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A mechanistic assessment of nutrient flushing at the catchment scale

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Summary Quantifying nutrient flushing mechanisms at the catchment scale is essential for model development and prediction of land use change and climate change effects on surface water quality. To date, the description of nutrient flushing at the catchment scale has been largely mechanistically weak. This paper mechanistically assesses the flushing mechanism of DOC, DON and DIN at the hillslope and catchment scale during two storm events, in a small catchment (WS10), H.J. Andrews Experimental Forest in the western Cascade Mountains of Oregon. Using a combination of natural tracer and hydrometric data, and end-member mixing analysis we were able to describe the exact flushing mechanism at the site. This mechanism involved vertical preferential flow to the soil–bedrock interface and then lateral downslope flow, with a finite source of DOC and DON in the organic horizon. Both specific UV absorbance (SUVA, 254 nm) and continuously measured raw fluorescence measured with a fluorometer increased during the storm events, suggesting DOC was more aromatic during stormflow compared to baseflow conditions. SUVA patterns in lateral subsurface flow from the hillslope and stream water in combination with hydrometric data enabled us to infer that the contribution of deep soil water and groundwater was higher during the falling limb compared to the rising limb of the hydrograph and contributed to the dilution of DOC, DON and SUVA values during storm events. Overall this study showed the value of using a combination of hydrometric data, natural tracer data, and in particular DOC quality indices such as SUVA and fluorescence to mechanistically assess nutrient flushing at the catchment scale.

Introduction

The hydrological controls on nutrient flushing at the catchment scale are poorly understood (Weiler and McDonnell,

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2006). During storm events and snowmelt periods, many studies have reported a significant increase in dissolved organic nitrogen (DON), dissolved organic carbon (DOC) and nitrate (NO_3-N), and attributed this increase to nutrient flushing (Creed et al., 1996; Boyer et al., 1997; McHale et al., 2002; McGlynn and McDonnell, 2003; Vanderbilt et al., 2003). Flushing of nutrients has been explained by (1) a rising water table that intersects high nutrient concentrations in the upper soil layer, (2) vertical transport of nutrients, by preferential or matrix flow through the (deeper less bio-active) soil to the soil–bedrock interface and then laterally downslope (Creed et al., 1996; Hill et al., 1999; Buttle et al., 2001), and (3) vertical transport of nutrients and then laterally within the soil profile (Gaskin et al., 1989). When these conceptual models are applied to the timescale of storm events (days) an infinite supply of nutrients is often assumed (Bishop et al., 2004; Weiler and McDonnell, 2006); although not many hydro-biogeochemical studies to date have tested this explicitly.

A mechanistic understanding of nutrient flushing is essential for model development for the prediction of land use change and climate change effects on surface water quality. Understanding the flushing mechanism during storm events is important, since stormflow contributes substantially to total DOC and nitrogen (N) export (Hinton et al., 1997; Bernal et al., 2005). Despite the many studies on nutrient flushing, the exact flushing mechanism remains mechanistically weak. For instance, while McGlynn and McDonnell (2003) found that the relative timing of riparian and hillslope source contributions to stream water explained stream DOC patterns, they could not determine what flushing mechanism at the hillslope occurred (i.e. if it was flushing mechanism 1, 2, or 3).

While patterns of DOC in shallow pore waters and in stream water provide evidence that the shallow soil is a primary source of high DOC concentrations to the stream (e.g., Boyer et al., 1997), we frequently do not know how these sources are hydrologically connected to the stream. Bishop et al. (2004) illustrated the importance of hydrological connectedness. They were able to identify the small riparian area as the only contributor to elevated stream DOC concentrations in a Swedish catchment during storm events, through a combination of hydrometric data and soil water DOC concentrations.

So how might we mechanistically asses flushing of nutrients? We know there are three possible flushing mechanisms with or without an infinite source of nutrients during storms that we can test as hypotheses in line with recommendations of Hooper (2001). Assessing sources of stream water is an initial step to reject one or more of these hypotheses. Bonell (1998) recommended that conclusions regarding the sources of stream water drawn from runoff hydrochemistry data at the hillslope and catchment scale should be supported by independent hydrometric data. End-member mixing analysis (EMMA) can be used as a hydro-chemical technique to resolve possible sources of channel stormflow. Numerous studies (Mulholland and Hill, 1997; Hagedorn et al., 2000; McHale et al., 2002; Inamdar and Mitchell, 2006; Bernal et al., 2006) have used this technique to investigate sources of and even biogeochemical controls on DOC and N. In addition to EMMA and hydrometric techniques, the chemical character of dissolved organic matter (DOM) (DOC:DON, specific UV absorbance (SUVA), fluorescence spectroscopy) can provide information to help elucidate sources of DOM at seasonal scales (McKnight et al., 1997; Hood et al.,2003, 2005) and during storms at the catchment scale (Hagedorn et al., 2000; Katsuyama and Ohte, 2002; Hood et al., 2006).

Measurements of matric potential at different depths in the soil may also provide critical information to enable rejection of one or more of the flushing mechanism hypotheses. In catchments with steep hillslopes, flushing mechanism 3, (vertical transport of nutrients and then lateral movement within the soil profile) may occur. Vertical and lateral flow vectors have been studied through detailed field experiments (Harr, 1977; Torres et al., 1998; Retter et al., 2006) and modeling studies (McCord et al., 1991; Jackson, 1992) with often contradicting results about the relative importance of lateral flow within the soil profile of hillslopes.

While several studies have identified the forest floor and upper soil layer as an important source of elevated DOC and N concentrations in stream water during storm events, whether this source is finite or infinite remains poorly understood. Concentrations of soluble nutrients (DOC, DON and inorganic N) may rise at the beginning of storm events or after prolonged dry periods for several reasons, and these have not been well differentiated. DOC and DON are produced in soils either from incomplete decomposition and mineralization or else via desorption of soluble nutrients (Kaiser and Zech, 1998; Kalbitz et al., 2000; Qualls and Richardson, 2003). Decomposition of soil organic matter occurs between storm events or during dry seasons, but the soluble products of decomposition are not removed until storms move water through the soil, causing stream concentrations to rise due to desorption and flushing. During conditions of high hydrologic flux, or when decomposition of organic matter is limited by temperature, flushing may exceed the production of soluble nutrients, and thus the supply of soluble nutrients from soils will decrease, resulting in a finite source of nutrients. When the supply of nutrients does not change during conditions of high hydrological flux the source of nutrients is infinite. The few studies that have focused on DOC concentrations in the upper soil profile during storm events concluded that DOC was an infinite source (Jardine et al., 1990; McGlynn and McDonnell, 2003). A synthesis of 42 studies that have focused on DOC and DON concentrations in the upper soil layer at coarser time scales in temperate forests (Michalzik et al., 2001) concluded that there was no dilution effect of precipitation for both DOC and DON concentrations, indicating an infinite source of DOM from the organic layer. In contrast Boyer et al. (1997) observed that DOC concentrations in shallow lysimeters decreased rapidly during the snowmelt season in an alpine catchment. This suggests that at their site DOC was a finite source at the time scale of about 4 months. Thus, detailed temporal measurements of nutrient concentrations in the organic horizon and shallow soil layer during storm events are essential to quantify whether DOC and N are a finite or infinite source during flushing of these solutes.

This study examines two storm events (December 2004 and May 2005 storm event) using a combination of continuous fluorescence measurements at the hillslope and catchment scale, hydrometric data and chemical measurements of soil water, groundwater, lateral subsurface flow and stream water to test the three flushing mechanism hypotheses. We address the following questions: (1) What is the lag time between start of rainfall and lateral subsurface flow, stream flow and internal hillslope hydrometric data, and peak time between start of rainfall and peak discharge of lateral subsurface flow and stream flow? (2) What is the DOC and N flushing pattern at the hillslope and catchment scale? (3) What sources of lateral subsurface flow and stream water can we identify with end-member mixing analysis? (4) Can hydrometric data be used to validate the end-member mixing analysis? (5) How do water and nutrient flow directions in the unsaturated zone shift through an event? (5) What pattern of DOC and N concentrations in the organic horizon, soil and groundwater do we observe?

Site description

This study was conducted in Watershed 10 (WS10), a 10.2 ha headwater catchment located on the western boundary of the H.J. Andrews Experimental Forest (HJA), in the western-central Cascade Mountains of Oregon, USA (44.2°N, 122.25°W) (Fig. 1). HJA has a Mediterranean climate, with wet mild winters and dry summers. Average annual rainfall is 2220 mm of which about 80% falls between October and April during storms characterized by long duration and low rainfall intensity. Light snow accumulations in WS10 are common but seldom exceed 30 cm, and generally melt within 2 weeks (Sollins et al., 1981). Elevations range from 470 m at the watershed flume to a maximum watershed elevation of 680 m at the southeastern ridge line. The watershed was harvested during May–June 1975 and is now dominated by a naturally regenerated second growth Douglas-fir (*Pseudotsuga menziesii*) stand. Several seep areas along the stream have been identified (Harr, 1977; Triska et al., 1984). These seep areas are related to the local topography of bedrock and/or saprolite, or to the presence of vertical, andesitic dikes approximately 5 m wide, which are located within the southern aspect 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 of the study hillslope ranged 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 deposits. Surface soils are well aggregated, but lower depths (70–110 cm) exhibit more massive blocky structure with less aggregation than surface soils (Harr, 1977). Soil textures change little with depth. Surface soils are gravelly loams, lower soil layers are gravelly silty clay loams or clay loams and subsoils are characterized by gravelly loams or clay loams (Harr, 1977). The soils are highly Andic and vary across the landscape as either Typic

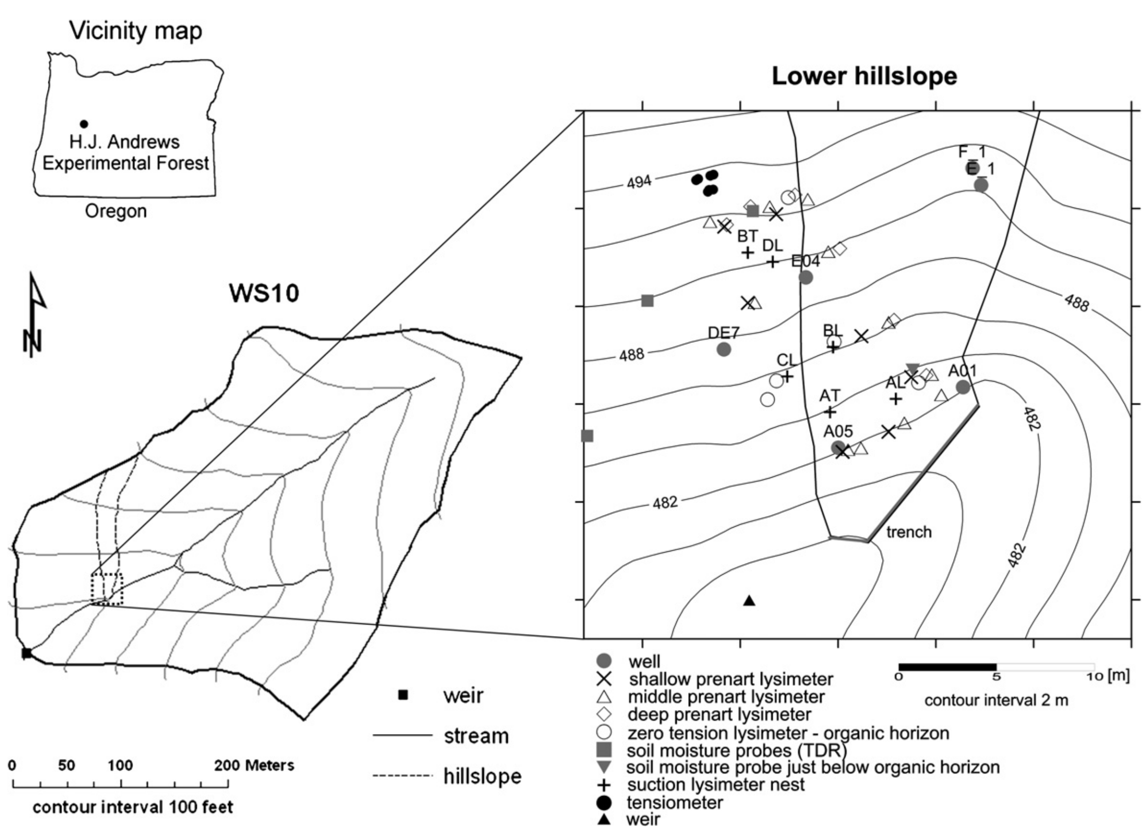

Figure 1 Map of WS10 showing the location of the hillslope study area and hillslope with the instrumentation.

Hapludands or as Andic Dystrudepts (Yano et al., 2005), and are underlain by 1–8 m relatively low permeability subsoil (saprolite), which formed in the highly weathered coarse breccia (Ranken, 1974; Sollins et al., 1981).

Benchmark hydrological studies (Harr, 1977; Ranken, 1974) were conducted at this site during the 1970s and the site was re-established by McGuire (2004) in 2002. As part of these 1970s studies, a total of 450 soil cores from 11 soil pits were collected at depths of 10, 30, 70 and 110 cm in the soil and 130, 150 and 250 cm in subsoil. These soil cores were analyzed for hydraulic conductivity, porosity, pore-size distribution, bulk density, soil moisture–tension relationships and stone-content (Ranken, 1974; Harr, 1977).

Methods

Instrumentation

To measure lateral subsurface flow at a natural seepage face a 10 m long trench was constructed (McGuire et al., 2007). 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) and verified by a water balance calculation (McGuire et al., 2007). We used a rounded value of 0.2 ha in all analyses. As part of the long term monitoring at the H.J. Andrews Experimental Forest, watershed discharge of WS10 has been measured with a trapezoidal flume since 1973. Since 1997 a V-notch weir has been used during the summer. Stage was measured with a Model 2 Stevens Instruments Position Analog Transmitter (PAT) (0.3 mm resolution).

We instrumented the gauged hillslope with four nests of porous cup suction lysimeters (Soil Moisture Equipment Corp., Model 1900, 2 bar) at 30, 70 and 110 cm depths, except for site AL, where the deepest lysimeter was installed at 80 cm depth (depth of bedrock) (Fig. 1). These suction lysimeters were installed in addition to four nests that were already installed (McGuire, 2004). Six plastic zero tension lysimeters were installed below the organic layer, with three measuring 10×10 cm installed at 20 cm depth, and two measuring 15×15 cm installed at 40 cm depth (Fig. 1). Twenty seven Prenart superquartz tension lysimeters (Prenart Equipment ApS, 0.5 bar) were installed at 20, 30–40 and 70–110 cm at a 30° angle according to the method described by Lajtha et al. (1999).

Transient saturation was measured with 69 maximum cork rise wells (3.18 cm diameter), and were screened for the lower 25 cm, the maximum water height observed by Harr (1977). We equipped three wells that showed consistent transient saturation and one well in the seepage area (A01) with 1-mm resolution capacitance water level recorders (TruTrack Inc., model WT-HR). We sampled with one well deep groundwater (A01 in the seepage area) and with four wells transient groundwater (Fig. 1) prior to, during, and after the December 2004 and May 2005 storm events and at three weekly intervals between the two storm events. All the wells were installed until refusal by a hand auger.

Soil water content (θ) was measured with water content reflectometers (WCR) (CS615, Campbell Scientific Inc.). The soil moisture probes were installed horizontally (i.e., with the slope) at three 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 from the slope base (McGuire, 2004).

Soil matric potential was measured by seven fast responding tensiometers (type: UMS T4, 1 bar porous cups), that were installed vertically in a triangle pattern, three tensiometers at 30 depth, three tensiometers at 70 cm depth and one tensiometer at 100 cm depth. The tensiometer triangle was located 25 m upslope from the base of the hillslope. We installed the tensiometers close to each other in a triangle to calculate unsaturated flow directions without bias of an elevation gradient. This enabled us to investigate the possible occurrence of an unsaturated lateral flow component during storms. Saturation was defined as pore pressure $\geqslant 0.25$ kPa.

Flow direction analysis

A plane was fitted through the total head values for each timestep at tensiometer locations at 30 cm depth and 70 cm depth, respectively. The direction of the lateral gradient was defined as the gradient parallel to the soil surface (46°) at the tensiometer triangle. The normal vectors to these planes defined the size of the lateral gradient at each depth. The direction of the vertical gradient was defined as normal to the soil surface. The vertical gradient between planes at 30 and 70 cm depth was calculated as the average of the gradients at the three tensiometer locations. The vertical gradient at 70 cm depth was calculated at the tensiometer location with three tensiometers at depths 30, 70 and 100 cm. The resultant flow direction from the lateral and vertical flow gradient was expressed as the deviation from the true vertical flow direction (Fig. 2).

Sampling

Throughfall, lateral subsurface flow, deep and transient groundwater, WS10 stream water and soil water (zero tension and tension) samples were collected prior to, during, and after the December 2004 and May 2005 storm events and at three weekly intervals between the two storm events. Throughfall was captured using the technique of Keim and Skaugset (2004). Tension lysimeters were evacuated to −50 kPa and allowed to collect water for 24 h. We used samples from porous cup tension lysimeters for the analysis of sulfate (SO_4^{2-}) and chloride (Cl^-), and samples from superquartz tension lysimeters for the analysis of DOC, TDN, NO_3-N, ammonium (NH_4-N) and UV absorbance at 254 nm (UV_{254}). All water samples except porous cup lysimeter samples were analyzed for DOC, TDN, NO_3-N, NH_4-N and UV_{254}. A subset of all water samples was analyzed for SO_4^{2-} and Cl^-. The gauged hillslope and watershed outlet were both sampled with 3700C Compact Portable Samplers with 24 polyethylene 500 ml bottles (Teledyne Isco) which allowed automatic collection of water samples, between 1

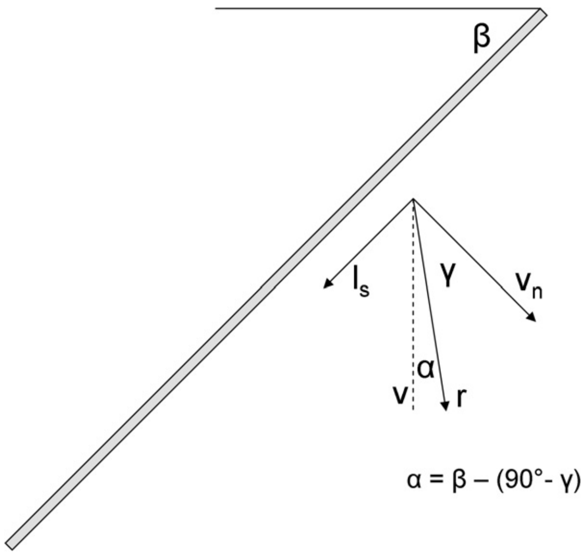

Figure 2 Schematic overview of gradients; l_s and v_n are the lateral (parallel to the slope) and vertical gradient (normal to slope), respectively, r is the resultant gradient of l_s and v_n, and v is the vertical. The flow direction deviation from the vertical is α.

and 4 h intervals during the two storm events. Fluorescence in the field at the gauged hillslope and watershed outlet were measured continuously at a 5 s interval during the two storm events using a field fluorometer (10-AU, Turner Designs Inc., Sunnyvale, CA) with a CDOM optical kit (P/N 10-303, Turner Designs Inc., Sunnyvale, CA) that measured within the 310—390 nm excitation and 410—600 nm emission wavelength spectrum.

Chemical analysis

DOC and TDN were measured with Pt-catalyzed high-temperature combustion (Shimadzu TOC-V CSH analyzer with TN unit). Nitrate-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 (NO_3-N and NH_4-N). Because DON was calculated by difference, values sometimes fell slightly below 0 mg l^{-1}. When negative DON values were smaller than 5% of TDN these values were considered to be 0 mg l^{-1}. When calculated negative DON values were larger than 5% of TDN we measured TDN and DIN again if sample volume permitted. If negative DON values remained larger than 5% after re-measurement DON and DIN were not used for further analysis. SO_4^{2-} and Cl^- were measured using a Dionex Model DX 500 Ion Chromatograph. UV absorbance (UV_{254}) was measured at 254 nm with a Hitachi V-2001 spectrophotometer. SUVA is UV_{254} normalized by DOC concentration.

End-member mixing analysis (EMMA)

We performed EMMA (Christopherson and Hooper, 1992; Burns et al., 2001; McHale et al., 2002; James and Roulet, 2006; Inamdar and Mitchell, 2006) to identify end-members of stream and lateral subsurface water during two storm events. The following solutes were used in EMMA: DOC, UV_{254}, Cl^- and SO_4^{2-}. EMMA relies on the assumption that mixing of end-members is a linear process, and thus solutes used in EMMA should behave conservatively and end-members should have time invariant compositions. We recognize that DOC and UV_{254} may behave non-conservatively. However, several studies have used DOC to identify expression of the organic horizon or shallow soil water in stream water (Brown et al., 1999; Inamdar and Mitchell, 2006; James and Roulet, 2006). In addition, Cl^- and SO_4^{2-} are considered quasi-conservative; Cl^- can sorb onto soils and be stored in plants by plant-uptake and SO_4^{2-} can undergo significant biological transformations (Swank et al., 1984). While Cl^- may behave quasi conservatively, the average Cl^- concentration of precipitation was 1.29 mg l^{-1} during the period 1990—2003 (PRIMET station, HJA), which is in the high range of Cl^- wet deposition in USA (NADP), and probably behaved relatively more conservatively in comparison to sites with lower Cl^- wet deposition values (<0.1 mg l^{-1}). Because the solutes used in EMMA may behave non- to quasi-conservatively, we used EMMA as an investigative tool to identify possible end-members for lateral subsurface flow and stream water.

Lateral subsurface flow and stream water concentrations of the four solutes were standardized by the mean value for the event. MATLAB was used to calculate the correlation matrix and to perform a principal component analysis resulting in the eigenvectors of the correlation matrix. Lateral subsurface flow and stream water samples were projected into the U space by multiplying the first two eigenvectors (U1 and U2) which implies a three component mixing model, with the standardized values. Median standardized values of potential end-members were projected in the U space in the same manner as the lateral subsurface flow and stream water samples. How well potential end-members bounded the observed lateral subsurface flow and stream water samples was investigated in the U mixing space. Potential end-members included throughfall water, organic horizon water, shallow and deep soil water, transient groundwater (well E04) and deep groundwater (grab samples of lateral subsurface flow and stream water prior to the storm event during baseflow conditions). End-members were selected based on the following criteria: for all storm events lateral subsurface flow and stream samples could be explained by more than one combination of three end-members; we did choose end-members combinations that were as similar as possible for stream water and lateral subsurface flow during individual storm events and bounded the solute space most complete. After selecting the end-members we used the EMMA model to calculate the contribution of each end-member to each sample during the two storm events for lateral subsurface flow and stream water, by solving the mass balance equations described by Burns et al. (2001, Eqs. (4)—(6)).

We evaluated the EMMA model by comparing EMMA predicted solute concentrations against measured concentrations and by comparing calculated end-member contributions to hydrometric data. We calculated Pearson correlation coefficients (r) between hydrometric data and EMMA derived contributions and squared Pearson correlation coefficient (R^2) between EMMA predicted solute concentrations and measured concentrations. We calculated also p values to test if these correlations were significantly different from zero which we defined at $p < 0.05$.

Results

Hydrological dynamics

The physical hydrological dynamics of the December 2004 and May 2005 storm events were evaluated through calculation of time lags of soil moisture, soil matric potential, deep (well A01) and transient groundwater, lateral subsurface flow and stream flow to the start of rainfall (Table 1 and Fig. 3) and time to peak of stream water and lateral subsurface flow from the start of rainfall (Fig. 3). During the December 2004 storm event responses of shallow soil moisture, shallow soil matric potential and lateral subsurface flow and stream flow to rainfall were similar and lagged rainfall by 8–12 h, except for the 30 cm soil moisture probe at the middle slope location that lagged rainfall by 17.8 h (Table 1). The soil moisture response at deep soil profile position and 122 cm (well E04) lagged rainfall by 15.7–25.7 h. The 15.7 h lag time is from the upper soil moisture probe location on the hillslope and precedes the soil moisture probe response at 70 cm by 1.7 h. While this may indicate preferential flow, the overall soil moisture response at 70 cm preceded the soil moisture response at 100 cm. Transient groundwater response in wells DE7 at 215.5 cm depth and A05 at 40.5 cm depth, lagged rainfall by 48.2 and 51.8 h, respectively.

During the May 2005 event, responses of deep groundwater, shallow soil moisture, shallow soil matric potential and lateral subsurface and stream flow to rainfall were similar and lagged rainfall by 45–48 h, except for the shallow soil moisture probe and tensiometers at the upper slope location that lagged rainfall by 31–33 h (Table 1). Deeper soil moisture and matric potential responded to rainfall by 45 and 63 h. Transient groundwater height observations were not available because sampling of wells during the storm affected the groundwater hydrographs to a large extent.

The faster response of stream water and lateral subsurface flow to rainfall for the December 2004 storm event compared to the May 2005 storm event was also reflected in the time to peak of stream water and lateral subsurface flow from the start of rainfall and peak flows during the two storm events. While the time to peak was 56 and 62 h for the December 2004 storm event for lateral subsurface flow and stream water, respectively, the time to peak for the May 2005 storm event was 118 and 117 h for lateral subsurface flow and stream water, respectively. In addition peak flows were higher during the December 2004 storm event compared to the May 2005 storm event (Fig. 3). Antecedent wetness conditions expressed as average soil moisture (from the lower soil pit) prior to the two events over 7 days (AMI_7) and 14 days (AMI_{14}) was 0.28 for the December 2004 and May 2005 storm event. Furthermore, total precipitation prior to the storm events over 7 days (API_7) and 14 (API_{14}) days were higher for the May 2005 storm event compared to the December 2004 storm event (Table 1). Gross precipitation was 200 and 100 mm and mean rainfall intensity was 1.5 and 0.5 mm h^{-1} for the December 2004 and May 2005 storm event, respectively, indicating that the difference in stream and lateral subsurface flow response between the two events was largely controlled by rainfall amount and intensity.

Table 1 Hydrological response timing to rainfall of December 2004 and May 2005 storms events

Site	Time lag from start rainfall event (h)	
	December storm 2004	May storm 2005
Soil moisture lower soil pit (30 cm)	8.33	45.17
Soil moisture lower soil pit (70 cm)	14	45.83
Soil moisture lower soil pit (100 cm)	17.83	49.83
Soil moisture middle soil pit (30 cm)	11.33	33
Soil moisture middle soil pit (70 cm)	17.33	49
Soil moisture middle soil pit (100 cm)	15.67	52.67
Soil moisture upper soil pit (30 cm)	17.83	47.83
Soil moisture upper soil pit (70 cm)	24.5	58.17
Soil moisture upper soil pit (100 cm)	25.67	62.17
Tensiometer (30 cm)	9.33	31.67
Tensiometer (70 cm)	16.33	52.67
Tensiometer (100 cm)	19.67	58.33
Groundwater (well E04)	19	–
Groundwater (well DE07)	51.83	–
Groundwater (well A05)	48.17	–
Groundwater (well A01)	11.83	44
Lateral subsurface flow	9.67	45.17
WS10 outlet	9.5	44.67
Antecedent wetness conditions		
AMI_7 and AMI_{14} (m^3/m^3)	0.28	0.28
API_7 (mm)	24	52
API_{14} (mm)	66	80

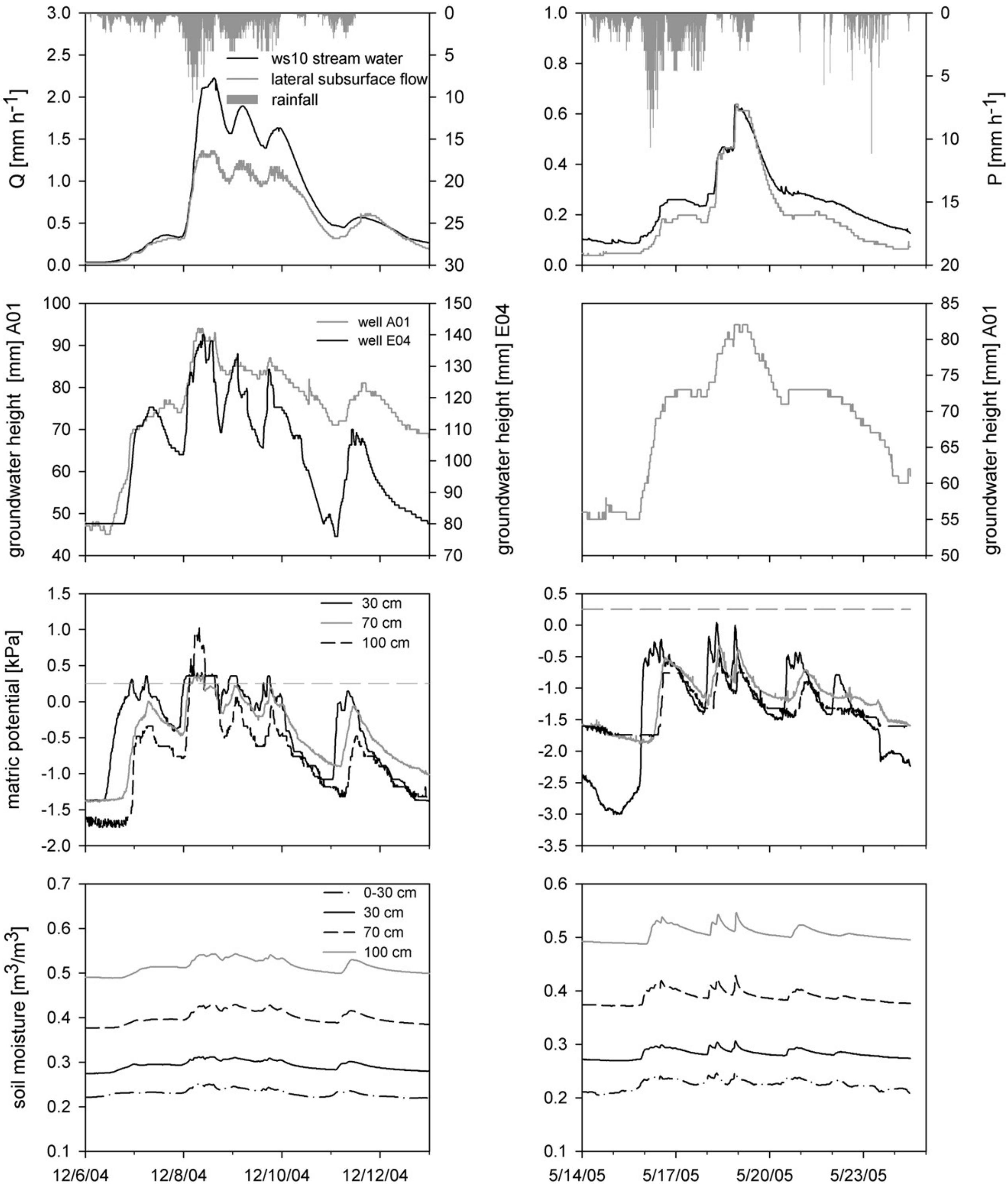

Figure 3 Hydrological dynamics during the December 2004 and May 2005 storm event.

DOC and N flushing pattern at the hillslope and catchment scale

DOC concentrations in lateral subsurface flow during the December 2004 storm event showed a dilution pattern, with a maximum concentration of 4.18 mg l^{-1} (Fig. 4a). DON showed maximum concentrations on the rising limb of the storm with a 1.8 times increase during the rising limb of the hydrograph. DIN concentrations during the storm did increase with maximum concentrations around the hydrograph peak. SUVA and raw fluorescence increased 2.4 and 1.8 times, respectively, on the rising limb during the storm event. DOC, SUVA, raw fluorescence and DON all showed a clockwise hysteresis pattern; higher DOC and DON concentrations and SUVA, and raw fluorescence values on the rising limb compared to the falling limb of the hydrograph. The

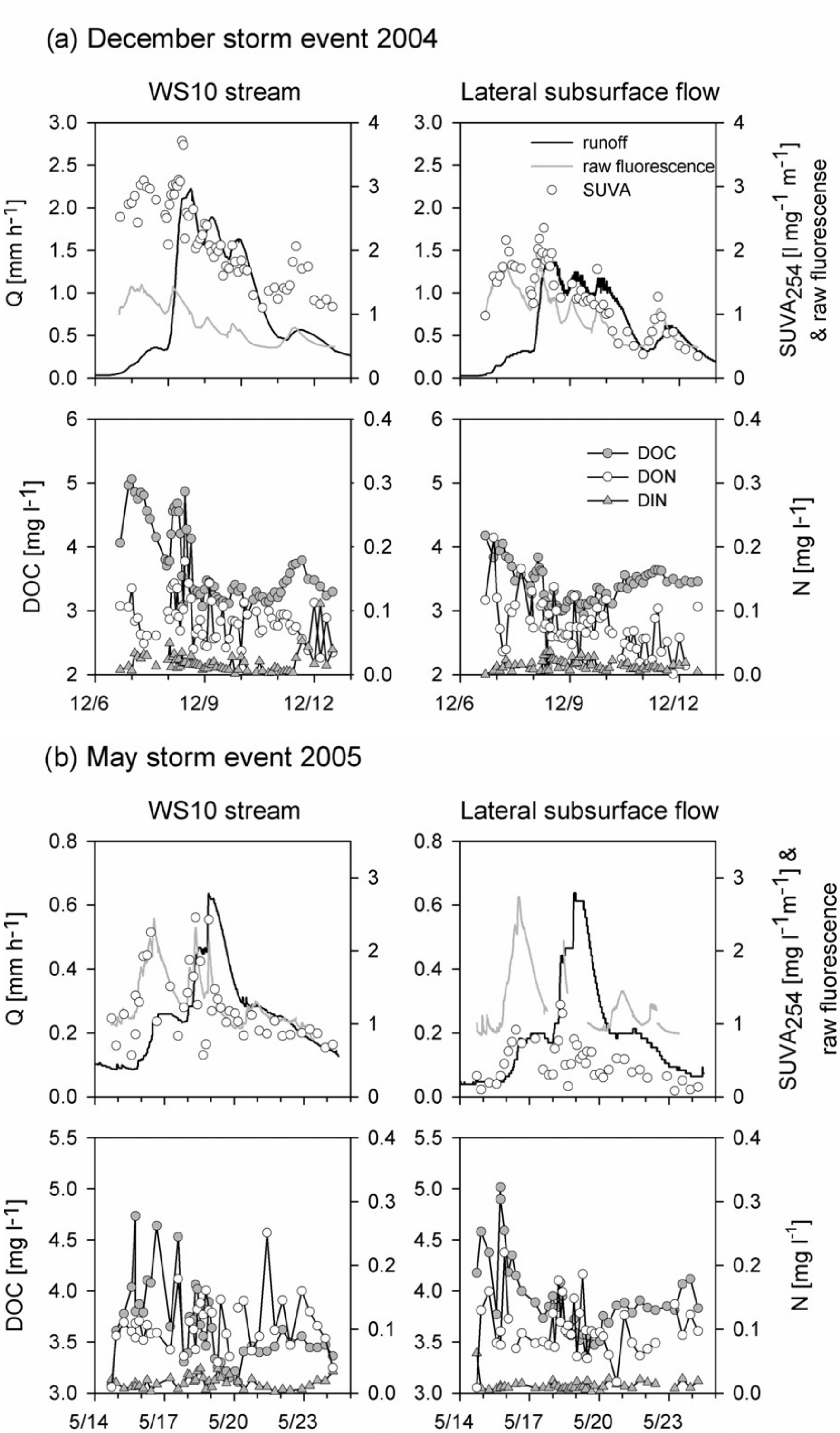

Figure 4 SUVA, raw fluorescence, DOC, DON and DIN concentrations in stream water and lateral subsurface flow, during (a) the December 2004 and, (b) May 2005 storm event.

flushing pattern (clockwise hysteresis pattern) of DON was not clear because of high variability of DON concentrations.

DOC concentrations in stream water increased 1.2 times and DON concentrations increased 1.7 on the rising limb of the December storm event (Fig. 4a). Highest DIN concentrations were found during the last hydrograph peak of the storm. SUVA and raw fluorescence increased both 1.5 times, during the rising limb of the storm. DOC, SUVA, raw fluorescence and DON all showed a clockwise hysteresis pattern. For lateral subsurface flow, the flushing pattern (clockwise hysteresis pattern) of DON was not clear because of high variability of DON concentrations.

During the May storm both lateral subsurface flow and stream water showed a DOC, SUVA, raw fluorescence and DON clockwise hysteresis pattern (Fig. 4b). Stream DOC and subsurface flow DOC increased 1.5 and 1.2 times, respectively. DON in stream and subsurface flow water did not show a clear flushing pattern (clockwise hysteresis pattern) because of high variability in DON concentrations during the storm. DON concentrations on the rising limb of the storm hydrograph increased by 11.7 and 25.8 times, respectively. DIN concentrations in stream water were highly variable and increased from 0.021 to 0.039 mg l^{-1} on the rising limb of the storm. DIN concentrations in lateral subsurface flow, were also highly variable and showed (after the first high DIN (0.0628 mg l^{-1}) sample) an increase from 0.0076 to 0.0198 mg l^{-1} on the rising limb. SUVA and raw fluorescence values in stream water increased 2.3 and 2.4 times, respectively, on the rising limb of the storm. SUVA and raw fluorescence in lateral subsurface flow increased on the rising limb of the storm 4.4 and 2.8 times, respectively.

Runoff sources of lateral subsurface flow and stream water

We used end-member mixing analysis (EMMA) to evaluate the contribution of runoff components to lateral subsurface flow and stream water during the December 2004 and May 2005 storm. The principal component analysis we used for EMMA indicated that between 78% and 95% of the variability in lateral subsurface flow and stream water during the December and May storm could be explained by two principal components. This indicates that variation in lateral subsurface flow and stream water could be accounted for by three end-members.

Lateral subsurface flow water during the December storm event was bounded by the three end-members: deep groundwater, throughfall and organic horizon water (Fig. 5b). The proportion of organic horizon water was higher on the rising limb of the hydrograph compared to the falling limb of the hydrograph, while on the falling limb of the hydrograph the proportion of throughfall water increased (Fig. 6). Stream water during the December storm event was bounded by three end-members: deep groundwater, throughfall and organic horizon water (Fig. 5a). During the storm the maximum proportion of througfall was 49% during the falling limb of the hydrograph, while the maximum proportion of organic horizon water was 36% during the rising limb of the hydrograph.

Lateral subsurface flow during the May storms was bounded by deep groundwater, throughfall and transient groundwater end-members (Fig. 5d). Deep soil water projected close to the end-member throughfall in the lateral subsurface flow U-mixing space. Maximum contribution (54%) to runoff by transient groundwater was found on the rising limb of the hydrograph. Throughfall contribution to runoff increased during the storm with highest values

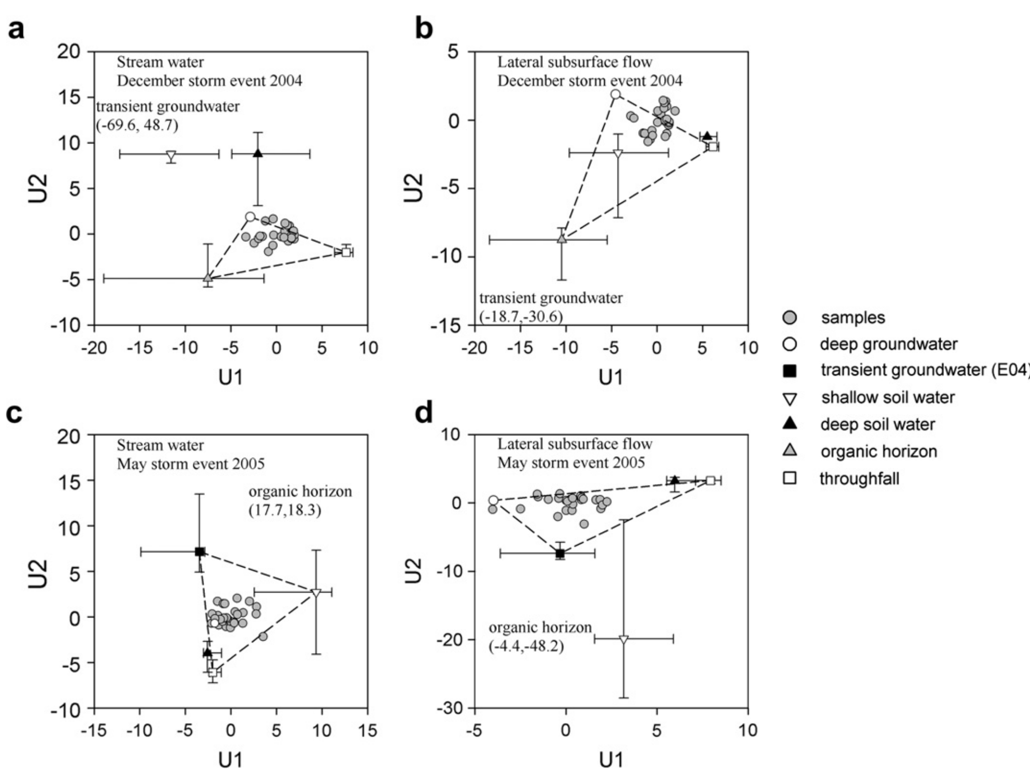

Figure 5 EMMA for (a) stream water during the December 2004 storm event, (b) lateral subsurface flow during the December 2004 storm event, (c) stream water during the May 2005 storm event and (d) lateral subsurface flow during the May 2005 storm event. Medians and the 25th and 75th percentiles of each possible end-member are plotted. U1 and U2 median coordinates are given for end-members outside the graph range. Note differences in scale between graphs.

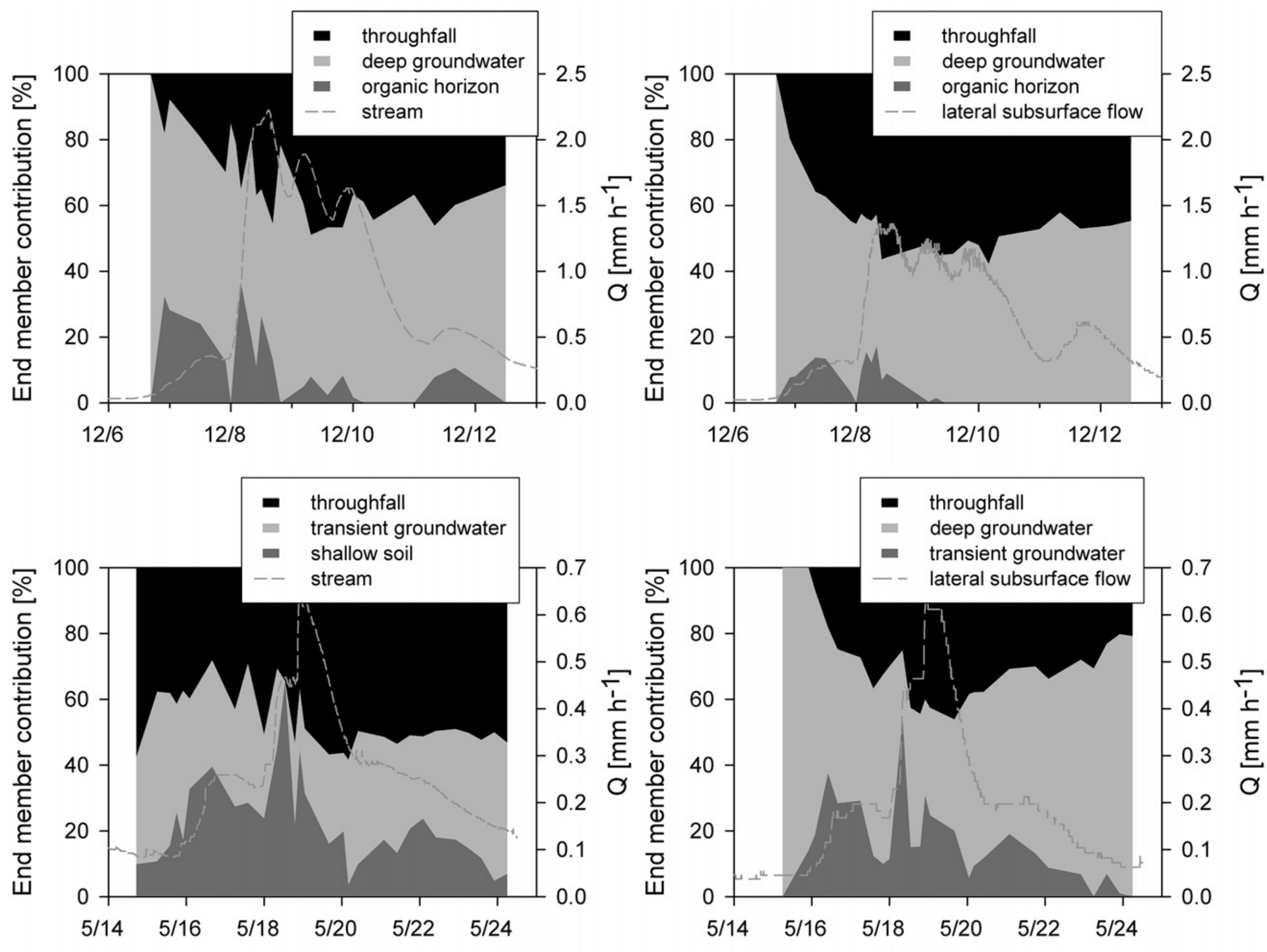

Figure 6 End-member derived contributions during the December 2004 and May 2005 storm events.

(46%) at the hydrograph peak. Stream water during the May storm was bounded by the end-members throughfall, shallow soil water and transient groundwater (Fig. 5c). As in the lateral subsurface flow mixing U-space, deep soil water and throughfall projected close to each other in the stream water mixing U-space. The end-member organic horizon was projected in the same positive U-mixing space as shallow soil water, however organic horizon did not bound the solutes as completely as shallow soil water. Shallow and throughfall water contributions to runoff varied the most during the storm (compared to transient groundwater contributions), with higher contributions of shallow soil water than throughfall during the rising limb and a reversed pattern during the falling limb of the hydrograph (Fig. 6).

Validating EMMA

We validated the EMMA by calculating squared Pearson correlation coefficient (R^2) between predicted solute concentrations and measured concentrations. For both storm events R^2 ranged between 0.66–0.99 and 0.47–0.92 for lateral subsurface flow and stream water, respectively (Table 2). This indicates that the EMMA model was a moderate to strong predictor of lateral subsurface flow and stream water solute concentrations.

Table 2 Squared Pearson correlation coefficients (R^2) between EMMA predicted solute concentrations and measured solute concentrations for stream water and lateral subsurface flow during the December 2004 and May 2005 storm events ($p < 0.001$ for all R^2)

	December 2004 event		May 2005 event	
	Stream water	Lateral subsurface flow	Stream water	Lateral subsurface flow
Cl	0.89	0.92	0.47	0.97
SO_4^{2-}	0.87	0.66	0.67	0.92
DOC	0.92	0.80	0.58	0.91
UV_{254}	0.89	0.72	0.60	0.99

To further evaluate the EMMA derived contributions of end-members for stream and lateral subsurface flow water we compared these contributions to hydrometric measurements (Fig. 7) at the hillslope study area. The Pearson correlation coefficient between water height in well A01 and EMMA derived deep groundwater contribution to subsurface lateral flow was −0.90 ($p < 0.001$) during the December event and −0.92 ($p < 0.001$) during the May event. Further-

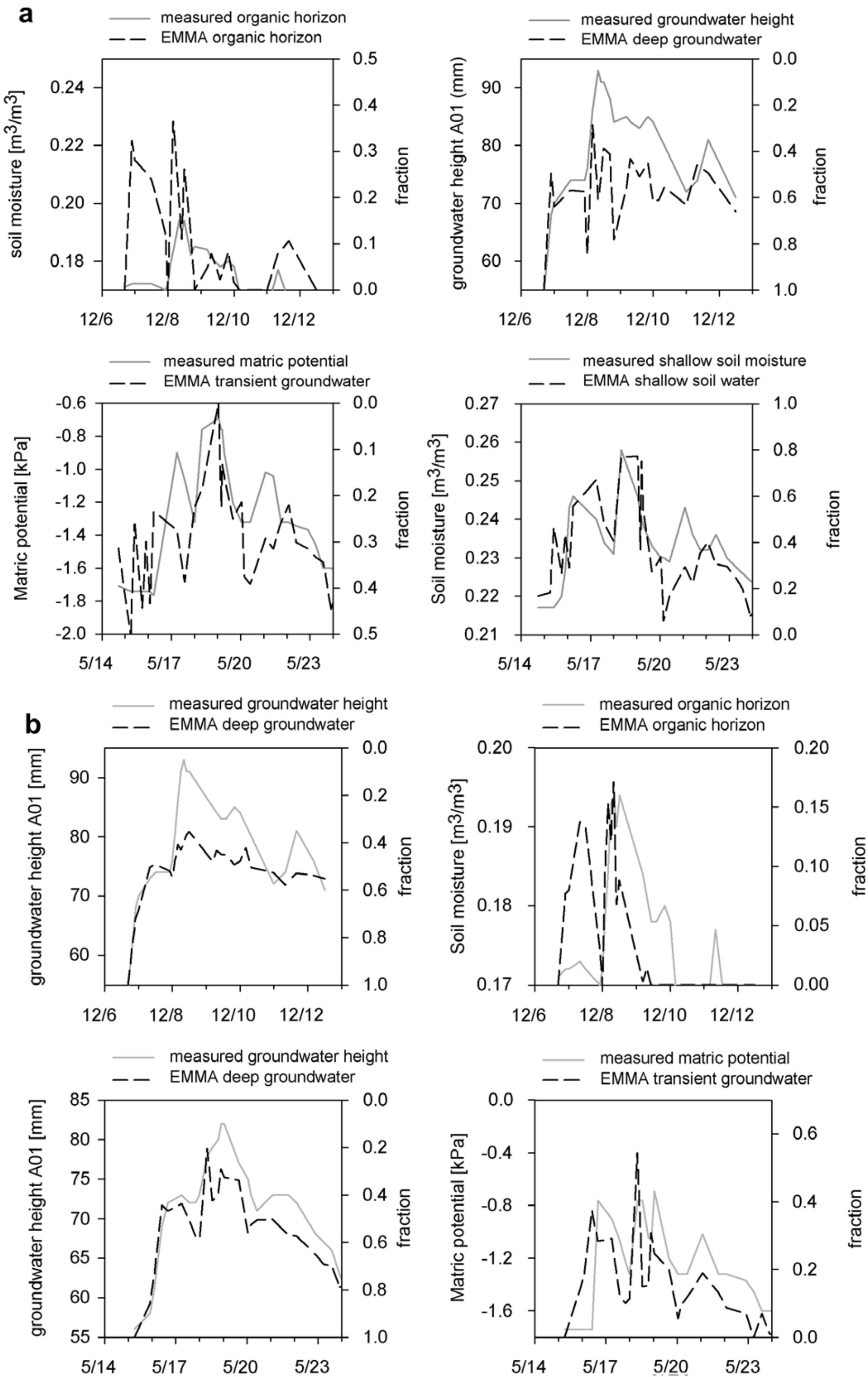

Figure 7 Comparison of EMMA derived contributions with hydrometric data for (a) stream water and (b) lateral subsurface flow.

more, the timing of EMMA derived deep groundwater contributions were in close agreement with the measured water height in well A01 (Fig. 7b). The Pearson correlation ($r = 0.52$, $p < 0.01$) for the organic horizon EMMA derived contribution to lateral subsurface flow and soil moisture measured at this soil profile position for the December event was smaller than the Pearson correlation for deep groundwater. The organic horizon EMMA derived contribution was likely overestimated at the start of the event, since the EMMA derived contribution was much higher than the soil moisture contribution (Fig. 7b).

Soil matric potential at 100 cm depth located 5 m upslope from well E04 was used as a proxy for transient groundwater in well E04 during the May 2005 storm event, because the transient groundwater hydrograph was affected by sampling during this event. The Pearson correlation coefficient of EMMA derived deep groundwater to stream water during the December event was −0.58 ($p < 0.01$) and the timing of EMMA derived deep groundwater was in general agreement with the water height in well A01 (Fig. 7a). For the May event, the Pearson correlation between transient groundwater EMMA derived contribution to lateral subsurface flow and soil matric potential at the deep soil profile position was 0.52 ($p < 0.01$). The Pearson correlation coefficient of organic horizon was low ($r = 0.36$) for stream water during the December 2004 event with a $p < 0.1$ and not significant; during the start of the event, the EMMA organic horizon derived contribution was largely overestimated (Fig. 7a). The Pearson correlations for the EMMA derived contribution of transient groundwater and shallow soil water to stream water during the May event were −0.66 ($p < 0.001$) and −0.65 ($p < 0.001$), respectively, and timing of these contributions and measurements were generally in agreement.

Flow direction analysis

The flow direction analysis was done to test if a lateral flow component within the soil profile is an important part of the flushing mechanism. The flow direction analysis based on the tensiometer triangle installed 25 m upslope showed that the direction of flow was mainly directed vertically during the December and May storm events (Fig. 8). Flow direction (r) with a positive deviation (α) from the vertical flow direction (v) is considered a lateral flow component. Flow direction parallel to the slope of the hillslope is characterized by an α of 46°. During the December event the maximum deviation from the vertical flow direction at 30 cm depth was 2.4° and most of the time (77%) smaller than zero and thus directed into the hillslope. During the May event maximum α at 30 cm depth was 10°, and α was 36% of the time <0°. Although the maximum deviation from the vertical flow direction at 70 cm depth was 25° during the December event and coincided with positive pore pressures at 100 cm depth (Fig. 8), 86% of the time α was <10°. During the May event maximum α was 19°, however, α was 65% of the time <10°. The negative changes of α (flow direction changes in upslope direction) during both storm events coincide with large positive changes in rainfall intensity (Figs. 3 and 8), indicating that changes in rainfall intensity are the driving force for changes in flow direction at both depths. In general these results show that a significant lateral flow at considerable lengths of time does not exist at 30 and 70 cm depth.

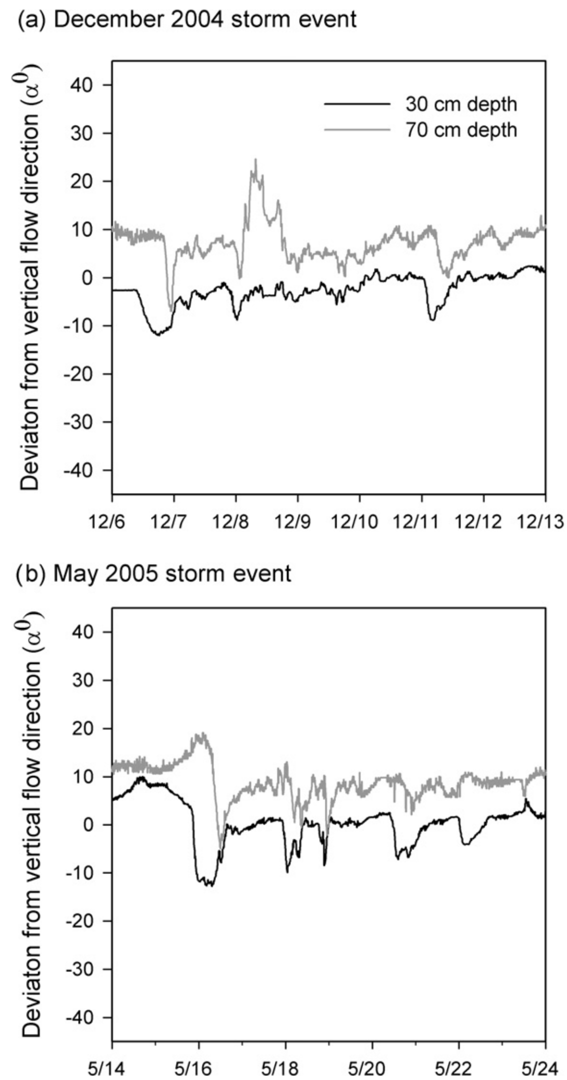

Figure 8 Flow direction at 30 and 70 cm depth during (a) the December storm event and (b) during the May storm event.

DOC and N in organic horizon, soil and groundwater

DOC and N in throughfall, from the organic horizon and in soil water were sampled frequently during the December 2004 and May 2005 storm events to investigate if DOC and N were a limited or unlimited supply during these storm events. Pre-storm mean DOC and DON concentrations in the organic horizon during the December storm, between 12/02 and 12/09, decreased from 11.7 to 7.4 mg l^{-1} and from 0.45 to 0.14 mg l^{-1}, respectively (Fig. 9). Between 12/09 and 12/12 both DOC and DON concentrations in the organic horizon increased slightly. DON increased in throughfall during the storm. In contrast DOC in throughfall showed a dilution pattern. The increase in DIN concentration in the organic horizon during the storm is probably to some extent caused by the increase in DIN concentration in throughfall. DOC concentrations at 20 and 30–40 cm depth did not show significant variation during the storm, while at 70–110 cm DOC increased slightly. DON soil solution concentrations did show variation during the storm: (1) at 20 cm depth, DON decreased from 0.2 to 0.1 mg l^{-1}

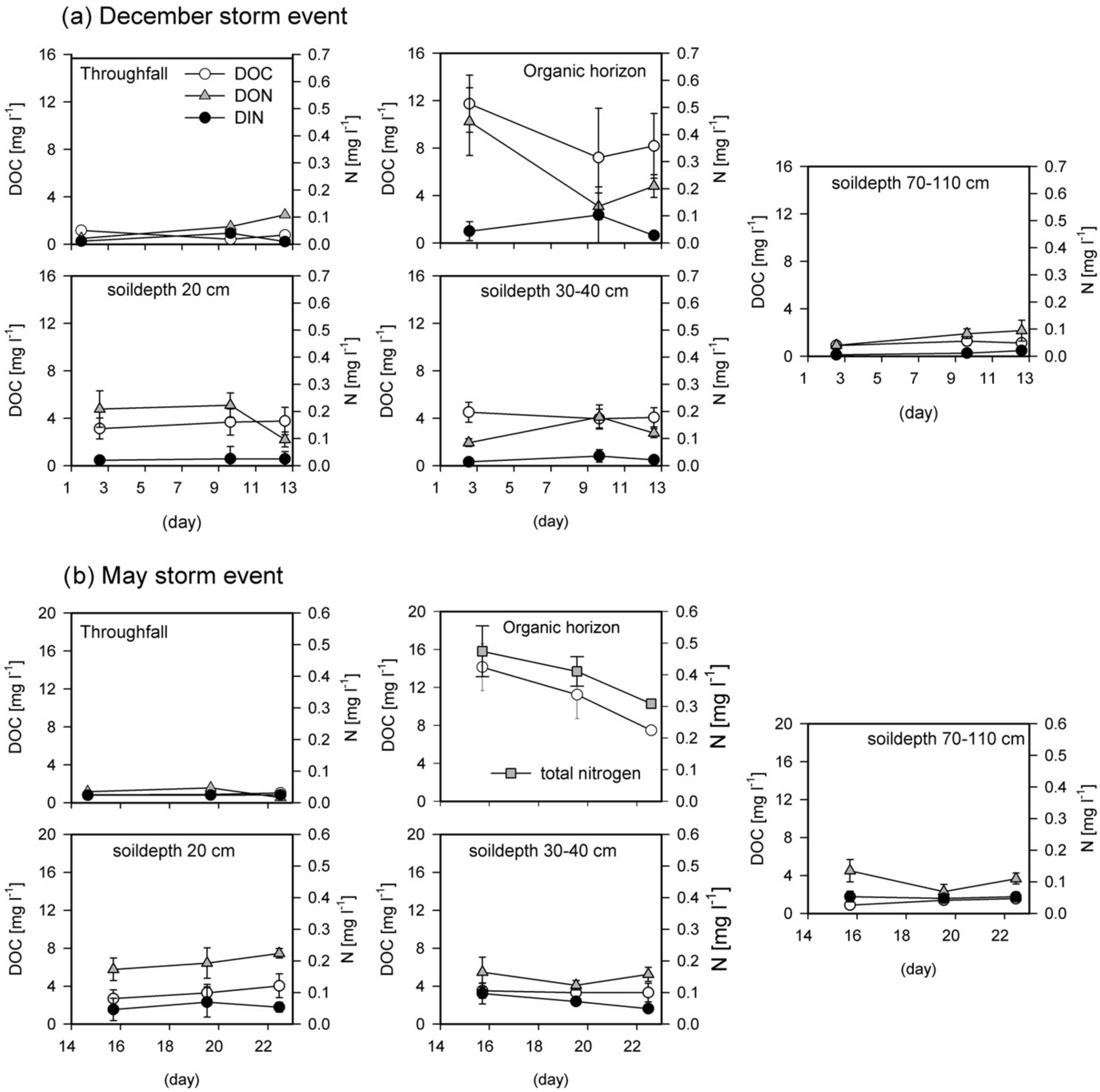

Figure 9 Mean (±SE) DOC, DON and DIN concentrations in throughfall, organic horizon water, and soil water at 20, 30—40 and 70—110 cm depth during (a) the December 2004 storm event, and (b) the May 2005 storm event.

between 12/09 and 12/12, (2) DON showed an overall increase in concentration at 30—40 cm depth compared to pre-storm DON, with a peak at 12/09, and (3) DON increased from 0.04 to 0.1 mg l^{-1} at 70—110 cm depth. DIN at 20 cm depth did not show any variation, while it showed some variation at deeper soil depths.

During the May storm in 2005, DOC and DIN concentrations showed little variation in throughfall, while DON concentrations decreased between 05/19 and 05/22. The decrease in DOC and total nitrogen (TN) during the storm in the organic horizon indicates a dilution pattern, and a finite source of DOC and N. DIN data was not available for the organic horizon. DOC and DON concentrations increased at 20 cm soil depth during the storm, while DOC and DON concentrations at 30—40 cm depth did not show a large amount of variation. DOC concentrations increased at 70—110 cm soil depth, from 0.9 to 1.6 mg l^{-1}, and in contrast DON concentrations decreased at this soil depth range.

EMMA indicated that organic horizon, deep groundwater and transient groundwater were important end-members. Furthermore, the flow vector analysis suggested a possible strong connection between the organic horizon and groundwater. To elucidate the connectedness between the organic horizon and transient and deep groundwater (well A01) we compared organic horizon DOC and N concentrations and SUVA values with transient and deep groundwater (well

A01) DOC and N concentrations and SUVA values during the two storm events. During the December storm event DOC and DON concentrations and SUVA values of the organic horizon and transient groundwater were very similar, while deep groundwater (well A01) was characterized by lower values (Table 3). This suggests in combination with the flow vector analysis that vertical preferential flow caused high DOC, DON concentrations and SUVA values in transient groundwater.

Discussion

While many studies (e.g., Boyer et al., 1997; Vanderbilt et al., 2003; Hood et al., 2006) described higher stream nutrient concentrations on the rising limb compared to the falling limb of the hydrograph, description of the exact flushing mechanism has been difficult. In the literature three different flushing hypotheses have been described: (1) a rising water table that intersects high nutrient concentrations in the upper soil layer, (2) vertical transport of nutrients, by preferential or matrix flow through the (deeper less bio-active) soil to the soil–bedrock interface and then laterally downslope, and (3) lateral transient flow within the shallow soil profile. It is difficult to reject one or more of these hypotheses because we need a variety of hydrological and chemical approaches to do so. However, it is important given that a mechanistic understanding of flushing of nutrients is essential for model development for prediction of land use change and climate change effects on surface water quality.

The main objective of our paper was to mechanistically assess nutrient flushing at the catchment scale, through measurements at the point, hillslope and catchment scale. We used hydrometric data (groundwater level observations, soil matric potential and soil moisture measurements) to validate our chemical end-member analysis of different sources of lateral subsurface flow and stream water. Lateral subsurface and stream water both showed highest DOC and DON, and SUVA values during the rising limb of the hydrograph during the December and May storm events. EMMA indicated generally three different sources for lateral subsurface flow and stream water during the December and May storm events: (1) organic horizon water or shallow soil water or transient groundwater, (2) deep groundwater and (3) throughfall. EMMA derived deep groundwater contributions to stream water and lateral subsurface flow were in good agreement with deep groundwater level variations in seepage well A01. Soil moisture dynamics in the organic horizon were in agreement with the EMMA derived organic horizon water contribution to stream water and lateral subsurface flow, although EMMA likely over-estimated the organic horizon contribution during the rising limb of the hydrograph. Furthermore, deep soil matric potential patterns were in agreement with EMMA derived transient groundwater contributions to stream water and lateral subsurface flow. The flow direction analysis and high DOC and DON concentrations and SUVA values in transient groundwater suggest vertical preferential flow to depth and a strong connection between the organic horizon/shallow soil and transient groundwater. DIN concentrations in transient groundwater were higher than DIN concentrations in organic horizon water indicating that these high DIN concentrations were not caused exclusively by a preferential flow mechanism. High DIN concentrations in transient groundwater were likely the result of a combination of ammonification and subsequent nitrification of organic N (van Verseveld et al., submitted for publication).

Groundwater heights above the bedrock were very shallow (about 10–15 cm) and the predominantly vertical flow component in the unsaturated zone during the storm events reject flushing mechanisms 1 and 3. Our results support flushing mechanism 2: vertical transport of nutrients through preferential flow and then laterally downslope at the soil bedrock interface occurred at our site. Furthermore, DOC and DON were a finite source in the organic horizon, while DOC and DON concentrations from shallow and deep lysimeters did not show large temporal variation. This suggests that the DOC and DON flushing pattern observed in lateral subsurface flow and stream flow was caused by organic horizon dynamics. However, the combination of EMMA, SUVA and hydrometric data showed evidence that flushing mechanism 2 including a finite source of DOC and DON is not sufficient to explain our observations. Mixing of different sources of water both spatially and temporally needs to be included to explain nutrient flushing mechanistically. We will describe this in more detail in the following sections.

Mixing at hillslope and catchment scale

The three end-members from EMMA were different between the December 2004 and May 2005 storm event. For lateral subsurface flow and both storm events EMMA resulted in three distinct groups of end-members: (1) deep groundwater, (2) throughfall/deep soil water and (3) shallow soil water, organic horizon water and transient groundwater. Furthermore, the end-members from group 3 could be used interchangeably for lateral subsurface flow without affecting how complete the solute space was bounded by the end-members. The interchangeability of these end-mem-

Table 3 Mean (SE) of DOC, DON, DIN and SUVA in transient and deep groundwater (well A01) during December 2004 and May 2005 storm events

	December 2004 event			May 2005 event		
	Organic horizon	Transient groundwater	Deep groundwater (A01)	Organic horizon	Transient groundwater	Deep groundwater (A01)
DOC (mg l^{-1})	9.0 (1.3)	10.8 (2.0)	3.4 (0.07)	12.9 (1.2)	4.7 (0.7)	3.7 (0.2)
DON (mg l^{-1})	0.27 (0.06)	0.23 (0.11)	0.075 (0.006)	n.a.	0.21 (0.04)	0.049 (0.009)
DIN (mg l^{-1})	0.049 (0.017)	0.86 (0.51)	0.026 (0.006)	n.a.	0.81 (0.23)	0.028 (0.005)
SUVA (l mg^{-1} m^{-1})	5.5 (0.5)	4.8 (3.2)	1.3 (0.2)	4.9 (0.4)	2.5 (0.2)	0.6 (0.1)

bers is in agreement with our conceptual model of vertical preferential flow causing transient groundwater to keep partly an organic horizon/ shallow soil water signal. The end-members of group 3 were not interchangeably for stream water during both storm events: during the December 2004 event organic horizon water and during the May 2005 storm event transient groundwater were end-members that had to be included to bound the solute space as complete as possible. Transient groundwater from well E04 plotted differently from organic horizon water (December 2004 event) and organic horizon and shallow soil water (May 2005 storm event) for stream water with respect to the stream water samples. This indicates that at the catchment scale transient groundwater with another signature than transient groundwater from well E04 contributed to stream water.

Since the end-members throughfall and deep soil water at the hillslope scale projected close to each other in the U-mixing space we were not able to separate these two end-members. At the hillslope scale we did choose throughfall since it encompassed the variability in samples well, and throughfall was a likely end-member for the following reasons. Hydrograph separation of storm events (November—December 2002) based on conservative isotopes (δ18O) at the hillslope and catchment scale (McGuire, 2004) with TRANSEP (Weiler et al., 2003) showed event water contributions of <30%. When we would have used deep soil water as an end-member instead of throughfall the contribution of event water for the May 2005 storm event would have been in disagreement with the hydrograph separation results based on $\delta^{18}O$. Deep groundwater, transient groundwater and soil water may be considered 'old' water, while organic horizon water and throughfall may be considered 'new' water. Using deep soil water instead of throughfall, and organic horizon instead of transient groundwater would have resulted in an underestimation of new water (2.8%). In addition, we used throughfall as an end-member at the catchment scale since we were able to separate throughfall and deep soil water for the December storm. The reason we could not separate throughfall and deep soil water during the May storm was that deep soil water changed on a seasonal scale to a more throughfall signature because of dilution: average Cl^- concentrations in deep soil water were 1.49 mg l^{-1} in December and diluted to 0.56 mg l^{-1} in April and stayed low throughout the rest of the study period. The EMMA derived new water contributions (throughfall and organic horizon) at the catchment scale and hillslope scale, were higher than the range of $\delta^{18}O$-derived new water contributions (McGuire, 2004). EMMA derived new water contributions during the December storm were 43% and 49%, and during the May storm were 34% and 29%, respectively, at the catchment and hillslope scale. This over-estimation of the new water contribution may have been caused by the inability to separate the end-members throughfall and deep soil water in the end-member mixing space and high variability in the end-members.

Conceptual model of DOC and DON flushing

The clockwise hysteresis patterns of DOC and DON during the December and May storm event at the hillslope and catchment scale has also been observed in other studies at this site (Hood et al., 2006) and at other sites (Buffam et al., 2001; McGlynn and McDonnell, 2003). The response times of soil and groundwater, and lateral subsurface and stream flow to the start of rainfall indicated that the rapid increase in DOC and DON during the early response of the December and May storm, at the hillslope and catchment scale, was mainly derived from a shallow soil water source near the stream. At the hillslope scale depth to bedrock increased upslope from about 0.3—0.6 m at the hillslope stream interface to 3—8 m at the ridge of the hillslope. This increase in depth to bedrock for the lower hillslope above the trench is illustrated in Fig. 11. Thus, shallow soil depths at the soil stream interface enabled water to move relatively quickly to the soil—bedrock interface resulting in high DOC and DON concentrations during the early response of storms (Fig. 12a).

Later in the event, but still on the rising limb more upslope sources became important (Fig. 12b). For example during the December event well E04 started responding to rainfall 19 h after rainfall started. Travel time from this hillslope position is about 24 h based on a average subsurface flow velocity of 0.5 m h^{-1}, that was calculated from a Br^- tracer injection in this well during a sprinkler experiment (Graham, unpublished data), and is in agreement with subsurface flow velocity calculations at this hillslope by McGuire (2004). Thus, the second peak and subsequent peaks in DOC, SUVA and raw fluorescence during the December storm event were derived from at least the lower 15—20 m of the hillslope.

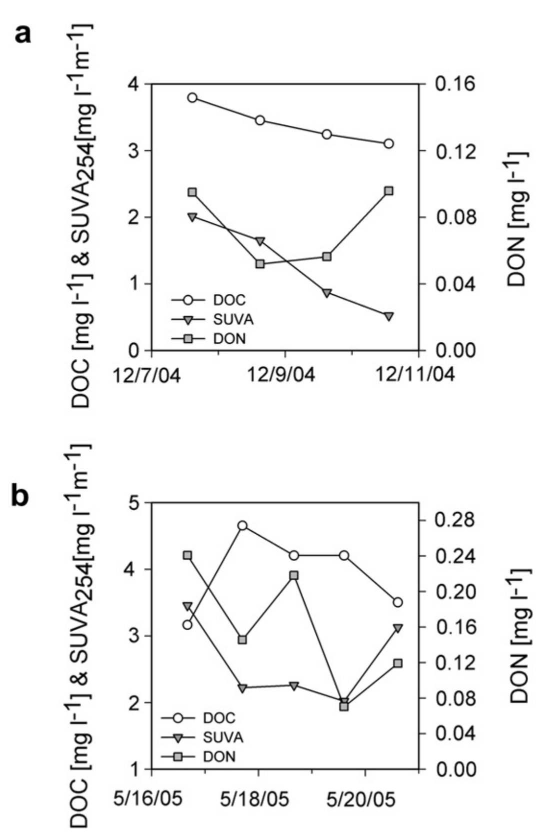

Figure 10 DOC, DON concentrations and SUVA values in (a) deep groundwater (well A01) during the December storm event, and (b) transient groundwater (well E04) during the May storm event.

The organic and shallow soil horizon were important contributors to high DOC, DON concentrations and SUVA values in lateral subsurface flow and stream water during storm events based on hydrometric data and EMMA. However, the question remains what caused the clockwise hysteresis pattern of DOC, DON and SUVA. The organic horizon showed a dilution pattern during the December and May storm events, which indicates that DOC and DON were both a limited source during storm events. Since transient groundwater and the organic horizon were strongly connected the decreasing DOC and DON concentrations at the organic horizon during storm events explain lower DOC and DON concentrations during the falling limb of the lateral subsurface flow and stream water hydrograph. Indeed, DOC and DON concentrations patterns in deep (well A01) and transient groundwater during the December and May event support this, respectively (Fig. 10). However, organic horizon SUVA values did not change much during the storm events, and SUVA remained high in transient groundwater during the storm events (Table 2). Thus, while the organic horizon dynamics explain the lower DOC and DON concentrations, it does not explain the lower observed SUVA values during the falling limb of the lateral subsurface flow and stream water hydrograph. EMMA showed maximum values of throughfall contribution which was likely a mix between throughfall and deep soil water during the falling limb of the lateral subsurface flow and stream water hydrograph. Deep soil water, deep groundwater and throughfall to a lesser extent were characterized by low SUVA values. We argue that deep groundwater/deep soil water contribution was higher during the falling limb than the rising limb of the storms at the hillslope and catchment scale and caused lower SUVA values and lower DOC and DON concentrations during the falling limb of the hydrograph (Fig. 12c). Deep groundwater is fed by mostly slow drainage of deep soil water throughout the year that likely extends much higher upslope where soil depths reach up to 8 m, than the lower 15–20 m of the hillslope that is characterized by transient groundwater dynamics. Slow drainage results in preferential retention of aromatic carbon which explains the low SUVA values of deep groundwater and lateral subsurface flow. For example during the December and May storm events average DOC and DON concentrations and SUVA values were lower in deep groundwater (well A01) than in transient groundwater (Table 3). In addition, SUVA values decreased in deep groundwater during the December storm

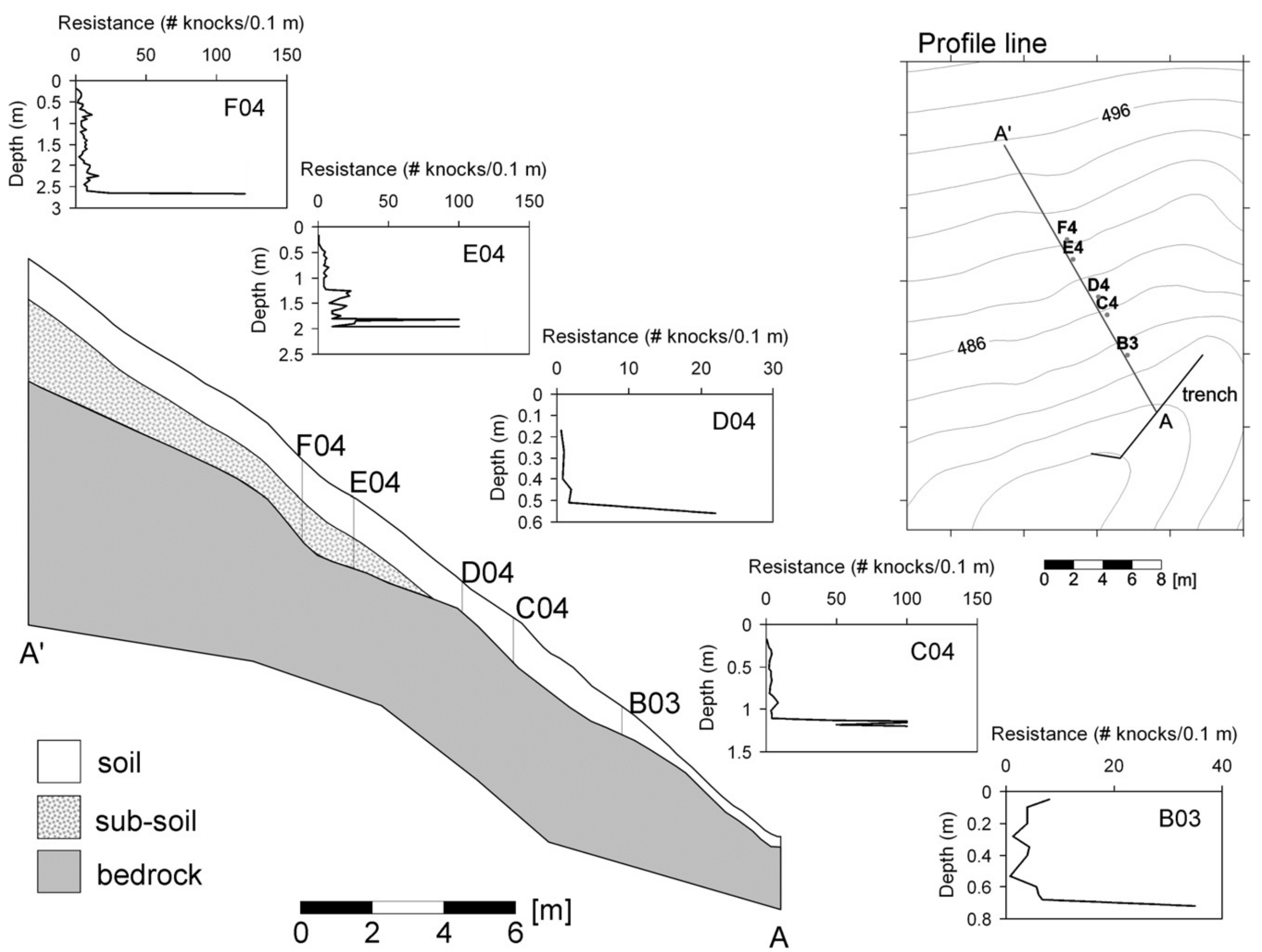

Figure 11 Cross-section of the hillslope above the trench along the profile line A–A′. Depth to bedrock and soil resistance was measured with a knocking pole. Maximum soil depth was assumed to be 1.1 m based on Ranken (1974) and Harr (1977). Depth to bedrock was defined as at least 20 knocks per 0.1 m.

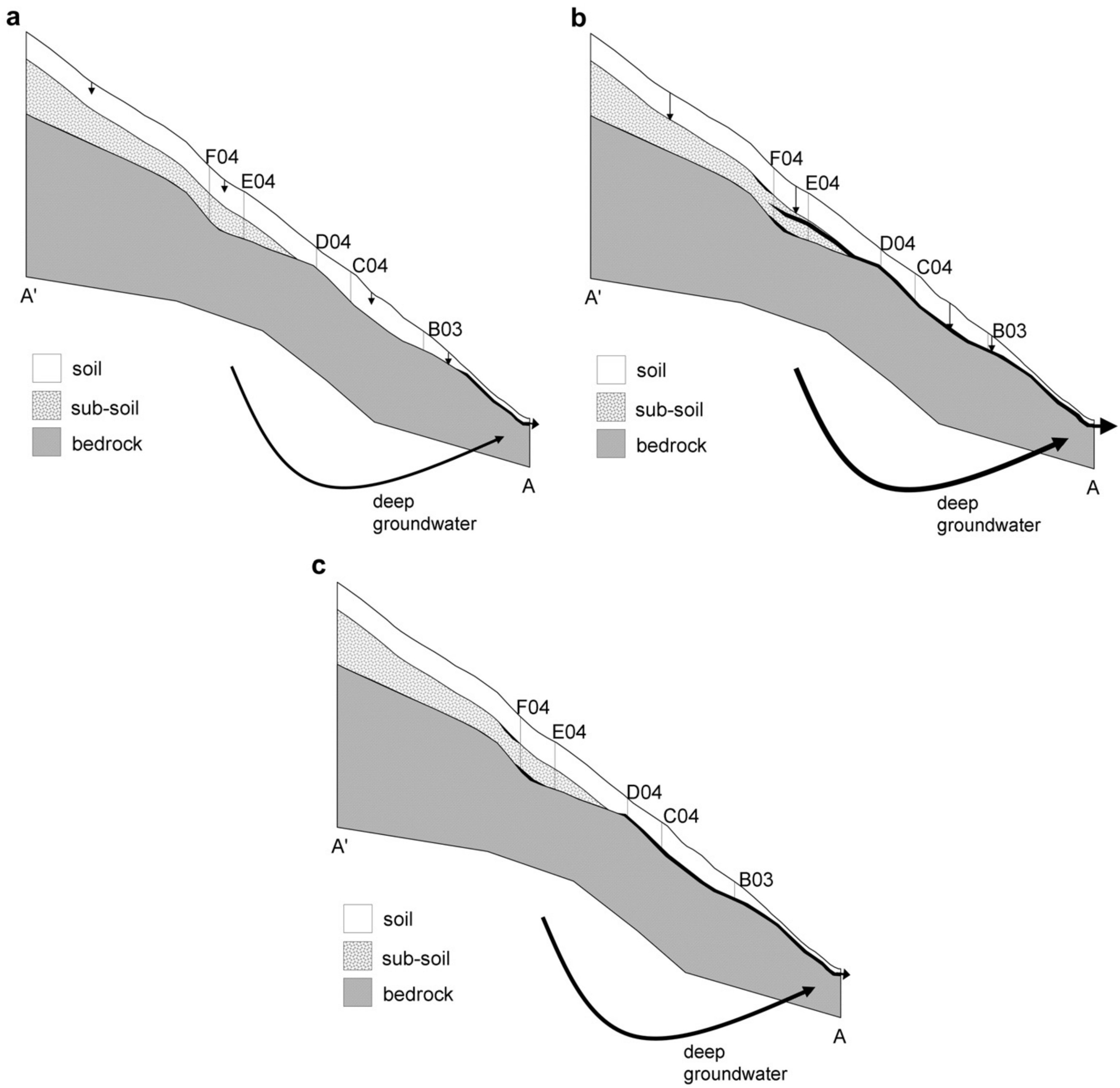

Figure 12 Conceptual model of nutrient flushing during (a) start of the storm with vertical flow that reaches the soil bedrock interface of the lower hillslope section resulting in transient groundwater at this location, and contribution of deep groundwater/deep soil water, resulting in the first rapid increase of DOC, DON, SUVA and raw fluorescence, (b) later in the storm event on the rising limb of the hydrograph vertical flow reaches greater depths and more upslope sources of transient groundwater become important, and contribution of deep groundwater/deep soil water increases, causing DOC, DON, SUVA and fluorescence to remain high, (c) during the falling limb of the hydrograph, transient groundwater contribution moves downslope and decreases while deep groundwater/deep soil water contribution remains high compared to the start of the storm, resulting in a dilution pattern of DOC, DON, SUVA and raw fluorescence. Furthermore, the finite source of DOC and DON in the organic horizon during the storm event contributes to decreasing concentrations of these solutes during the storm.

event (Fig. 10). Furthermore, comparing groundwater height dynamics of deep groundwater (A01) and transient groundwater (E04) suggests that deep groundwater contributed more during the falling limb of the December storm event. Thus, the clockwise hysteresis pattern was caused by a combination of a finite source of DOC and DON in the organic horizon and higher contribution of deep groundwater/deep soil water on the falling limb of the lateral subsurface flow and stream flow hydrograph. Flushing mechanism 2 alone could not explain our observations. The change in mixing of water sources during storm events had to be included.

Concluding remarks

We mechanistically assessed nutrient flushing at the hillslope and catchment scale during a December and May storm event. We posed the three following flushing mechanisms as hypotheses: (1) a rising water table that intersects high nutrient concentrations in the upper soil layer, (2) vertical transport of nutrients, by preferential or matrix flow through the (deeper less bio-active) soil to the soil–bedrock interface and then laterally downslope, and (3) vertical transport of nutrients and then laterally within the soil profile, and tested these hypotheses based on a combination of hydrometric and natural tracer data.

Sources and flowpaths of stream water and lateral subsurface flow were examined at the storm event scale through the use of hydrometric and natural tracer data. End-members from end-member mixing analysis were essentially grouped in the following categories: (1) organic horizon water or shallow soil water or transient groundwater, (2) deep groundwater and (3) throughfall. Detailed measurements of DOC and DON concentrations in the organic horizon showed a dilution pattern. High DOC and DON concentrations and SUVA values in the organic horizon and transient groundwater suggested vertical preferential flow and a strong connection between the organic horizon and transient groundwater. Groundwater was characterized by maximum groundwater levels of 10–15 cm. Furthermore, the unsaturated flow vector analysis showed that flow in the unsaturated zone was predominantly vertical during both storm events. Thus, hydrometric data in combination with natural tracers enabled us to reject flushing mechanism 1 and 3, and to accept flushing mechanism 2 that included a finite source of DOC and DON in the organic horizon.

However, DOM quality, expressed as SUVA was needed to further refine our conceptual model based on flushing mechanism 2. During the early response of the December and May storm events DOC and DON were mainly transported from near stream zones, while upslope sources ($\sim$20 m upslope) became more important later in the event, but still on the rising limb of the hydrograph. The organic horizon DOC and DON dilution pattern and the strong connection between the organic horizon and transient groundwater during the storms could explain the lower DOC and DON concentrations during the falling limb of the hydrograph, resulting in a clockwise hysteresis pattern. However, SUVA that also showed a clockwise hysteresis pattern did not change significantly in the organic horizon and transient groundwater during storms. We argued based on hydrometric data and SUVA that the contribution of deep groundwater/deep soil water was higher during the falling limb compared to the rising limb of the hydrograph and had a dilution effect of DOC and DON concentrations and SUVA values.

This study showed the importance of combining hydrometric and tracer data that enabled us to mechanistically assess nutrient flushing at our site and to develop a conceptual model of how DOC and DON were transported from the soil to the stream at the hillslope and catchment scale during storm events. In addition it demonstrated the value of using SUVA as a measure of DOM quality. Without SUVA we would not have been able to refine our accepted flushing mechanism hypothesis of vertical transport of nutrients by preferential flow to the soil–bedrock interface and then lateral movement downslope.

We assessed the flushing mechanism at our site during two storm events with different precipitation amounts and intensities and concluded that the same flushing mechanism occurred during these two storm events. However, extending this result to storm events of rather different magnitude or to storm events with different antecedent wetness conditions at our study site is difficult. Virtual experiments driven by field intelligence (Weiler and McDonnell, 2006) may provide a way to define the first order controls on nutrient flushing at the hillslope and catchment scale and a promising future research direction to extrapolate beyond the observed storm events at our study site. Extending the result of this study to other sites with different topography, soil types, soil depths and rainfall patterns is even more limited. Functional intercomparison of hillslopes and small catchments (Uchida et al., 2006) may yield further insights into the first order controls on hydro-biogeochemical processes at different sites and the role of site conditions in the hydro-biogeochemical response of these sites. Currently, we are investigating the possibility of such a functional intercomparison of our study site and other well studied sites.

Acknowledgements

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