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# The role of hillslope hydrology in controlling nutrient loss

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SUMMARY

Hydrological controls on DOC and N transport at the catchment scale were studied for five storm events from the fall of 2004 through the spring of 2005 in WS10, H.J. Andrews Experimental Forest in the western Cascade Mountains of Oregon. This catchment is devoid of any riparian zone and characterized by hillslopes that issue directly into the stream. This enabled us to compare a trenched hillslope response to the stream response without the influence of riparian zone mixing. DOC and N concentrations and dissolved organic matter (DOM) quality (specific UV-absorbance (SUVA) and C:N of DOM) were investigated at the plot scale, in lateral subsurface flow from the trenched hillslope and stream water at the catchment outlet at the annual and seasonal scale (transition vs. wet period) during baseflow and stormflow conditions. DON was the dominant form of total dissolved nitrogen (TDN) in all sampled solutions, except in transient groundwater, where DIN was the dominant form. Organic horizon leachate and transient groundwater were characterized by high SUVA, and high DOC and total N concentrations, while SUVA and DOC and DON concentrations in lysimeters decreased with depth in the soil profile. This suggests vertical preferential flow without much soil matrix interaction occurred at the site. Deep groundwater (from a spring at the base of the hillslope) was characterized by low SUVA and low DOC and N concentrations. SUVA was always lower in lateral subsurface flow than in stream water at the seasonal scale, even during the wet period when other solutes were similar between lateral subsurface flow and stream water. This suggested mixing of deep groundwater and shallow transient groundwater was different at the hillslope scale compared to the catchment scale. DOC and DON sources were finite (production of DOC and DON from the hillslope soils appeared to be limited) at the seasonal scale since DOC and DON concentrations were significantly lower during the wet period compared to the transition period during stormflow conditions. This was also reflected in the DOC and DON peak and flow weighted storm event concentrations and antecedent soil moisture relationship where drier conditions (less prior flushing) resulted in the highest DOC and DON peak and flow weighted storm event concentrations. Results from this study showed the importance of the hillslope component in DOC and N transport at the catchment scale and underscore the importance of sampling solutes below the root zone (transient groundwater) and the value of using SUVA to fingerprint DOC sources.



## Introduction

Controls on dissolved organic matter (DOM) losses at the catchment scale are poorly understood, and yet DOM fluxes may have important consequences for both terrestrial and aquatic ecosystem function. DOM has the ability to form complexes with metals, and thus plays an important role in metal toxicity and transport (Leenheer et al., 1998). Dissolved organic nitrogen (DON) can represent a significant loss of nitrogen (N) (Sollins et al., 1980; Hedin et al., 1995; Perakis and Hedin, 2002; Vanderbilt et al., 2003) in unpolluted forested ecosystems, and may be a critical factor in maintaining N-limitation in these systems (Vitousek et al., 1998). In addition, dissolved organic carbon (DOC) is an important energy source to bacteria and some algae in streams (Kaplan and Newbold, 1993) and absorbs UV-radiation (Morris et al., 1995) that can damage aquatic organisms.

Recent research has focused on the hydrological controls on stream concentrations and quality of dissolved organic carbon (DOC) (McKnight et al., 2002; McGlynn and McDonnell, 2003; Inamdar and Mitchell, 2006; Park et al., 2007), dissolved organic nitrogen (DON) (Hill et al., 1999; Hagedorn et al., 2000; Buffam et al., 2001; Bernal et al., 2005), and nitrate ($NO_3$–N) (McHale et al., 2002; Ocampo et al., 2006). While these studies have improved our understanding of flushing and draining processes of nutrients at the catchment scale (as described by Hornberger et al., 1994; Boyer et al., 1997; Creed et al., 1996), quantifying spatial sources of these nutrients during storm events and across seasons remain

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poorly understood. The main reason is that it is difficult to separate different geomorphic units of the catchment. While hillslopes make up the largest part of catchments, research has been mostly focused on the riparian zone (Cirmo and McDonnell, 1997), such that sources of nutrients from the hillslope component are more poorly understood compared than those from the riparian zone.

One approach to increase our understanding of spatial sources of DOM and N at the catchment scale, is to isolate discrete landscape units and to understand their individual hydro-biogeochemical dynamics. While some studies have done this for the riparian zone (e.g., Hill, 1993; McDowell et al., 1992; Vidon and Hill, 2004) few studies have been able to isolate the hillslope hydro-biogeochemical response (McGlynn and McDonnell, 2003). It is difficult to observe hydro-biogeochemical expressions of hillslopes in the stream (Hooper, 2001), due to chemical transformations in the riparian zone (Hedin et al., 1998) or infrequent episodic flow into the riparian zone (McGlynn and McDonnell, 2003). An approach to quantify the hillslope response directly, without any riparian zone modulation, is to trench experimental hillslopes. A few trenched experimental hillslopes exist around the world (Woods and Rowe, 1996 (Maimai, New Zealand); Tromp-van Meerveld and McDonnell, 2006 (Panola, USA);Uchida et al., 2003 (Fudoji, Japan)) but these experiments have typically monitored only a handful of storms to work with (Tromp-van Meerveld and McDonnell, 2006), and often lack detailed biogeochemical data.

While isolating the hillslope or riparian zone has led to new insights into spatial sources of nutrients, questions remain about the hydrological controls on DOM and N export from the hillslope component at seasonal and storm event scales. It is especially important to understand the role of hillslopes in DOM and N export across different antecedent wetness conditions because several studies have suggested that seasonal variation in stream DOC, DON and $NO_3$–N is related to antecedent wetness conditions (Triska et al., 1984; Vanderbilt et al., 2003; Bernal et al., 2005) and many studies have reported significant increases in DON, DOC and $NO_3$–N during individual storm events (Creed et al., 1996; McHale et al., 2002; Boyer et al., 1997).

We report on work from a small well-studied hillslope trench within a headwater catchment at the H. J. Andrews Experimental Forest (HJA), Oregon. The catchment is well-suited for exploring questions of how hillslope hydrological processes control stream DOC and N concentrations. This study site has a unique feature: hillslopes that issue directly into the headwater stream without any riparian zone modulation. Riparian zone water storage was effectively removed from the site due to 1986 and 1996 debris flows that evacuated the valley bottom. This setup made it possible to isolate lateral subsurface flow from the hillslope trench and compare the hydro-biogeochemical response from this hillslope to the response of the whole array of hillslopes that make up this watershed. Furthermore, we explored the use of different indices of DOM quality (specific UV-absorbance (SUVA) and DOC:DON) to fingerprint terrestrial sources of DOM. Recent studies have demonstrated that SUVA can be used as a surrogate for the aromatic carbon content and molecular weight of DOC ( Chin et al., 1994; McKnight et al., 1997; Weishaar et al., 2003; Hood et al., 2005). The chemical character of DOM (DOC:DON, (SUVA)) has been used to identify terrestrial sources of DOM at seasonal scales (Hood et al., 2003, 2005; McKnight et al., 1997, 2001) and during storms at the catchment (Hagedorn et al., 2000; Hood et al., 2006; Katsuyama and Ohte, 2002) and plot scale (Kaiser and Guggenberger, 2005).

Our study builds upon a wealth of previous hydrological (Harr, 1977; McGuire, 2004) and biogeochemical (Sollins et al., 1980; Sollins et al., 1981; Triska et al., 1984) research at the site. The H.J. Andrews Experimental Forest is characterized by dry summers, a gradual wet up between October and December (transition period), and from December through late spring the watershed is persistently wet. This steady and progressive shift from dry to very wet conditions allowed us to explore the role of antecedent wetness and flow conditions on DOC and nitrogen (N) patterns at seasonal and storm event scales. Monitoring and sampling of lateral subsurface flow from the hillslope trench, and stream water at the catchment outlet between August 2004 and June 2005 during and between storm events allowed us to compare DOC and N concentrations and SUVA values between the transition period and the wet period at the hillslope and catchment scale, and between these two scales, during baseflow and stormflow conditions. In addition, sampling storm events at the hillslope and catchments scale during the transition and wet period enabled us to examine the role of antecedent wetness conditions on DOC and N concentrations and compare export rates between these two scales.

We address the following questions to improve our understanding of the hydrological controls on DOM and N fluxes from hillslopes in a small watershed: (1) What is the variation in DIN, DON and DOC concentrations and DOM quality (SUVA and DOC:DON) among sources from the plot scale, lateral subsurface flow and stream water on an annual scale? (2) What is the influence of flow conditions at the seasonal scale (transition vs. wet period) on the variation of solutes and DOM quality in lateral subsurface flow and stream water during baseflow and stormflow conditions? (3) What is the role of timing (transition vs. wet period) and under what flow conditions are the single gauged hillslope and catchment response similar with respect to the solutes and DOM quality? (4) Do peak and flow averaged DOC and N concentrations during storms at the catchment and hillslope scale increase with a decrease in antecedent soil moisture and antecedent precipitation conditions? (5) Is the total carbon and nitrogen export at the hillslope and catchment scale during storm events the same?

## Site description

The study was conducted in Watershed 10 (WS10), a 10.2 ha headwater catchment located in the H.J. Andrews Experimental Forest (HJA), in the western-central Cascade Mountains of Oregon, USA (44.2°N, 122.25°W) (Fig. 1). Elevations range from 470 m at the watershed flume to a maximum watershed elevation of 680 m. HJA has a Mediterranean climate, with dry summers and wet winters characterized by long, low intensity storms. Average annual rainfall is 2220 mm and about 80% falls between October and April. Snow accumulation in WS10 seldom exceeds 30 cm, and seldom persists for more than 2 weeks (Sollins et al., 1981). Atmospheric total bulk N deposition is low compared to other sites in USA and averages 1.6–2 kg N $ha^{-1}$ $yr^{-1}$ (Vanderbilt et al., 2003). The watershed was harvested in 1975 and is now dominated by a naturally regenerated second growth Douglas-fir (*Pseudotsuga menziesii*) stand. Seep areas along the stream have been observed (Harr, 1977; Triska et al., 1984), which are related to the local topography of bedrock and/or saprolite, or to the presence of vertical, andesitic dikes approximately 5 m wide, located within the south-facing hillslope (Swanson and James, 1975; Harr, 1977).

The hillslope study area is located on the south aspect of WS10, 91 m upstream from the stream gauging station (Fig. 1). The 125 m long stream-to-ridge slope has an average gradient of 37°, ranging from 27° near the ridge to 48° adjacent to the stream (McGuire, 2004). Elevation at the hillslope ranges from 480 to 565 m. The bedrock is of volcanic origin, including andesitic and dacitic tuff and coarse breccia (Swanson and James, 1975). The depth to unweathered bedrock ranges from 0.3 to 0.6 m at the stream–hillslope interface and increases gradually toward the ridge to approximately 3–8 m. Soils are about 1 m deep, and formed either in residual parent material or in colluvium originating from these

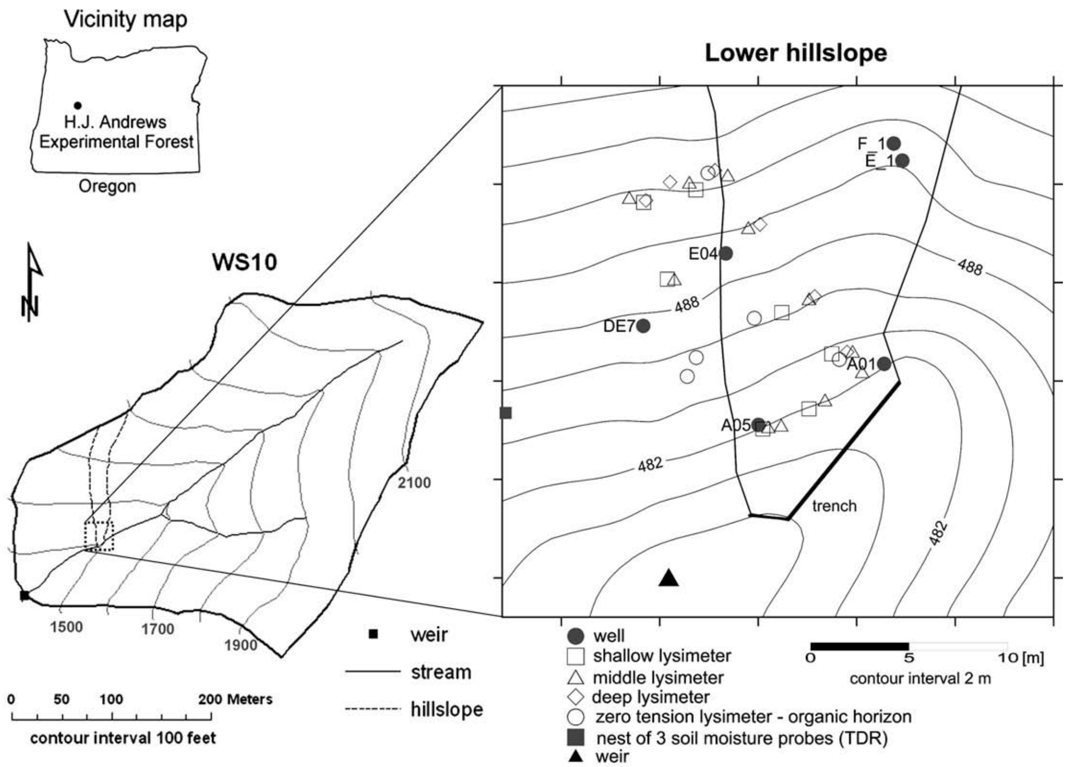


**Fig. 1.** Map of WS10 showing the location of the hillslope study area and lower hillslope with the instrumentation.

deposits. The soils are highly andic and vary across the landscape as either Typic Hapludands or as Andic Dystrudepts (Yano et al., 2005) and are underlain by 1–8 m relatively low permeability subsoil (saprolite), formed in the highly weathered coarse breccia (Ranken, 1974; Sollins et al., 1981). Soil textures range from gravelly, silty clay loam to very gravelly clay loam. Surface soils are well aggregated, but lower depths (70–110 cm) exhibit more massive blocky structure with less aggregation than surface soils (Harr, 1977).

## Methods

### *Infrastructure*

A 10 m long trench was constructed to measure subsurface flow at a natural seepage face (McGuire, 2004). Intercepted subsurface water was routed to a calibrated 30° V-notch weir that recorded stage at 10-min time intervals using a 1-mm resolution capacitance water-level recorder (TruTrack, Inc., model WT-HR). Rainfall was measured with a tipping bucket and storage gauge located in a small canopy opening on the hillslope. The drainage area of the hillslope was delineated topographically from a total station survey of the entire hillslope (0.17 ha, round to 0.2 ha in all analyses) and verified by a water balance calculation (McGuire, 2004). As part of the long-term monitoring at the H.J. Andrews Experimental Forest, discharge at the WS10 outlet was measured with a trapezoidal flume. During the summer a V-notch weir was used to measure discharge at the WS10 outlet. Stage was measured with a Model 2 Stevens Instruments Position Analog Transmitter (PAT) (0.001 ft resolution).

Soil water content ($\theta$) was measured with water content reflectometers (WCR) (CS615, Campbell Scientific, Inc.). The soil moisture probes were installed parallel to the slope at 3 depths (30, 70 and 100 cm) in three soil pits in the lower portion of the hillslope. The nests were located 15, 20 and 25 m upslope from the slope base (McGuire, 2004).

We installed six plastic 10 $\times$ 10 cm zero tension lysimeters just below (0.5 cm) the organic layer (Fig. 1). Twenty seven superquartz (Prenart Equipment ApS) tension (0.5 bar) lysimeters were installed at shallow (20 cm), middle (30–40 cm) and deep (70–110 cm) soil profile positions (Fig. 1) at a 30° angle following the method described by Lajtha et al. (1999).

We installed 69 maximum cork rise wells (3.18 cm diameter), that were screened for the lower 25 cm, the maximum water height observed by Harr (1977). All wells were installed until refusal by a hand auger. We sampled five wells located outside the seepage area that showed transient saturation and one well (A01) located in the seepage area (Fig. 1).

### *Sampling and chemical analysis*

Throughfall, lateral subsurface flow, WS10 stream water, soil water (zero tension and tension), transient and seepage groundwater samples were collected between August 2004 and June 2005 at 3-week intervals, and prior to, during, and after selected storm events. Throughfall was captured using the technique of Keim and Skaugset (2004). Grab samples at 3-week intervals and during storms were taken at the right fork during the transition period, and at the left fork during the whole study period. Prenart tension lysimeters were evacuated to −50 kPa and allowed to collect water for 24 h. These samples were not filtered because initial experiments with filtered soil solutions demonstrated that tension lysimeter samples did not need to be filtered (Lajtha et al., 2005). Other samples were filtered through combusted Whatman GF/F glass fiber filters (nominal pore size = 0.7 μm) and stored frozen until analysis. The gauged hillslope and watershed outlet were sampled with ISCO samplers during five storms, at 1–4 h intervals. Samples were analyzed for DOC, total dissolved nitrogen (TDN), nitrate, ammonium and UV-absorbance at 254 nm ($UV_{254}$). DOC and TDN were measured with Pt-catalyzed high-temperature combustion (Shimadzu TOC-V CSH analyzer with TN unit). $NO_3$–N was measured with the hydrazine sulfate reduction method and $NH_4^+ - N$ was determined by the Berthelot reaction method with a an Orion Scientific AC 100 continuous flow auto-analyzer (Westco Scientific Instruments, Inc., Danbury, CT). DON was calculated as the difference between TDN and DIN (nitrate and ammonium). Because DON was calculated by difference, values sometimes fell slightly below 0 mg $l^{-1}$. Negative DON values were considered to be 0 mg $l^{-1}$. $UV_{254}$ was measured with a Hitachi V-2001 spectrophotometer and SUVA is $UV_{254}$ normalized by DOC concentration.

### Data analysis

We divided the dataset into two periods: a transition period (transition from dry to wet conditions) and a wet period in order to investigate the influence of flow conditions on DIN, DOC, DON concentrations and SUVA. The transition and wet periods were defined by measurable hillslope discharge. The transition period was defined as the period with hillslope baseflow (between storm events) discharge $\leqslant$0.01 L $s^{-1}$, and the wet period was defined as the period with hillslope baseflow discharges >0.01 L $s^{-1}$. We subdivided the runoff record of these two periods into two different catchment response modes; baseflow and stormflow conditions. Stormflow conditions were defined as flow during and 12 h after storm events. The remainder of the runoff dataset was defined as baseflow conditions. A storm event was defined as a precipitation event of more than 10 mm and separated by at least 12 h periods with rainfall intensities smaller than 0.1 mm/h. We used the Wilcoxon ranksum to test for significant differences ($p < 0.01$) in DOC and N concentrations and SUVA for flow conditions within and between the transition and wet period. Hillslope discharge before 12-02-2004 was estimated from stream discharge with a second order polynomial because the hillslope discharge gauge failed. Average 95% confidence bounds of the second order polynomial on predicted values during this period were ±7.95 × $10^{-4}$ mm $h^{-1}$. Because of these small confidence bounds uncertainty resulting from calculations with estimated hillslope discharge was not quantified.

Pearson correlation coefficients ($r$) were calculated between antecedent wetness conditions as antecedent soil moisture at 30 cm depth and antecedent precipitation before a storm event and DOC, DON and DIN peak and flow weighted concentrations. The correlation was considered significant when $p < 0.1$. We used a 7-day, 14-day and 30-day average of soil moisture before a storm event as antecedent soil moisture indices ($AMI_7$, $AMI_{14}$ and $AMI_{30}$) and a 7-day, 14-day and 30-day total precipitation before a storm event as antecedent precipitation indices ($API_7$, $API_{14}$ and $API_{30}$). We used soil moisture data from the lower soil pit (Fig. 1), since that data was most reliable. All statistical and mathematical computations were made in MATLAB.

## Results

### Variation in DOC and N

To investigate variation in DOC and N concentrations between sources from the plot scale, lateral subsurface flow and stream water we compared average DOC, DON and DIN concentrations and average SUVA and DOC:DON values from throughfall, below the organic horizon, in shallow, middle and deep soil profile positions, transient and seepage groundwater, lateral subsurface flow and stream water. Furthermore, through this analysis we are able to identify sources that contributed to high DOC and N concentrations in lateral subsurface flow and stream water.

DOC and DON concentrations were low in throughfall, highest from just below the organic layer and then progressively decreased with depth into the soil profile (Table 1). This suggests a net release of both DOC and DON from the organic layer, and net removal of DON and DOC from solution below the organic layer. DOC and DON concentrations in transient groundwater were higher than soil water DOC and DON concentrations observed at the deep soil profile position. In addition, DOC and DON concentrations in transient groundwater were higher than the groundwater seep concentrations. DON and DOC concentrations of lateral subsurface flow and stream water were most similar to soil water DON and DOC concentrations at the middle soil profile depth.

SUVA values showed a maximum in the organic layer and transient groundwater solution (Table 1). SUVA values increased from throughfall to the organic horizon, and decreased from the organic layer to the deep soil layer (70–110 cm). SUVA values in stream water were most similar to SUVA values from deep soil water. Lateral subsurface flow showed a much lower SUVA value than WS10 stream water and was most similar to SUVA values from the groundwater seep.

DOC:DON did not show a clear trend with soil depth. Soil water from the middle soil profile position had the greatest DOC:DON ratio, while organic horizon, shallow and deep soil water had lower ratios. DOC:DON increased from deep soil water to seepage and transient groundwater. Lateral subsurface flow showed the greatest DOC:DON ratio, similar to the DOC:DON ratio of the groundwater seep. Stream water showed the second highest DOC:DON ratio. The DOC:DON ratio of throughfall was similar to the shallow soil water.

DIN was the dominant form of total dissolved nitrogen (TDN) in transient groundwater, while DON was the dominant form of TDN in the other solutions. DON as a fraction of TDN ranged from 0.71 to 0.92 in all solutions, while the fraction was 0.37 in transient groundwater. $NO_3$–N concentrations decreased with depth from the organic horizon to the deep soil profile position, but $NH_4$–N concentrations did not show a trend with depth. Low $NO_3$–N and $NH_4$–N concentrations ($\leqslant$0.01 mg $l^{-1}$) were found in throughfall, seep groundwater, lateral subsurface flow and WS10 stream water.

**Table 1**
Mean (± SD) of DOC, DON, $NH_4$–N, $NO_3$–N concentrations and DOC:DON and SUVA and number of samples [$n$].

| | DOC (mg $l^{-1}$) | DON (mg $l^{-1}$) | $NH_4$–N (mg $l^{-1}$) | $NO_3$–N (mg $l^{-1}$) | DOC:DON | $SUVA_{254}$ (L mg $C^{-1}$ $m^{-1}$) |
|---|---|---|---|---|---|---|
| Throughfall | 1.2 (0.5) [17] | 0.07 (0.04) [16] | 0.008 (0.008) [16] | 0.008 (0.008) [16] | 25 (21) [16] | 2.8 (0.8) [16] |
| Organic horizon | 12.3 (5.3) [51] | 0.45 (0.60) [40] | 0.072 (0.970) [40] | 0.045 (0.173) [40] | 35 (20) [38] | 5.3 (1.8) [37] |
| Shallow lysimeter | 9.1 (15.5)[a] [99] | 0.25 (0.29) [88] | 0.033 (0.053) [91] | 0.023 (0.083) [88] | 25 (20) [87] | 4.5 (6.4) [99] |
| Middle lysimeter | 4.3 (2.4) [93] | 0.16 (0.10) [81] | 0.028 (0.022) [83] | 0.010 (0.025) | 40 (44) [81] | 3.5 (2.0) [93] |
| Deep lysimeter | 1.4 (0.6) [65] | 0.10 (0.06) [56] | 0.033 (0.031) [57] | 0.005 (0.017) [56] | 21 (23) [56] | 1.8 (0.9) [64] |
| Groundwater seep | 4.0 (1.0) [9] | 0.07 (0.02) [8] | 0.014 (0.009) [8] | 0.013 (0.016) [8] | 63 (27) [8] | 0.9 (0.6) [8] |
| Transient groundwater | 8.5 (6.7) [23] | 0.32 (0.28) [18] | 0.261 (0.338) [18] | 0.297 (0.499) [18] | 32 (28) [18] | 5.4 (5.2) [22] |
| Lateral subsurface flow | 4.8 (1.3) [298] | 0.11 (0.07) [278] | 0.005 (0.005) [279] | 0.004 (0.005) [279] | 78 (223) [278] | 0.7 (0.5) [281] |
| Stream water | 5.1 (1.5) [302] | 0.14 (0.07) [283] | 0.007 (0.010) [283] | 0.004 (0.005) [283] | 51(72) [283] | 1.6 (0.7) [291] |

[a] High SD is caused by one lysimeter that was installed in an area with woody debris with high DOC concentrations.

*DOC and N during transition and wet period*

First, we compared DOC concentrations, DOC quality and N concentrations between the transition and wet period during baseflow conditions in lateral subsurface flow and stream water. DIN, DOC quality (expressed as DOC:DON and SUVA) in lateral subsurface flow during baseflow conditions were not different between the transition and wet period (Figs. 2 and 3a). Stream water during baseflow conditions followed the same pattern as lateral subsurface flow, except that DIN was significantly higher during the wet period. DOC and DON concentrations during baseflow conditions in stream water were significantly lower during the wet period, while in lateral subsurface flow only DOC was significantly lower during the wet period ($p > 0.01$ for hillslope water DON).

Secondly, we compared DOC concentrations, DOC quality and N concentration between lateral subsurface flow and stream water under baseflow conditions, during the transition and wet period. During the wet period under non-driven conditions, SUVA values of lateral subsurface flow were significantly lower than SUVA values of stream water, while DOC, DON and DIN concentrations and DOC:DON ratios of lateral subsurface flow and stream water were similar. During the transition period and baseflow conditions, DOM quality (DOC:DON and SUVA) between lateral subsurface flow and stream water was different; lateral subsurface flow had higher DOC:DON ratios and lower SUVA values. In addition, non-driven DON concentrations in lateral subsurface flow were lower than stream water during this period.

Thirdly, we compared DOC concentrations, DOC quality and N concentrations between the transition and wet period during stormflow conditions in lateral subsurface flow and stream water. During stormflow conditions, stream water SUVA values were not different between the transition and wet period, while DOC and DON concentrations were lower, DIN concentrations were higher, and DOC:DON ratios were higher during the wet period (Figs. 2 and 3b). Lateral subsurface flow followed the same pattern as stream water except for SUVA values that were significantly higher during the wet period, and DOC:DON ratios that were not different between the transition and wet period in lateral subsurface flow.

Finally, we compared DOC concentrations, DOC quality and N concentrations between lateral subsurface flow and stream water under stormflow conditions, during the transition and wet period. During the wet period and stormflow conditions SUVA values were significantly different between lateral subsurface flow and stream water. Stormflow DOC and DON concentrations and SUVA values during the transition period were each lower in lateral subsurface flow than stream water, while DOC:DON ratios were higher in lateral subsurface flow.

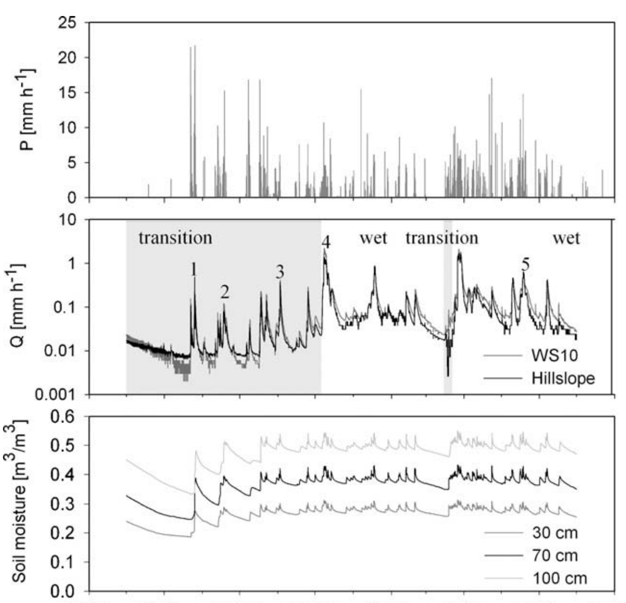


**Fig. 2.** Time series of hydrological data during the study period: (a) rainfall, (b) discharge from the hillslope and watershed with different hydrological conditions during the year: transition periods (light gray background) characterized by an increase in hillslope and watershed baseflow and soil moisture and a wet period (white background) characterized by high 'steady' hillslope and watershed baseflow conditions. The numbers in the graph refer to storms that were sampled and (c) soil moisture content ($m^3/m^3$).

*Antecedent wetness conditions and stormflow DOC and N*

We used five sampled storms (Fig. 2) to examine the influence of antecedent wetness conditions on peak and flow weighted DOC, DON and DIN in stream water and lateral subsurface flow (Tables 2 and 3). Three antecedent soil moisture indices were used: the 7-day, 14-day and 30-day antecedent soil moisture index ($AMI_7$, $AMI_{14}$ and $AMI_{30}$), and three antecedent precipitation indices were used: the 7-day, 14-day and 30-day antecedent precipitation index ($API_7$, $API_{14}$ and $API_{30}$).

The storm characteristics of these events as well as DOC, DON, DIN peak and flow weighted concentrations are summarized in Table 2. $API_7$, $API_{14}$ and $API_{30}$ were not significantly related to peak and flow weighted DOC, DON and DIN concentrations. $AMI_7$, $AMI_{14}$ and $AMI_{30}$ were similar (Table 2), and thus we calculated pearson correlations between $AMI_7$ and peak and flow weighted DOC, DON and DIN in stream water and lateral subsurface flow. The concentration of all solutes except DIN decreased with an increase in $AMI_7$ at 30 cm depth. DOC, DON peak and flow weighted concentrations in stream water were more weakly correlated to $AMI_7$ than these solutes in lateral subsurface flow (Table 3). Both DIN peak and flow weighted DIN in stream water and lateral subsurface flow were not significantly related to $AMI_7$. In addition DON peak in stream water was not significantly related to $AMI_7$.

*Storm event export rates of C and N at hillslope and catchment scale*

The export rates of DOC, DON and DIN for all five storms were smaller at the hillslope than watershed scale (Fig. 4a–c). DON was the dominant form of total nitrogen export during all storms. The DON:TDN ratios during storms 4 and 5, both storms during the wet period, were 0.84 and 0.87 at the watershed scale for storm 4 and 5, respectively, and 0.84 and 0.90 at the hillslope scale for storm 4 and 5, respectively. In contrast DON:TDN ratios for storms during the transition period were >0.94.

The highest DOC, DON and DIN export rates were observed during storm 4. For the watershed and hillslope scale during storm 4, export rates of DOC were 4.4 and 3.0 kg/ha/storm, respectively. Rates of DON export for the watershed and hillslope scale were 0.11 and 0.08 kg/ha/storm, respectively. Rates of DIN export for the watershed and hillslope scale were 0.020 and 0.014 kg/ha/storm, respectively.

## Discussion

Quantifying spatial sources of soluble nutrients at the catchments scale is one of the greatest challenges faced in hydro-biogeochemical research. Isolating the hillslope component has been difficult in past studies because so few trenched experimental hillslopes exist around the world in catchments where active biogeochemical research is done. These trenched experimental hillslopes

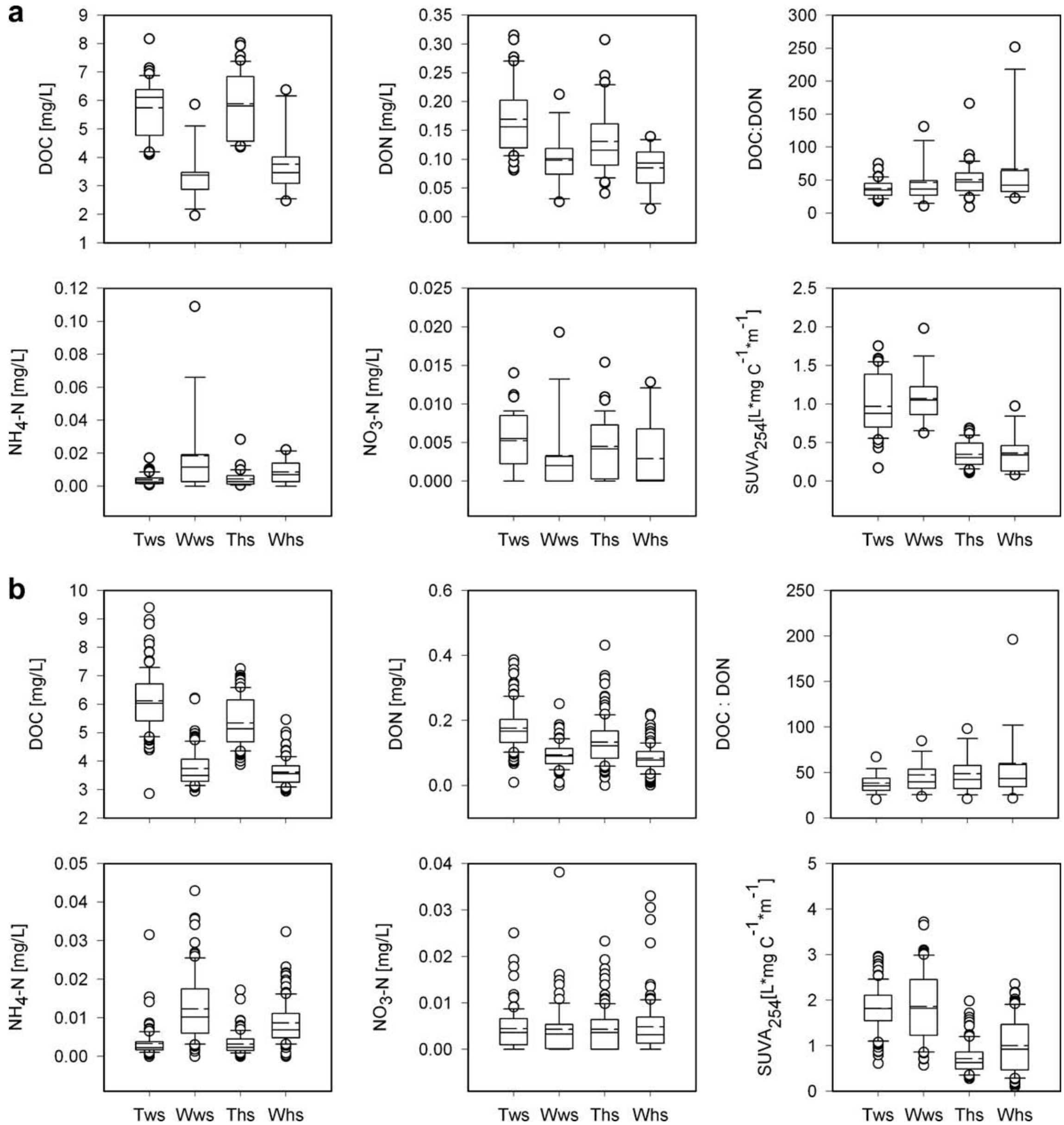


**Fig. 3.** Box plots of DOC, DON, $NH_4$–N, $NO_3$–N concentrations, DOC:DON and SUVA during (a) baseflow conditions and (b) stormflow conditions, during different hydrological conditions (T = transition period, W = wet period) for stream water at WS10-oulet (ws) and lateral subsurface flow from the trenched hillslope (hs). The dashed line in the box plot is the average value and the solid line is the median value. The boundary of the box indicates the 75th percentile. The error bars above and below the box indicate, respectively, the 90th and 10th percentile. Circles are outliers.

often lack detailed hydro-biogeochemical data across a wide range of antecedent wetness conditions. In addition, it is extremely difficult to quantify the representativeness of a single experimental hillslope for the whole array of hillslopes that make up a catchment. Single gauged hillslopes only sample part (tens of meters) of the hillslope component and, more importantly, most catchments have a riparian zone that transforms the biogeochemical signal of the hillslope component en route to the stream channel.

Our work exploits a rather unique experimental design where a trenched hillslope is compared to the stream response in a headwater catchment without a riparian zone. This natural experimental design allowed us to study the hydrological controls on DOM and N export from the hillslope component at seasonal and storm event scales unimpeded by riparian dynamics. Because of the installation of a 10 m wide trench to capture lateral subsurface flow, we were also able to compare the hydro-biogeochemical signal from the single gauged hillslope to the overall hydro-biogeochemical response of the whole array of hillslopes that make up the catchment, by examining when the study hillslope acted in concert with the stream and when hillslope dynamics were different from the stream response.

The fundamental question of this study is whether the single gauged hillslope is representative of the whole array of hillslopes that make up the catchment. We state the null hypothesis that the chemistry (DOC, DON and DIN concentrations and DOM quality) at the single gauged hillslope is the same as the chemistry at the catchment outlet. First, we will discuss the acceptance or rejection of the null hypothesis at the seasonal level (contrasting the wet seasons and the transition season), and then we will present hydrological and biogeochemical explanations why the null hypothesis was accepted or rejected. Finally, we will discuss storm responses, in particular the difference in C and N storm export

**Table 2**
Storm event characteristics and DOC, DON and DIN peak and flow weighted average concentrations for lateral subsurface flow and stream water.

| | Storm 1 | Storm 2 | Storm 3 | Storm 4 | Storm 5 |
|---|---|---|---|---|---|
| Start date | 08-24-04 | 09-16-04 | 11-01-04 | 12-06-04 | 05-14-05 |
| End date | 08-29-04 | 09-20-04 | 11-04-04 | 12-12-04 | 05-24-05 |
| Gross precipitation (mm) | 71 | 44 | 42 | 200 | 100 |
| 10-min max. rainfall intensity (mm/h) | 21.7 | 15.2 | 6.1 | 10.7 | 14.8 |
| Rainfall duration (h) | 39 | 74 | 49 | 132 | 195 |
| Runoff ratio WS10 (%) | 6.3 | 9.7 | 20 | 74.5 | 36.7 |
| Runoff ratio hillslope (%) | 4.2 | 5.6 | 15.2 | 55.6 | 37 |
| $AMI_7$ ($m^3/m^3$) | 0.193 | 0.242 | 0.274 | 0.278 | 0.282 |
| $AMI_{14}$ ($m^3/m^3$) | 0.191 | 0.237 | 0.278 | 0.279 | 0.279 |
| $AMI_{30}$ ($m^3/m^3$) | 0.193 | 0.231 | 0.266 | 0.274 | 0.279 |
| *Stream water* (mg $l^{-1}$) | | | | | |
| DOC peak | 9.4 | 7.5 | 6.7 | 5.1 | 4.7 |
| DON peak | 0.39 | 0.25 | 0.30 | 0.18 | 0.25 |
| DIN peak | 0.030 | 0.022 | 0.015 | 0.053 | 0.039 |
| Flow weighted average DOC | 7.6 | 5.9 | 5.3 | 3.6 | 3.6 |
| Flow weighted average DON | 0.24 | 0.14 | 0.17 | 0.09 | 0.11 |
| Flow weighted average DIN | 0.010 | 0.007 | 0.009 | 0.016 | 0.019 |
| *Lateral subsurface flow* (mg $l^{-1}$) | | | | | |
| DOC peak | 8.0 | 6.5 | 5.8 | 4.2 | 5.0 |
| DON peak | 0.73 | 0.25 | 0.19 | 0.21 | 0.22 |
| DIN peak | 0.033 | 0.027 | 0.017 | 0.036 | 0.063 |
| Flow weighted average DOC | 6.5 | 5.0 | 4.6 | 3.2 | 3.7 |
| Flow weighted average DON (mg $l^{-1}$) | 0.20 | 0.11 | 0.12 | 0.08 | 0.10 |
| Flow weighted average DIN | 0.008 | 0.007 | 0.008 | 0.016 | 0.011 |

**Table 3**
Pearson correlation coefficients ($r$) between DOC, DON and DIN flow weighted average and peak concentrations of WS10 stream water and lateral subsurface flow and $AMI_7$.

| | $AMI_7$ Pearson correlation coefficient ($r$) | |
|---|---|---|
| | WS10 stream water | Lateral subsurface flow |
| DOC peak (mg $l^{-1}$) | $-0.94^{**}$ | $-0.97^{***}$ |
| DON peak (mg $l^{-1}$) | $-0.79$ | $-0.93^{**}$ |
| DIN peak (mg $l^{-1}$) | 0.25 | 0.26 |
| Flow weighted average DOC (mg $l^{-1}$) | $-0.93^{**}$ | $-0.94^{**}$ |
| Flow weighted average DON (mg $l^{-1}$) | $-0.86^{*}$ | $-0.91^{**}$ |
| Flow weighted average DIN (mg $l^{-1}$) | 0.55 | 0.53 |

* $p < 0.1$.
** $p < 0.05$.
*** $p < 0.01$.

rates between the hillslope and catchment scale and C and N storm event concentrations during the study period. Again we will consider hydrological and biogeochemical controls that explain our observations.

*Contrasting hillslope and catchment*

Lateral subsurface flow during the transition period was characterized by lower DON concentrations and higher DOC:DON than stream water during baseflow conditions, while DIN and DOC concentrations showed no difference. Lateral subsurface flow DON and DOC concentrations were lower than stream water concentrations during stormflow conditions within the transition period. Thus, for the transition period we reject the null hypothesis.

The single gauged hillslope response was not significantly different from the catchment response (with respect to DOC, DON and DIN concentrations and DOC:DON ratios) during the wet period, during both baseflow and stormflow conditions. However, SUVA in lateral subsurface flow was significantly lower than SUVA in stream water during the wet period during both baseflow and stormflow conditions. Thus, for the wet period we also reject the null hypothesis.

*Hydrological explanations*

The difference in SUVA we observed in lateral subsurface flow and stream water suggests that sources of DOM at the single gauged hillslope and catchment scale were not similar during the wet period and illustrates the value of using SUVA as a fingerprinting tool. Transient groundwater was high in DON, DOC and DIN concentrations, and was the only water source where DON was not the dominant form of TDN. Average values of DOC, DON and DOM quality (SUVA) in transient groundwater were similar to observed values in organic horizon and shallow soil water, suggesting a vertical preferential flow mechanism without much soil matrix interaction. Jardine et al. (1989a) found that if preferential flow at the pedon scale was dominant, DOC was non-reactive with the solid phase because it bypassed the soil matrix. DOM and DIN concentrations and SUVA in deep soil water was lower than transient groundwater, indicating that flow paths with significant soil matrix interaction undergo preferential retention of aromatic DOM and loss of DIN. Many other studies (Hagedorn et al., 2000; Yano et al., 2004; Kaiser and Guggenberger, 2005; Jardine et al., 1989b) have found preferential retention of aromatic DOM with depth.

Transient groundwater represents one source of lateral subsurface flow and stream water. Another source of lateral subsurface flow and stream water is seepage groundwater. Stream water during summer low flow conditions is sustained by different seeps in WS10 (e.g., Triska et al. (1984) identified five different seeps in WS10). These seepage areas are characterized by low SUVA values during summer low flow conditions. During the transition period the contribution of transient groundwater will increase and SUVA values in stream water and lateral subsurface flow reflect the ratio between the two water sources. We argue that the ratio of seep groundwater to transient groundwater from vertical preferential flow at the single gauged hillslope was larger than the ratio at the catchment scale during the whole study period. The difference in mixing at the hillslope scale compared to the catchment scale

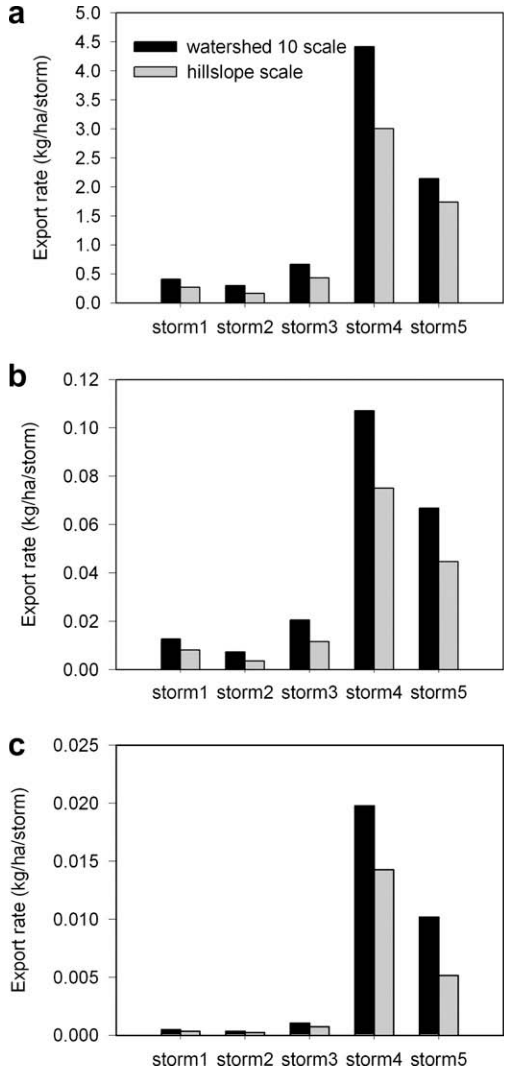


**Fig. 4.** Export rates of: (a) DOC, (b) DON and (c) DIN, during sampled storms at the watershed and hillslope scale.

inferred from SUVA measurements may have caused the difference in DOC and DON concentrations between lateral subsurface flow and stream water during the transition period. However, in the next section we discuss why the difference in DOC and DON concentrations between lateral subsurface flow and stream water during the transition period was likely largely biogeochemical controlled.

*Biogeochemical explanations*

An explanation could be that the lower observed SUVA during the wet period in lateral subsurface flow was caused by bio-available carbon compounds with a low aromatic and nitrogen content that were rapidly processed in the WS10 stream. However, this does not explain the observed low SUVA values in stream water (range: 0.17–0.88) and lateral subsurface flow (range: 0.14–0.41) before storm 1 during low flow conditions. During these conditions flow paths are characterized by long residence times and thus processing of these bio-available carbon compounds within the hillslope would occur.

Algae were observed in the bedrock channel of WS10, are characterized by low C:N ratios, and higher stream DON concentrations during the transition period may have been caused by by-products of in-stream production. In addition, $N_2$-fixing alder was present in the right fork of watershed 10, which can influence stream N concentrations (Compton et al., 2003; Cairns and Lajtha, 2005). During low flow conditions, when in-stream processes as by-products of algae production (autochthonous input) and leaching of leaf litter (allochthonous input) (Meyer et al., 1998) are likely more important than transport of DOM from the terrestrial to the stream environment (Mulholland and Hill, 1997; Hagedorn et al., 2000) these sources likely contributed significantly to elevated stream DON concentrations during the transition period. While there was a difference in mixing of sources between the hillslope and catchment scale during the transition period inferred from SUVA measurements, we argue that in-stream processes were the dominant control on higher DOC and DON concentrations in stream water. Grab samples during stormflow conditions from the hillslope trench, right fork and left fork during the transition period showed that average DOC and DON concentrations were higher at the right fork (DOC: 9.7; DON: 0.28 mg $l^{-1}$, $n = 4$) and left fork (DOC: 7.3; DON: 0.17 mg $l^{-1}$, $n = 4$) compared to the hillslope trench (DOC: 5.0; DON: 0.11 mg $l^{-1}$, $n = 4$). This indicates that sources more upstream in the catchment caused the higher DOC and DON concentrations during stormflow conditions at the WS10 stream outlet compared to lateral subsurface flow. Average SUVA values from the right and left fork were 3.54 and 2.13, respectively, and average DOC:DON ratios were 37 and 44, respectively, suggesting a terrestrial source of DOM. Grab samples ($n = 58$, during the wet period) were taken from the left fork (DOC: 3.8 mg $l^{-1}$; DON: 0.10 mg $l^{-1}$, $n = 58$) during the whole study period that were not different in DOC and DON concentrations compared to lateral subsurface flow (DOC: 4.1 mg $l^{-1}$; DON: 0.09 mg $l^{-1}$, $n = 56$) and stream water (DOC: 3.9 mg $l^{-1}$; DON: 0.10 mg $l^{-1}$, $n = 56$) at the catchment outlet during the wet period. This lack of difference indicates that DOC and N concentrations were controlled mainly by lateral subsurface flow and not in-stream processes during the wet period with storms characterized by high runoff ratios (Table 2), consistent with the findings of Mulholland and Hill (1997). During the transition period storms were characterized by small runoff coefficients (Table 2) and a lower discharge regime (Fig. 2b). In addition, DOC and DON concentrations were higher at the left, right fork and catchment outlet compared to lateral subsurface flow during the transition period. The hydrological observations as runoff coefficients and discharge regime and spatial sampling within the catchment indicated that in-stream processes were the dominant control during the transition period.

*Storm responses*

*C and N export rates at the hillslope and catchment scale*

We used mean flow weighted DOC, DON and DIN concentrations and storm flow totals to assess what caused lower C and N export rates during storm events at the hillslope scale compared to the catchment scale. The difference in DOC export for storm 5 was caused by a storm difference since flow weighted mean DOC concentration were lower in stream water and thus hydrological controlled. The difference in DOC export during storms 1–4 and the difference in DON export during all storms between the catchment and hillslope was an effect of lower mean flow weighted concentrations in lateral subsurface flow and lower storm totals at the hillslope scale. These differences were both hydrological (lower storm totals) and biogeochemical controlled since higher DOC and DON concentrations in stream water at the WS10 outlet likely resulted from in-stream processes.

McGlynn and McDonnell (2003) found that hillslope DOC export accounted for 22–36% of total catchment DOC export in a Maimai catchment, New Zealand. The remaining 64–78% originated in riparian and channel zones. At our site we observed that hillslope DOC export during five storm events accounted for a range of 56–

82% of total WS10 catchment DOC export. In WS10 hillslopes issue water directly into the stream without significant riparian zone modulation and this caused very likely higher hillslope DOC export contributions to total catchment DOC export than reported by McGlynn and McDonnell (2003).

*Antecedent wetness conditions control C and N storm event concentrations*

High solute (DOC, DON) concentrations during storms after dry antecedent wetness conditions have been reported by others (Grieve, 1991; Vanderbilt et al., 2003; Cooper et al., 2007; Inamdar et al., 2006). Storm DOC and DON peak and flow weighted concentrations at the hillslope and catchment scale generally decreased during the sequence of storms (Table 2), with an increase in antecedent soil moisture. The $AMI_7$ at 30 cm soil depth can be considered as an index of how much flushing in the soil profile occurred prior to a storm event. $AMI_{14}$ and $AMI_{30}$ were not different from $AMI_7$. Furthermore, $API_7$, $API_{14}$ and $API_{30}$ were not significantly related to DOC and N peak and flow weighted concentrations. This suggests that solute concentrations during storm events were not controlled by rainfall events and thus flushing in the soil profile up to a month prior to these events. Rather, our results indicate that DOC and DON in the soil profile were exhausted rapidly during the transition period and stayed 'constant' during the wet period as a result of long-term precipitation patterns reflected in the soil moisture pattern at 30 cm depth. We calculated the Pearson correlation coefficient between $AMI_7$ and total precipitation before each storm event since August 1, 2004 (long-term precipitation) to evaluate if the soil moisture pattern at 30 cm reflected long-term precipitation during the transition period. During the transition period the Pearson correlation was 0.95 ($p < 0.1$) and this result supports the explanation that $AMI_7$ reflected long-term precipitation patterns. Thus the observed pattern of storm DOC and DON peak and flow weighted concentrations was largely hydrological controlled and was likely caused by rapid exhaustion of DOC and DON during the transition period as a response to flushing during storm events over time. We did not find a significant relationship between $AMI_7$ and DIN concentrations during storms. This is likely caused by the high biological demand of nitrate and ammonium in this environment.

*Biogeochemical control on DIN in transient groundwater?*

It is not likely that the high DIN concentrations in transient groundwater were caused exclusively by a preferential flow mechanism. Transient groundwater DIN concentrations were higher than organic horizon DIN concentrations, indicating net production of nitrate and ammonium in transient groundwater. Sollins et al. (1981) also found higher nitrate concentrations in suction lysimeters at 2 m depth than at 0.3 m depth at the same location in WS10. They hypothesized that this difference may have been caused by a decrease in bio-available C compounds below the rooting zone such that nitrifiers were able to compete for reduced N with heterotrophic bacteria. We observed high DOC and DON concentrations in transient groundwater 'below' the rooting zone, suggesting that a significant C source was available below the rooting zone, although the lability of this DOM is unknown. Transient groundwater was only sampled frequently from one well (E04) during storm 5 within the study period. $NO_3$–N increased until 5/17/05 during the rising limb of the storm, while $NH_4$–N decreased until 5/17/05 (Fig. 5). This indicates that during this period of the storm autotrophic and/or heterotrophic nitrification occurred. After 5/17/05, $NO_3$–N began to decrease during the remainder of the storm while at the same time $NH_4$–N increased until 5/20/05. The increase in $NH_4$–N may have been caused by dissimilatory nitrate reduction to ammonium (DNRA). DNRA is an anaerobic microbial pathway that transforms $NO_3$–N to $NH_4$–N and has been

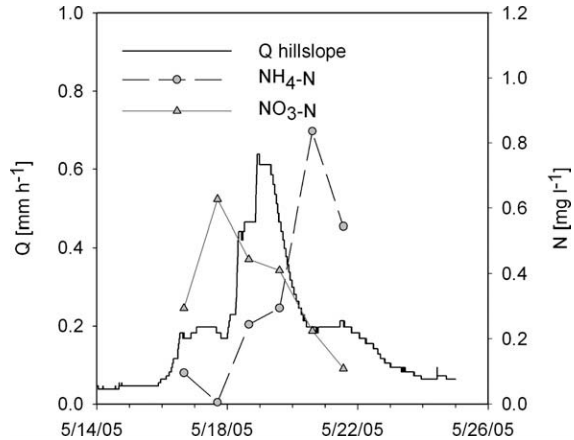


**Fig. 5.** Hillslope discharge and $NO_3$–N and $NH_4$–N patterns in transient groundwater from well E04, during storm 5.

documented in soils and sediments (Buresh and Patrick, 1978; Tiedje, 1988; Silver et al., 2001). Conditions that favor DNRA are available $NO_3$–N, (labile) C and a low redox potential and could have occurred after 5/17/05 during the storm. Thus, the high $NO_3$–N and $NH_4$–N concentrations in transient groundwater we observed could be the result of the co-occurrence of nitrification and DNRA. Another explanation we cannot rule out is that the pattern of $NO_3$–N and $NH_4$–N in transient groundwater was simply caused by ammonification and nitrification. Since groundwater was transient, and thus the soil at this depth was likely not sufficient anoxic to favor DNRA, the observed $NO_3$–N and $NH_4$–N concentration patterns were most likely caused by ammonification and subsequent nitrification of organic N.

## Conclusions

The high observed DOC and N concentrations in transient groundwater underscore the importance of measuring DOC and N concentrations at different depths within the soil profile. High DOC and N concentrations and SUVA values in transient groundwater did indicate the occurrence of vertical preferential flow at our site. During the wet period the chemistry with respect to concentrations at the hillslope and catchment scale was the same. However, SUVA showed that mixing of water sources may be different between the hillslope and catchment scale. This result underscores that similar results (nutrient concentrations during the wet period) can be the outcome of different processes, and it shows the value of using multiple lines of measurements to investigate the complex hydrologic and solute response of a steep forested catchment.

We explained the differences in chemistry between the catchment and hillslope scale by a dominant hydrological and a dominant biogeochemical control (in-stream processes) during the wet and transition period, respectively. Small runoff coefficients and a low discharge regime suggested a dominant biogeochemical control during the transition period. However, we acknowledge that the role of in-stream processes remains somewhat uncertain since the hillslope was not representative of the catchment during the transition and wet period. Only a few studies have attempted to separate hydrological controls from biogeochemical controls as in-stream processes across seasons, and more research is needed to fully clarify when and how these controls drive solute responses in forested catchments.

Antecedent wetness conditions controlled DOC and DON concentrations in lateral subsurface flow and stream water during storm events; more prior flushing (expressed as $AMI_7$) resulted in lower DOC and DON peak and flow weighted concentrations during storms. In addition, DOC and DON concentrations in lateral subsurface flow and in stream water during stormflow conditions were lower during the wet period compared to the transition period. Both of these results suggest that the production of DOC and DON in soils lagged behind the flushing of these nutrients. If DOC and DON production is seasonally limited, this has important consequences for the interpretation of soil solution concentrations in end-member mixing analysis (EMMA) and annual calculations of solute losses from limited soil solution data. Since EMMA requires conservative behavior of tracers and time invariance of end-member compositions, limitation of DOC and DON on a seasonal scale violates the EMMA assumptions.

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