of DON concentrations and THF contributions (Figures 3–5 and Spearman correlations in Table 3) suggested that THF was likely responsible for the export of DON from PPBW. However, a comparison of EMMA-predicted and observed DON concentrations (Figure 7) indicated that the EMMA model consistently underestimated the observed DON concentrations. The EMMA model failed because none of the selected end-members had sufficiently high DON concentrations to enclose the stream DON values. Peak DON concentrations in stream-

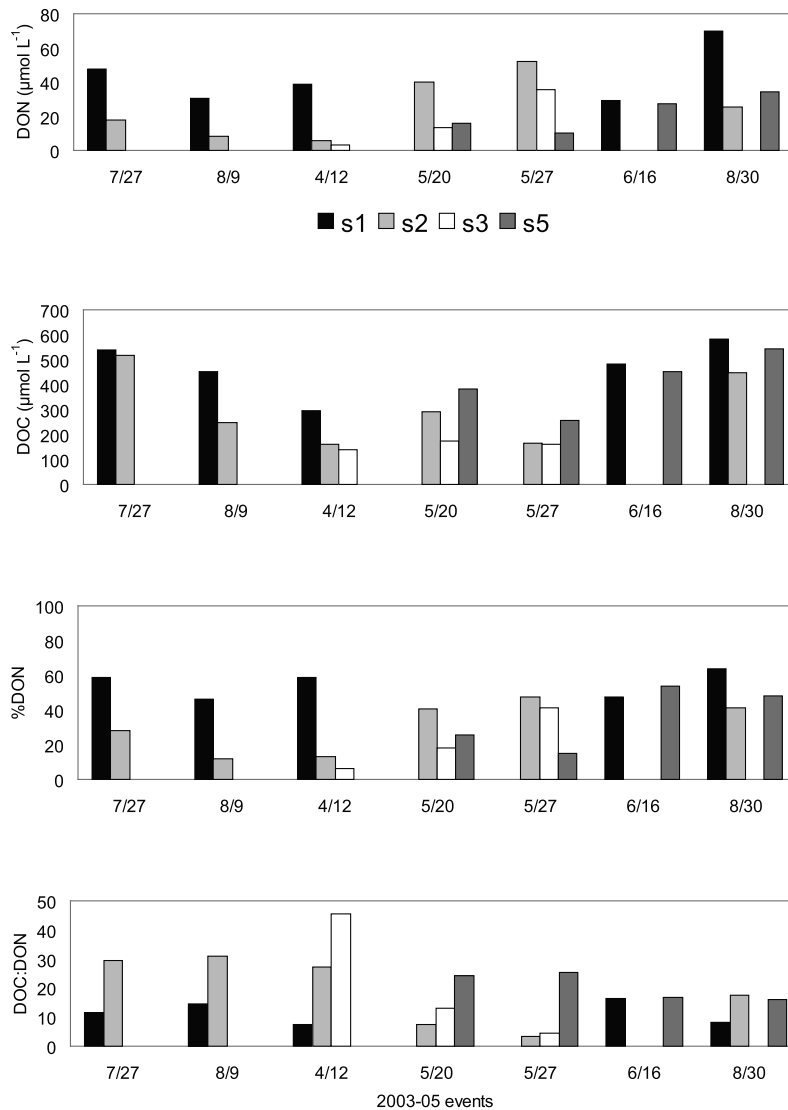


Figure 8. Flow-weighted mean DON and DOC concentrations ($\mu\text{mol L}^{-1}$), %DON, and DOC:DON ratios for the seven selected events.

flow from the catchments were frequently greater than $50 \mu\text{mol N L}^{-1}$ (Figures 3–5) while DON concentrations for the end-members (THF, SGW, RW) were much lower (Table 4).

[42] Our EMMA results are in contrast to a similar analysis by *Hagedorn et al.* [2000] who were able to successfully use EMMA to explain the storm event DON concentrations. *Hagedorn et al.* [2000] used throughfall, “topsoil” and “subsoil” as the end-members for their EMMA model. The topsoil end-member included the litter/Mor layer and had a mean DON concentration of $69 \mu\text{mol N L}^{-1}$ followed by a throughfall value of $31 \mu\text{mol N L}^{-1}$ [*Hagedorn et al.*, 2000, Table 2]. DON concentrations of conifer throughfall (THFC) from our study were similar to *Hagedorn et al.* [2000] throughfall values, but our other end-members did not have DON concentrations as high as the “topsoil” concentration of $69 \mu\text{mol N L}^{-1}$. Further-

more, unlike our observations, DON concentrations in *Hagedorn et al.*’s study peaked on the recession limb and were synchronous with the DOC concentrations. *Hagedorn et al.* [2000] attributed the delayed expression of DON and DOC peaks to the “flushing” of topsoil.

[43] Although our EMMA model failed to reproduce the DON concentrations, the strong correspondence in temporal patterns of DON and THF precludes us from ruling out the influence of THF on DON. This is further supported by the correspondence between event water contributions ($\delta^{18}\text{O}$ values) and DON concentrations (Figure 6). We hypothesize that THF contributions were instrumental in mobilizing a large pool of DON as THF percolated through the DON-rich litter layer. The DON-rich mixture of THF and litter leachate was then transported to receiving streams via saturation overland flow. *Hill et al.* [1999] also alluded to the possibility of throughfall acquiring a higher DON

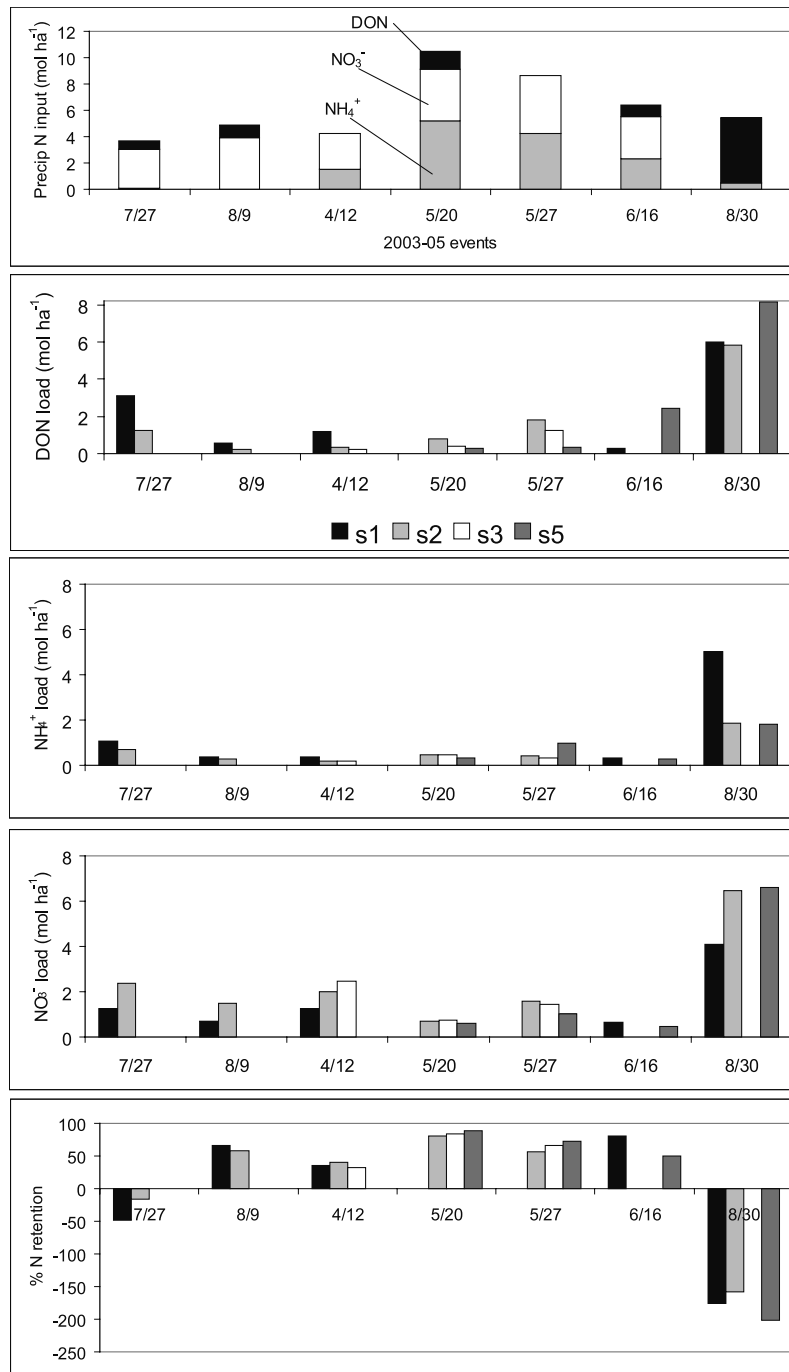


Figure 9. N input from precipitation (mol N ha^{-1}), fluxes of DON, NH_4^+ , and NO_3^- (mol N ha^{-1}), and % N retention for the seven selected storm events.

concentration as it percolated through the organic soil horizon and therefore did not attempt to predict the DON concentrations on the basis of throughfall (event water) contributions.

[44] Litter DON concentrations (Table 2) in our study however were not sufficiently elevated to explain the peak DON values observed during storm events (Figures 3–5). It is likely that our limited litter sampling (2 samplers and only 5 data points) may have underestimated the DON concentrations of the litter layer in PPBW. Both litter samplers

were placed on dry locations on hillslopes and away from the saturated areas. Previous field and laboratory studies have shown that concentrations of DON from litter leachate increase with increasing wetness and throughfall input [Michalzik *et al.*, 2001; Park and Matzner, 2003]. It is possible that litter in saturated areas at PPBW had much higher concentrations of DON. Another source that could contribute to the litter DON pool is the presence of large woody debris on the forest floor. Hafner *et al.* [2005] found that DON concentrations in coarse woody debris exceeded

those recorded for litter leachate and throughfall. We had no measurements of the contributions of woody debris to DON in our study.

[45] Other sources of DON that have been identified in previous studies include: in-stream processes [Brookshire *et al.*, 2005; Chapman *et al.*, 2001] and the hyporheic zone [Wondzell and Swanson, 1996]. Contribution from in-stream processes is typically expected to be higher during baseflow conditions [Mulholland and Hill, 1997]. The higher DON concentrations during baseflow for the third-order S1 stream could suggest some in-stream production of DON. However, it is very unlikely that the marked increases in DON during storm events in this study could be attributed to within stream production. Similarly, flushing (or piston displacement) of DON from the hyporheic zone can also be discounted as a major source of DON in PPBW. Hyporheic zone water is pre-event water (“old” water). The $\delta^{18}\text{O}$ results (Figure 6) indicated a strong correspondence between event (“new”) water and DON suggesting that hyporheic zone (pre-event water) was likely not a major contributor of DON.

4.3. How Do the Storm-Event Patterns of DON Differ From Those of DOC, NH_4^+ , and NO_3^- and What Does This Indicate About the Flow Paths and Transport Mechanisms for DON?

[46] A number of studies have compared DON, DOC, and NO_3^- concentrations to help ascertain the flow paths for DON. McHale *et al.* [2000] found a positive correlation between discharge and DON, which was similar to DOC, and suggested that both DON and DOC were being “flushed” [after Hornberger *et al.*, 1994] from the catchment. Hagedorn *et al.* [2000, 2001] found DOC and DON peaks on the recession limb and attributed the DON signature to mobilization of DON during its passage through the forest canopy and organic-rich topsoil. In contrast, Buffam *et al.* [2001] reported DOC and DON peaks on the rising limb of the hydrograph but were unable to conclusively identify the transport mechanisms. Vanderbilt *et al.* [2003] looking at monthly DON concentrations reported DON peaks on the rising limb of fall storms and attributed this pattern to the flushing of decomposing leaf litter. Similarities in relationships of DOC and DON are to be expected since these solutes are both DOM (dissolved organic matter) constituents that are not chemically distinct from each other. However, the correlations of DON with streamflow discharge have been consistently weaker than those for DOC, leading many researchers to conclude that sources and/or transport mechanisms differed for these two solutes [Hagedorn *et al.*, 2000, 2001; Michalzik *et al.*, 2001; McHale *et al.*, 2000; Ito *et al.*, 2005; Willett *et al.*, 2004].

[47] Our observations showed a clear separation between storm event DON and DOC chemographs across all events and catchments, with the peak DOC concentration consistently lagging behind the DON peak. Inamdar and Mitchell [2006] previously identified throughfall and riparian waters as the source of DOC in PPBW and attributed the DOC export to the flushing (or piston displacement) of DOC from riparian and hillslope-bench saturated areas by a rising water table [e.g., Creed and Band, 1998]. Groundwater elevations in saturated areas in PPBW consistently reached

a maximum (closest to the soil surface) after peak discharge [Inamdar and Mitchell, 2006, Figures 3 and 6] thus supporting the delayed expression of DOC. The peak in DON concentrations prior to the peak in groundwater elevations suggests that the DON exports were influenced less by the rising groundwater and the flushing of the mineral soil than DOC. Our results suggest that DON in stream water during events was primarily derived from THF and litter layer. In contrast DOC contributions were derived from the flushing of the DOC-rich surficial mineral soil by a rising water table as well as from THF.

[48] Concentrations for NH_4^+ followed a very similar pattern to DON across all events suggesting similar flow paths and export mechanisms as DON. This was not surprising since NH_4^+ concentrations were also highest in THF and litter leachate. Storm event patterns of NO_3^- varied with seasons and between catchments (Figures 3–5). The storm event expression of NO_3^- in streamflow was attributed to NO_3^- concentrations and contributions from THF and SGW [Inamdar and Mitchell, 2006]. When throughfall NO_3^- concentrations were low (as in case of the summer events), the stream NO_3^- concentrations followed the SGW contributions (dilution curve). During these events the NO_3^- pattern clearly did not match the DON trend. Alternately, high throughfall NO_3^- concentrations (during spring events) produced a pronounced increase in stream NO_3^- concentrations with a peak in concentrations at or before the discharge peak [Inamdar and Mitchell, 2006]. The importance of NO_3^- rich throughfall in influencing stream NO_3^- concentrations has been highlighted in previous studies [Hagedorn *et al.*, 2001; Hill *et al.*, 1999; Inamdar and Mitchell, 2006]. The agreement in temporal patterns of NO_3^- and DON for the spring events (Figure 5) lends further support to our hypothesis that THF is an important contributor to these solutes in stream water during storms.

[49] While we have identified sources of DON and DOC (THF, litter, and mineral soil) as important in influencing the expression of DON and DOC during storm events it is also possible that the mobility (adsorption/desorption kinetics) of DON and DOC could have also influenced the concentrations and temporal patterns of these solutes during storm events. Work of Qualls and Haines [1991], Kaiser [2001] and Gu *et al.* [1995] has shown that DON is composed of greater proportion of hydrophilic organic matter while DOC is predominantly hydrophobic. It is generally recognized that the hydrophobic fractions of DOM are preferentially adsorbed to the soil [Jardine *et al.*, 1989; Kaiser and Zech, 1998] while a greater proportion of hydrophilic DOM constituents remain in solution. This would suggest that DON is more mobile than DOC. Similar assessments have also been made by Aitkenhead-Peterson *et al.* [2003], Kalbitz *et al.* [2000] and Ussiri and Johnson [2004]. The greater mobility of DON vis-à-vis DOC could also explain the early expression of DON and the delayed response of DOC during storm events.

4.4. How Do DON Exports Vary Among Catchments of Varying Size and Wetness?

[50] Flow-weighted mean DON concentrations, %DON (Figure 8), and peak concentrations during events (Figures 3–5) all increased consistently with catchment size for the nested catchments S3 (1.6 ha), S2 (3.4 ha), and

S1 (696 ha). Similarly, the flux of DON (Figure 9) also increased with catchment size across the nested catchments. In contrast, nitrate flux decreased with catchment size, resulting in little difference in the total N flux among the nested catchments (Figure 9). Surface-saturated area % and areal extent of wetness (as characterized by DWI) increased from catchments S3 to S1 (Table 1). Data for riparian, wetland and topsoil water (Table 2) clearly showed that saturated areas were significant sources of DON, second only to throughfall and litter. Furthermore, saturated areas also serve as loci for interception of DON-rich THF and the delivery of DON-rich THF and litter-leachate via saturation overland flow. We therefore attribute the increase in DON with increase catchment size to a concomitant increase in saturated areas.

[51] Saturated areas including riparian zones and wetlands have been identified as important locations for transformation of inorganic N species to organic forms [Devito and Dillon, 1993a, 1993b; Hill, 1996]. The loss of nitrate N at these locations has been attributed to microbial immobilization and denitrification [Bischoff *et al.*, 2001; Hill, 1996]. Devito and Dillon [1993a, 1993b] found that wetlands (beaver ponds and sphagnum swamps) were sinks for inorganic N but sources of organic N, resulting in a net balance of total N at these landscape positions. The increase in DON with basin area along with a simultaneous decrease in nitrate N was also reported by Hood *et al.* [2003] for high-elevation alpine and subalpine catchments, but they attributed the change in DON to the standing stocks of C and N in catchment soils.

[52] In comparison to the consistent behavior of the nested catchments for DON, the response of wetland catchment S5 was mixed. DON concentrations at S5 were lower than S2 and S3 for the spring 2004 events (Figure 8) but high for the summer events of 2005. A similar pattern was repeated for the DON flux (Figure 9). An important difference between S2 and S3 versus S5 was that saturated areas in S2 and S3 were variably saturated over time while S5 enclosed a large valley-bottom wetland, which was continually wet (note AGI values for R1 versus R5 in Table 5). The largest catchment S1 contained both: variably saturated areas and some wetlands. Moisture conditions in the spring of 2004 were very wet with frequent storm events while the summer of 2005 was much drier (AGI values in Table 5) with infrequent storm events. It is possible that the wet conditions and frequent storm events of spring 2004 resulted in lower accumulation of DON in the S5 wetland while the long, dry periods of summer 2005 allowed for larger accumulations of DON and consequently greater exports of DON during the events of summer 2005. Accumulation of DOM in the soil/litter layers following dry periods have been reported previously [Kalbitz *et al.*, 2000; McDowell and Wood, 1984].

[53] In contrast to the variable DON response, concentrations of DOC from S5 were consistent and always exceeded the values from catchments S2 and S3 (Figure 8). Clearly this suggests that wetland processes or mechanisms that were responsible for the variable response of DON did not affect the DOC flux. Previous studies have also reported differences between DOC and DON responses from wetlands [Chapman *et al.*, 2001; McHale *et al.*, 2004; Ito *et al.*, 2005; Willett *et al.*, 2004]. Ito *et al.* [2005] reported increases in both

DON and DOC concentrations with the proportion of wetlands in watersheds located in the Adirondack Mountains of New York, but also noted that the influence of wetlands on DOC was stronger. Willett *et al.* [2004] found that histosol-dominated catchments in Wales, U.K., exported greater amounts of DOM, but the ratio of DOC:DON varied seasonally and during storm events. Our observations confirm that wetlands have a greater influence on DOC than DON concentrations.

4.5. DON Exports and Atmospheric N Deposition

[54] Watersheds subject to elevated atmospheric N deposition have typically been reported to export N predominantly in inorganic form [Aber *et al.*, 2003]. PPBW is subject to some of the highest rates of N deposition in the US (573 mol N ha⁻¹: annual average for 2003–2004 from NADP Weather Station at Chautauqua, NY; 35 km southwest of PPBW; NADP site, 2006) and our storm-event data (Figure 9) revealed that most of the wet deposition occurred predominantly as inorganic N. At PPBW, the exports of N during baseflow occurred primarily in inorganic form (largely NO₃⁻) however significant amounts of organic N were also exported, especially during storm events. The amounts of DON were also influenced by the catchment size and the % saturated or wetland area. These observations suggest that despite high inorganic N deposition rates, watersheds like PPBW can still export significant quantities of DON during storm events, especially in catchments with substantial proportions of saturated areas and/or wetlands. Pellerin *et al.* [2006] reviewed DON export patterns from 348 forested and human-dominated watersheds subject to a wide range of atmospheric N deposition and also concluded that watershed characteristics and climate may be more important controls on DON exports from forested watersheds than N loading from atmospheric sources.

[55] Annual N export from catchment S1 was estimated by Inamdar *et al.* [2006] at 231 mol N ha⁻¹ (for the period May 2003 to June 2004). A comparison with the annual precipitation input of 573 mol N ha⁻¹ (NADP site, 2006) indicates an annual N retention rate of 60% in PPBW. Storm event data presented for S1 (Figure 9) also showed that except for the two largest events (27 July 2003 and 30 August 2005) N retention rates for events varied between 41 and 81%. The events of 27 July and 30 August, however, show that net export of N from the watershed could occur during large, intense events. Recent work on N cycling in terrestrial ecosystems has shown that N losses from watersheds could occur despite high N biotic demand and that a large portion of this loss or “leak” occurs in the form of DON [Hedin *et al.*, 1995; Perakis and Hedin, 2002; Neff *et al.*, 2003]. Results from PPBW suggest that “leakage” of DON is likely to be facilitated by large intense storm events, and especially those that occur after extended dry periods.

5. Conclusions

[56] This study highlighted important differences between storm event expressions of DON vis-à-vis DOC and inorganic N species. The peak in DON concentration consistently preceded the DOC peak across multiple catchments and events suggesting that the two solutes were derived

from different sources in the watershed. We attributed the exports of DON to throughfall and litter layer while DOC contributions occurred from throughfall, litter and flushing of the surficial soils by a rising water table. Storm event patterns of NH_4^+ were similar to DON across all seasons indicating similar sources and flow paths for the two solutes. However, unlike DON, the trajectory of storm-event NO_3^- concentrations varied with seasons suggesting different sets of biotic and abiotic controls for the two solutes.

[57] Storm-event DON concentrations and %DON increased with catchment size. We attributed this response to the areal extent of saturated areas/wetlands within the catchments. A wetland catchment that consistently yielded high DOC concentrations during storm events varied considerably with regard to DON values. This differential response indicates that exports of DON and DOC from wetlands may be mediated by different set of processes and need to be further explored. This study also showed that watersheds subject to high inorganic N deposition may still yield substantial amounts of DON under certain conditions. Occurrence of storm events and watershed features such as saturated areas and/or wetlands were identified are the important factors regulating DON dynamics.

[58] **Acknowledgments.** This project was funded through a USDA-NRI New Investigator award (2002-00847) to S. Inamdar. We are very grateful to the Gowanda Water Department for providing access to the PPB watershed. Joanna Tuk Riley and Julia Graham are thanked for sample collection and data management. Pat McHale and David Lyons provided the water chemistry results expeditiously. The comments and suggestions of the editors and reviewers were very helpful and constructive.

References

- Aber, J. D., K. J. Nadelhoffer, P. A. Steudler, and J. M. Melillo (1989), Nitrogen saturation in forest ecosystems, *BioScience*, 39, 378–386.
- Aber, J. D., C. L. Goodale, S. V. Ollinger, M. L. Smith, A. H. Magill, M. E. Martin, and R. A. Hallett (2003), Is nitrogen deposition altering the nitrogen status of northeastern forests?, *BioScience*, 53, 375–389.
- Aitkenhead-Peterson, J. A., W. H. McDowell, and J. C. Neff (2003), Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters, in *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*, edited by S. Findlay and R. Sinsabaugh, pp. 26–70, Elsevier, New York.
- Ameel, J. J., R. P. Axler, and C. J. Owen (1993), Persulfate digestion for determination of total nitrogen and phosphorus in low-nutrient waters, *Am. Environ. Lab.*, 10, 1–111.
- Arheimer, B., L. Andersson, and A. Lepisto (1996), Variation of nitrogen concentration in forest streams—Influences of flow, seasonality and catchment characteristics, *J. Hydrol.*, 179, 281–304.
- Bernal, S., A. Butturni, and F. Sabater (2005), Seasonal variation of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream, *Biogeochemistry*, 75, 351–372.
- Bischoff, J. M., P. Buckaveckas, M. J. Mitchell, and T. Hurd (2001), N storage and cycling for a forested wetland: Implications for watershed N processing, *Water Air Soil Pollut.*, 128, 97–114.
- Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight (1997), Response characteristics of DOC flushing in an Alpine catchment, *Hydrol. Processes*, 11, 1635–1647.
- Brookshire, E. N. J., H. M. Vallett, S. A. Thomas, and J. R. Webster (2005), Coupled cycling of dissolved organic nitrogen and carbon in a forest stream, *Ecology*, 86, 2487–2496.
- Buffam, I., J. N. Galloway, L. K. Blum, and K. J. McGlathery (2001), A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream, *Biogeochemistry*, 53, 269–306.
- Burns, D. A., P. S. Murdoch, G. B. Lawrence, and R. L. Michel (1998), Effect of groundwater springs on NO_3^- concentrations during summer in Catskill Mountains streams, *Water Resour. Res.*, 34, 1987–1996.
- Burns, D. A., J. J. McDonnell, R. P. Hooper, N. E. Peters, J. E. Freer, C. Kendall, and K. J. Beven (2001), Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA), *Hydrol. Processes*, 15, 1903–1924.
- Buttle, J. M. (1994), Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins, *Prog. Phys. Geogr.*, 18, 16–41.
- Campbell, J. L., J. W. Hornbeck, W. H. McDowell, D. C. Buso, J. B. Shanley, and G. E. Likens (2000), Dissolved organic nitrogen budgets for upland forested ecosystems in New England, *Biogeochemistry*, 49, 123–142.
- Chapman, P. J., A. C. Edwards, and M. S. Cresser (2001), The nitrogen composition of streams in upland Scotland: Some regional and seasonal differences, *Sci. Total Environ.*, 265, 65–83.
- Christopherson, N., and R. P. Hooper (1992), Multivariate analysis of stream water chemical data: The use of principal component analysis for the end-member mixing problem, *Water Resour. Res.*, 28, 99–107.
- Creed, I. F., and L. E. Band (1998), Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics, *Water Resour. Res.*, 34, 3105–3120.
- Currie, W. S., J. D. Aber, W. H. McDowell, R. D. Boone, and A. H. Magill (1996), Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests, *Biogeochemistry*, 35, 471–505.
- Devito, K. J., and P. J. Dillon (1993a), The importance of runoff and winter anoxia to the P and N dynamics of a beaver pond, *Can. J. Fish. Aquat. Sci.*, 50, 2222–2234.
- Devito, K. J., and P. J. Dillon (1993b), The influence of hydrologic condition and peat oxia on phosphorous and nitrogen dynamics of a conifer peatland, *Water Resour. Res.*, 29, 2675–2685.
- Driscoll, C., et al. (2003), Nitrogen pollution in the northeastern United States: Sources, effects, and management options, *BioScience*, 53, 357–374.
- Goller, R., W. Wilcke, K. Fleischbein, C. Valarezo, and W. Zech (2006), Dissolved nitrogen, phosphorus, and sulfur forms in the ecosystem fluxes of a montane forest in Ecuador, *Biogeochemistry*, 77, 57–89.
- Gu, B., J. Schmitt, Z. Chen, L. Liang, and J. F. McCarthy (1995), Adsorption and desorption of different organic matter fractions on iron oxide, *Geochim. Cosmochim. Acta*, 59, 219–229.
- Hafner, S. D., P. M. Groffman, and M. J. Mitchell (2005), Leaching of dissolved organic carbon, dissolved organic nitrogen, and other solutes from coarse woody debris and litter in a mixed forest in New York State, *Biogeochemistry*, 74, 257–282.
- Hagedorn, F., P. Schleppli, P. Waldner, and H. Fluhler (2000), Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments—The significance of water flow paths, *Biogeochemistry*, 50, 137–161.
- Hagedorn, F., J. Bucher, and P. Schleppli (2001), Contrasting dynamics of dissolved inorganic and organic nitrogen in soil and surface waters of forested catchments with Gleysols, *Geoderma*, 100, 173–192.
- Hedin, L. O., J. J. Armesto, and A. H. Johnson (1995), Patterns of nutrient loss from unpolluted, old-growth temperate forests—Evaluation of biogeochemical theory, *Ecology*, 76, 493–509.
- Hill, A. R. (1993), Nitrogen dynamics of storm runoff in the riparian zone of a forested watershed, *Biogeochemistry*, 20, 19–44.
- Hill, A. R. (1996), Nitrate removal in stream riparian zones, *J. Environ. Qual.*, 25, 743–755.
- Hill, A. R., W. A. Kemp, J. M. Buttle, and D. Goodyear (1999), Nitrogen dynamics of subsurface storm runoff on forest Canadian Shield hill slopes, *Water Resour. Res.*, 35, 811–824.
- Hinton, M. J., S. L. Schiff, and M. C. English (1998), Sources and flow-paths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield, *Biogeochemistry*, 41, 175–197.
- Hjerdt, K. N., J. J. McDonnell, J. Seibert, and A. Rodhe (2004), A new topographic index to quantify downslope controls on local drainage, *Water Resour. Res.*, 40, W05602, doi:10.1029/2004WR003130.
- Hood, E., D. M. McKnight, and M. W. Williams (2003), Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States, *Water Resour. Res.*, 39(7), 1188, doi:10.1029/2002WR001738.
- Hornberger, G. M., K. E. Bencala, and D. M. McKnight (1994), Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, *Biogeochemistry*, 25, 147–165.
- Howarth, R. W., et al. (1996), Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences, *Biogeochemistry*, 35, 75–139.
- Inamdar, S. P., and M. J. Mitchell (2006), Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales, *Water Resour. Res.*, 42, W03421, doi:10.1029/2005WR004212.
- Inamdar, S. P., N. O'Leary, M. J. Mitchell, and J. T. Riley (2006), The impact of storm events on solute exports from a glaciated forested watershed in western New York, USA, *Hydrol. Processes*, 20, 3423–3439.

- Ito, M., M. J. Mitchell, C. T. Driscoll, and K. M. Roy (2005), Nitrogen input-output budgets for lake-containing watersheds in the Adirondack region of New York, *Biogeochemistry*, *72*, 283–314.
- Jardine, P. M., N. L. Weber, and J. F. McCarthy (1989), Mechanism of dissolved organic carbon adsorption on soil, *Soil Sci. Soc. Am. J.*, *53*, 1378–1385.
- Kaiser, K. (2001), Dissolved organic phosphorus and sulfur as influenced by sorptive interactions with mineral subsoil horizons, *Eur. J. Soil Sci.*, *52*, 489–493.
- Kaiser, K., and W. Zech (1998), Rates of dissolved organic matter release and sorption in forest soils, *Soil Sci.*, *163*, 714–725.
- Kalbitz, K., S. Solinger, J. H. Park, B. Michalzik, and E. Matzner (2000), Controls on the dynamics of dissolved organic matter in soils: A review, *Soil Sci.*, *165*, 277–304.
- Lovett, G. M., K. C. Weathers, and W. V. Sobczak (2000), Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York, *Ecol. Appl.*, *10*, 73–84.
- Matzner, E. (1988), Der Stoffumsatz zweier Waldökosysteme im Solling, *Ber. Forschungsz. Waldökosysteme/Waldsterben Uni Göttingen, Reihe A*, *40*, 1–217.
- McDowell, W. H. (2003), Dissolved organic matter in soils—Future directions and unanswered questions, *Geoderma*, *113*, 179–186.
- McDowell, W. H., and T. Wood (1984), Podzolisation: Soil processes control dissolved organic carbon concentrations in stream water, *Soil Sci.*, *137*, 23–32.
- McGlynn, B. L., and J. J. McDonnell (2003), Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, *Water Resour. Res.*, *39*(4), 1090, doi:10.1029/2002WR001525.
- McHale, M. R., M. J. Mitchell, J. J. McDonnell, and C. P. Cirimo (2000), Nitrogen solutes in an Adirondack watershed: Importance of dissolved organic nitrogen, *Biogeochemistry*, *48*, 165–184.
- McHale, M. R., J. J. McDonnell, M. J. Mitchell, and C. P. Cirimo (2002), A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed, *Water Resour. Res.*, *38*(4), 1031, doi:10.1029/2000WR000102.
- McHale, M. R., C. P. Cirimo, M. J. Mitchell, and J. J. McDonnell (2004), Wetland nitrogen dynamics in an Adirondack forested watershed, *Hydrol. Processes*, *18*, 1853–1870.
- Michalzik, B., and E. Matzner (1999), Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem, *Eur. J. Soil Sci.*, *50*, 579–590.
- Michalzik, B., K. Kalbitz, J. H. Park, S. Solinger, and E. Matzner (2001), Fluxes and concentrations of dissolved organic carbon and nitrogen—A synthesis of temperate forests, *Biogeochemistry*, *52*, 173–205.
- Mitchell, M. J., G. McGee, P. McHale, and K. C. Weathers (2001), Experimental design and instrumentation for analyzing solute concentrations and fluxes for quantifying biogeochemical processes in watersheds, paper presented at the 4th International Conference on Long Term Ecological Research (LTER) in East Asian and Pacific Region, Natl. Sci. Found., Lake Hovsgol, Mongolia. (Available at [http://www.ansp.org/~goulden/2001_MLTER_Meeting_Papers/15-21Mitchell_edited_\(new\).pdf](http://www.ansp.org/~goulden/2001_MLTER_Meeting_Papers/15-21Mitchell_edited_(new).pdf))
- Moore, T. R., W. Desouza, and J. F. Koprivnjak (1992), Controls on the sorption of dissolved organic carbon in soils, *Soil Sci.*, *154*, 120–129.
- Mulholland, P. J., and W. R. Hill (1997), Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects, *Water Resour. Res.*, *33*, 1297–1306.
- Neff, J. C., F. S. Chapin, and P. M. Vitousek (2003), Breaks in cycle: Dissolved organic nitrogen in terrestrial ecosystems, *Front. Ecol. Environ.*, *1*, 205–211.
- Park, J., and E. Matzner (2003), Controls on the release of dissolved organic carbon and nitrogen from a deciduous forest floor investigated by manipulations of aboveground litter inputs and water flux, *Biogeochemistry*, *66*, 265–286.
- Pellerin, B. A., W. M. Wolheim, C. S. Hopkinson, W. H. McDowell, M. R. Williams, C. J. Vorosmarty, and M. L. Daley (2004), Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U. S. rivers and streams, *Limnol. Oceanogr.*, *49*, 910–918.
- Pellerin, B. A., S. S. Kaushal, and W. H. McDowell (2006), Does anthropogenic nitrogen enrichment increase organic nitrogen concentrations in runoff from forested and human-dominated watersheds?, *Ecosystems*, *9*, 852–864.
- Perakis, S. S., and L. O. Hedin (2002), Nitrogen loss from unpolluted South American forests mainly via dissolved organic compounds, *Nature*, *415*, 416–419.
- Phillips, R. A. (1988), Relationship between glacial geology and stream-water chemistry in an area receiving acid deposition, *J. Hydrol.*, *101*, 267–273.
- Qualls, R. G., and B. L. Haines (1991), Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem, *Soil Sci. Soc. Am. J.*, *55*, 1112–1123.
- Schiff, S. L., K. J. Devito, R. J. Elgood, P. M. McCrindle, J. Spoelstra, and P. Dillon (2002), Two adjacent forested catchments: Dramatically different NO_3^- exports, *Water Resour. Res.*, *38*(12), 1292, doi:10.1029/2000WR000170.
- Tipping, E. (1981), The adsorption of aquatic humic substances by iron oxides, *Geochim. Cosmochim. Acta*, *45*, 191–199.
- Ussiri, D. A. N., and C. E. Johnson (2004), Sorption of organic carbon fractions by spodosol mineral horizons, *Soil Sci. Soc. Am. J.*, *68*, 253–262.
- Vance, G. F., and M. B. David (1992), Dissolved organic carbon and sulfate sorption by spodosol mineral horizons, *Soil Sci.*, *154*, 136–144.
- Vanderbilt, K. L., K. Lajtha, and F. J. Swanson (2003), Biogeochemistry of unpolluted forested watersheds in the Oregon Cascades: Temporal patterns of precipitation and stream nitrogen fluxes, *Biogeochemistry*, *62*, 87–117.
- Wigington, P. J., Jr., T. D. Davis, M. Tranter, and K. N. Eshleman (1990), Episodic acidification of surface waters due to acidic deposition, *Acidic Deposition: State Sci. Technol. NAPAP Rep. 12*, Natl. Acidic Precip. Assess. Program, Washington, D. C.
- Willett, V. B., B. A. Reynolds, P. A. Stevens, S. J. Ormerod, and D. L. Jones (2004), Dissolved organic nitrogen regulation in freshwaters, *J. Environ. Qual.*, *33*, 201–209.
- Williams, M. W., E. Hood, and N. Caine (2001), Role of organic nitrogen in the nitrogen cycle of a high elevation catchment, Colorado Front Range, *Water Resour. Res.*, *37*, 2569–2581.
- Wondzell, S. M., and F. J. Swanson (1996), Seasonal and storm dynamics of the hyporheic zone of a 4th order mountain stream. II: Nitrogen cycling, *J. N. Am. Benthol. Soc.*, *15*, 20–34.
- Yavitt, J. B., and T. J. Fahey (1985), Chemical composition of interstitial water in decaying lodgepole pine bole wood, *Can. J. For. Res.*, *15*, 1149–1153.

S. P. Inamdar, Bioresources Engineering, University of Delaware, 260 Townsend Hall, 531 South College Avenue, Newark, DE 19716, USA. (inamdar@udel.edu)

M. J. Mitchell, Faculty of Environment and Forest Biology, College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210, USA.