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Export of dissolved organic carbon and nitrogen from Gleysol dominated catchments – the significance of water flow paths

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Abstract. In this study, we estimated whether changes in hydrological pathways during storms could explain the large temporal variations of dissolved organic carbon (DOC) and nitrogen (DON) in the runoff of three catchments: a forest and a grassland sub-catchment of 1600 m^2 delineated by trenches, and a headwater catchment of 0.7 km^2.

The average annual DOC export from the sub-catchments was 185 kg DOC ha^{-1} y^{-1} for the forest, 108 kg DOC ha^{-1} y^{-1} for the grassland and 84 kg DOC ha^{-1} y^{-1} for the headwater catchment. DON was the major form of the dissolved N in soil and stream water. DON export from all catchments was approximately 6 kg N ha^{-1} y^{-1}, which corresponded to 60% of the total N export and to 50% of the ambient wet N deposition. DOC and DON concentrations in weekly samples of stream water were positively correlated with discharge. During individual storms, concentrations and properties of DOC and DON changed drastically. In all catchments, DOC concentrations increased by 6 to 7 mg DOC l^{-1} compared to base flow, with the largest relative increment in the headwater catchment (+350%). Concentrations of DON, hydrolysable amino acids, and phenolics showed comparable increases, whereas the proportion of carbohydrates in DOC decreased at peak flow. Prediction of DOC and DON concentrations by an end-member mixing analysis (EMMA) on the base of inorganic water chemistry showed that changes in water flow paths largely explained these temporal variability. According to the EMMA, the contribution of throughfall to the runoff peaked in the initial phase of the storm, while water from the subsoil dominated during base flow only. EMMA indicated that the contribution of the DOC and DON-rich topsoil was highest in the later stages of the storm, which explained the highest DOC and DON concentrations as the hydrograph receded. Discrepancies between observed and predicted concentrations were largest for the reactive DOC compounds such as carbohydrates and phenolics. They occurred at base flow and in the initial phase of storms. This suggests that other mechanisms such as in-stream processes or a time-variant release of DOC also played an important role.

Introduction

Dissolved organic carbon is an important component of solutions in terrestrial and aquatic ecosystems through its influence on acidity and mobility of nutrients and contaminants (Eshleman & Hemond 1985; Qualls et al. 1991). DOC contains a range of organic compounds, from simple sugars to complex fulvic and humic acids (McKnight et al. 1985; McDowell & Likens 1988; Guggenberger & Zech 1993). Concentrations and composition of DOC change as a result of both biotic and abiotic processes when it moves through the ecosystem (McDowell & Likens 1988; Meyer 1990; Guggenberger & Zech 1993). Despite considerable information on various aspects of DOC cycling, little is known about the nitrogen fraction of DOC (Northup et al. 1995; Creed & Band 1998). However, DON is a dominant vehicle of N leached from forest floors (Yavitt & Fahey 1984; Qualls et al. 1991), of N transported by subsurface runoff (Hill et al. 1999), and of N exported from catchments (Hedin et al. 1995; Arheimer et al. 1996).

In catchments, DOC export during storms may account for a substantial proportion of the total DOC export (Sedell & Dahm 1990; Hinton et al. 1997). Easthouse et al. (1992) and Hinton et al. (1998) showed that the large temporal variations of DOC concentrations and properties in streams were caused by changes in water flow paths contributing to the runoff. Other studies identified in-stream processes such as throughfall onto the stream, stream channel expansion at increasing discharge, and DOC production by algae as important regulators for variations in DOC concentrations (Kaplan & Bott 1982; Tate & Meyer 1983; Mulholland & Hill 1997). To understand the mechanisms regulating DOC export from catchments, there is a need for an interdisciplinary approach, which combines (1) the identification of water flow paths through the catchment with (2) the analysis of the composition of stream water DOC as an indicator for the DOC origin (Cronan 1990; Meyer 1990; Kaplan & Newbold 1993).

In this study, we measured concentrations, fluxes, and properties of DOC and DON in the soil solution, in the runoff of small sub-catchments and in a stream draining a headwater catchment. To determine whether variations in concentrations and properties of DOC and DON during storms were consistent with variations in water flow paths, we conducted an end-member mixing analysis (EMMA) based on inorganic chemistry (Christophersen et al. 1990; Mulder et al. 1995). This way we were able to track the fate of DOC and DON through the ecosystem and to separate effects of changing water flow paths and in-catchment processes.

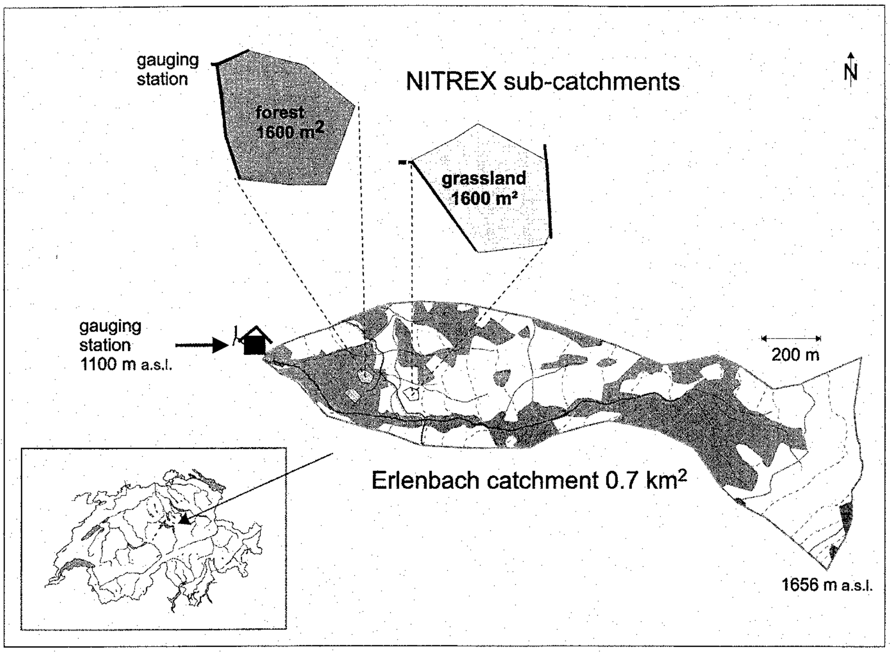

Figure 1. Experimental area of the Erlenbach headwater catchment in Switzerland and the spatial arrangement of the forest and grassland sub-catchments.

Materials and methods

Study site

The study area was located in the Alptal (47°03 N, 8°43 E), a south-north oriented valley in the Prealps of central Switzerland (Figure 1). The mean air temperature was 6 °C. The parent rock material was Flysch, consisting of alternating calcareous sandstones with argillite and bentonite shists. Major soil types were clayey Gleysols of low permeability with a water table close to the surface throughout the year.

Erlenbach headwater catchment. The Erlenbach headwater catchment covered 0.7 km^2, consisting of 40% forest (mainly *Picea abies* (L.)) and 60% grassland (Figure 1, Keller 1990). The average slope was 20% and had a western aspect. At some locations open ditches draining waterlogged soils were dug to improve slope stability. The stream channel was steep and narrow and did not have a riparian zone.

Runoff was continuously measured with a large V-notch weir. The average annual water balance (1978–1993) showed that the total amount of precipitation, 2190 mm, was partitioned into 1740 mm of runoff (80%) and 450 mm of evapotranspiration (20%) (Burch 1994). The stream water was sampled flow-proportionally and bulked every week.

Experimental sub-catchments. At mid-slope within the headwater catchment, three sub-catchments of 1600 m^2 were set up to study N cycling within the NITREX project (Schleppi et al. 1998). One grassland and two forested areas were hydrologically delineated by 80 cm deep trenches. Since the clayey subsoils had a low permeability and water levels were high throughout the year ($<$ 50 cm depth), it was assumed that deep seepage was small compared to surface and lateral subsurface runoff. This was supported by a closed water balance (Schleppi et al. 1998). In this study, we only used data from the control forest and the grassland sub-catchment.

In the forest sub-catchments, vegetation and soil formed a mosaic pattern, which was closely related to the micro-topography. *Picea abies* (L.) and *Vaccinium* sp. grew on mounds where water tables were below 40 cm depth. The soil type was an umbric Gleysol with an oxidised Bw horizon and a mor type humus layer. In depressions, the water table frequently reached the surface. The mineral soil consisted of a permanently reduced Bg horizon overlain by a muck humus (mollic Gleysol). The depressions were too wet for tree growth and the ground vegetation was dominated by *Caltha palustris*, *Petasites albus*, *Poa trivialis* and *Carex ferruginea*.

In contrast to the forest sub-catchments, the grassland sub-catchment showed no distinct micro-relief. The grassland had been a fallow for 15 years and the vegetation consisted mainly of *Poa trivialis* and *Carex ferruginea*. The soil was better drained than the depressions of the forest stand. A mollic epipedon was found on top of a thin Bw horizon and a permanently reduced Bg horizon.

Soil properties and soil solution characteristics were strongly influenced by the carbonic parent rock material and the depths of the water table (Tables 1 and 4). Redox potentials showed a vertical decrease, whereas soil pH, electrical conductivity (EC) and concentrations of base cations and iron all increased with depth.

Water tables were recorded automatically every ten minutes by an ultrasonic device in both soil types, mounds and depressions. The discharge was permanently measured with V-notch weirs at the outlet of the sub-catchments. Samples of the runoff were taken proportionally to the measured discharge and collected weekly. As in the headwater catchment, this enabled us to estimate element exports by multiplying measured concentrations and discharges.

Table 1. Selected properties of soil types.

Horizon (depth)	pH ($CaCl_2$)	Redox potential[a] [mV]	C content[b] [g kg^{-1}]	N content[b] [g kg^{-1}]	Dissolved Fe[c] [mg l^{-1}]	Texture[d] % clay/silt/sand
Mound						
LF (0–5 cm)	3.3		423	19		
A (5–10 cm)	4.6	+600 to +800	70	4.1	0.26	47/47/6
Bw1 (10–20 cm)	5.2	+400 to +700	27	1.8	0.35	
Bw2 (20–50 cm)	5.9	+200 to +600	14	0.9	0.52	46/46/5
Depression						
LF (0–2 cm)			423	19		
A (2–10 cm)	5.4	+100 to +600	156	8.5	0.17	51/45/4
BA (10–20 cm)	6.1	0 to +400	86	4.8	4.36	44/44/11
Bg (20–50 cm)	6.9	–250 to +100	16	0.8	8.4	43/42/15

[a] Measured with Pt electrodes (*n* = 20 per depth).
[b] Measured with a Carlo Erba C/N analyser.
[c] Measured in the soil solution.
[d] From Schleppi et al. (1998).

Monitoring of DOC and DON during storms

In all catchments, runoffs were sampled with a high temporal resolution during four storms in the summer 1998. Flow-proportional automatic sampling devices (ISCO 2900, Lincoln, NE, USA) were connected to the permanent discharge measurements in all catchments. The sampling rates were adjusted to collect one sample per 0.9 mm runoff.

Sampling of soil solution

Soil solution samples were collected in soil plots of 20 m^2 within the experimental site from 1996 until 1998. Three plots were located on mounds, 6 plots in wet depressions of the forest, and 3 plots in the better drained grassland. Five of the plots, one on a mound and four in depressions, received additional N inputs simultaneously added to rainfall by sprinklers. Five control plots received the equivalent amount of additional nonamended rainwater, whereas 2 plots did not receive any additional inputs. Soil solution was sampled with horizontally installed porous glass filter plates (Ø 90 mm, maximal pore radius < 16 μm) at 5 and 10 cm depths, and with suction cups at 30, 50 and 100 cm depths. To avoid a steady flow towards the suction devices, which would alter the redox conditions in their vicinity, the suction was applied only once a week, to collect a volume sufficient for the analyses. In the waterlogged depressions, a suction of 5 kPa was applied to the suction plates, and 15 kPa to the suction cups. In the mounds, suction plates were evacuated with 10 kPa, and suction cups with 30 kPa. Sampling was performed weekly and bulked every two weeks per depth and plot.

The amount of rainfall was monitored in intervals of 10 minutes on a tower above the forest and on open land close to the research site. Bulk deposition was sampled weekly on the grassland sub-catchment. Throughfall was collected on 10 plots in the forest with polyethylene (PE) funnels (Ø 15 cm). Sampling was conducted weekly and bulked every two weeks.

Sample preparation and analyses

All solution samples were collected in acid-washed PE bottles, filtered (0.45 μm, Schleicher & Schuell ME25) within the next 48 h and stored at 4 °C. For elemental analyses, sub-samples were acidified with concentrated HNO_3 to 2.5% by volume. If time until analysis exceeded 1 month, samples were stored frozen.

All samples were analysed for major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe_{tot}, Al_{tot}) by inductively-coupled plasma atomic emission spectrometry (Perkin Elmer ICPAES OPTIMA 3000, Norwalk, CT), anions (Cl^-, NO_3^-, SO_4^{2-},

$H_2PO_4^-$) by ion chromatography (DIONEX DX-120, Sunnyvale, CA), and NH_4^+ colorimetrically by automated flow injection analysis (Perkin Elmer FIAS-300).

Dissolved organic carbon (DOC) was measured with a Shimadzu TOC-500 analyser (detection limit: 0.5 mg DOC l^{-1}). Total dissolved nitrogen (TDN) was estimated by alkaline persulfate digestion converting all nitrogen to nitrate (Solorzano & Sharp 1980). In contrast to the original procedure, the autoclave bottles were tightly closed. This improved the reproducibility of the method considerably. Nitrate was then measured photometrically at 210 nm with a spectrophotometer (model UV-160 Shimadzu, Inc., Kyoto, Japan). DON was obtained by substracting the concentration of inorganic species from TDN. Recovery of the standards glycine, purine, pyridine and humic acid (Fluka, Buchs, Switzerland) was between 95 and 101%. The coefficient of variation of the TDN measurements for a reference soil solution (n = 10) was below 3%. However, the detection limit for DON depended on the background of inorganic N. In bulk deposition and stream water during snowmelt, both typically with high inorganic N and low DON concentrations, the detection limit was about 0.1 mg l^{-1}. In the soil solutions of the subsoil, which contained no mineral N, DON measurements were reproducible even at concentrations of 0.05 mg N l^{-1}.

Dissolved organic matter characterisation. To characterise DOC, soil and stream water samples were fractionated into hydrophilic and hydrophobic DOC by the use of Amberlite XAD-8 resin columns (Aiken & Leenheer 1993). The DOC sorbing at pH 2 on XAD-8 resin is operationally defined to be hydrophobic, while hydrophilic DOC passes through the columns. The molar UV absorptivity of DOC at 285 nm was measured in 1 cm quartz window cuvettes with a double beam Shimadzu UV-160 spectrophotometer. Hydrolysable amino-acids were analysed according to a modified procedure of Allen (1981) (Michalzik, pers. comm.). 1.5 ml of sample were hydrolysed with 0.6 ml of 32% NaOH for 2 h. After neutralization, amino acids were measured colorimetrically at 570 nm using a ninhydrin reaction with cystein and glycin as standards. Phenol concentrations were measured according to Swaine and Hillis (1959) with Folin-Denis reaction. Hydrolysable carbohydrate content was determined by the phenol-sulfuric acid method (Chaplin 1994), using a 5% phenol solution and glucose as a standard. If concentrations of hydrolysable amino-acids, phenols, and hydrolysable carbohydrates were below the detection limit, samples were concentrated 3 to 5 times by freeze-drying to achieve accurate measurements. The validity of the concentration step was tested by DOC measurements and by conducting the same procedure for standards and blanks.

End-member mixing analysis (EMMA)

To determine whether variations DOC and DON concentrations and properties during storms were consistent with changes in hydrologic flow paths, we conducted an end-member mixing analysis (EMMA) (Christophersen et al. 1990; Mulder et al. 1995). EMMA allows the identification of the contribution of observed water sources or flow paths (the so called end-members) to runoff based upon their water chemistry using a least-square regression technique. In order to be used successfully in EMMA, solutes must (1) differ significantly between end-members, and (2) mix conservatively. In our case, the variables used for EMMA were electrical conductivity (EC), Ca^{2+}, SO_4^{2+}, and Cl^-. Potential end-members are those water sources which reproduce the concentrations of selected solutes in runoff water, when mixed in appropriate proportions under various hydrological conditions (Mulder et al. 1995).

The relative contribution of the end-members to the runoff was estimated by solving the following set of simultaneous equations:

$$f_1 c_{i,1} + f_2 c_{i,2} + f_3 c_{i,3} = c_{i,r}, \tag{1}$$

$$f_1 + f_2 + f_3 = 1, \tag{2}$$

where c_i is the concentration of the variables i = (Ca^{2+}, Cl^{-1}, SO_4^{2-}, EC), the subscripts 1, 2, and 3 refer to the end-members (flow paths), r refers to runoff sample; and f refers to the runoff fraction contributed by the end-members. Solute concentrations were normalised relative to their standard deviations during the storm event. Calculations were performed with the non-negative least square fitting procedure of MATLAB. To evaluate if uncertainty in the inorganic composition of the end-members caused errors in the estimates of flow path contributions, we performed another EMMA based on variation in the measurements (± standard deviation). The contributions of end-members changed by less than 10%. Thus, the results of our mixing analyses appeared to be robust.

Results

DOC and DON in throughfall and in the soil

The DOC and DON concentrations and characteristics showed a distinct change from throughfall to the soil solution (Table 2). In the precipitation, DOC and DON concentrations were low. They increased in the throughfall and in the topsoil, then decreased across the B horizon indicating retention in

Table 2. Concentrations and characteristics of DOC in precipitation, throughfall, and soil solution. Means and standard deviations.

	DOC [mg l^{-1}]	Carbohydrates [% of DOC]	Phenolics [% of DOC]	Hydrophobic DOC [% of DOC]	Molar UV absorptivity [L cm^{-1} mol C^{-1}]	DON [mg l^{-1}]	Amino acids [% of DON]
Precipitation	1.6	< d.l.	< d.l.	n.d.	n.d.	<0.10	n.d.
Throughfall	9.6	21 ± 4	15.6 ± 4	n.d	120 ± 15	0.44 ± 0.15	83 ± 5
Mound (3 plots)							
Mor layer (5 cm)	33.1 ± 5.2	9.3 ± 0.4	9.9 ± 0.8	71 ± 4	450 ± 52	0.96 ± 0.10	59 ± 7
Bw horizon (30 cm)	9.1 ± 2.5	4.8 ± 0.9	3.5 ± 0.9	60 ± 3	240 ± 39	0.31 ± 0.10	25 ± 8
Depression (9 plots)							
A horizon (5 cm)	15.3 ± 4.8	9.2 ± 0.9	7.7 ± 1.0	65 ± 4	370 ± 42	0.63 ± 0.13	45 ± 9
Bg horizon (30 cm)	9.7 ± 2.8	4.6 ± 1.0	3.9 ± 0.4	60 ± 3	230 ± 32	0.35 ± 0.12	27 ± 6
Cv horizon (100 cm)	2.1 ± 0.5	4.2 ± 0.4	2.1 ± 0.3	n.d.	90 ± 18	0.1 ± 0.03	20 ± 3

d.l. detection limit.
n.d. not determined.

the mineral soil. However, DOC concentrations of the reduced mineral soil in the depressions, averaging 10 mg l^{-1}, were higher than concentrations found in Podzols or Cambisols, which are usually lower than 2 mg l^{-1} (Guggenberger & Zech 1993). This suggests that the retention of DOC is low under reducing conditions. Sorption of DOC is low, either because of a high pH due to reduction decreasing anion exchange sites or because of the reductive dissolution of Fe-oxides as indicated by high Fe concentrations and low redox potentials in the subsoil (Hagedorn et al. 2000). The pH of the mineral soil solution was high (7.5–8.5), but was not significantly correlated with DOC concentrations. In contrast, dissolved Fe showed a significant correlation with DOC and DON concentrations in the subsoil (r^2 = 0.83*** for DOC and r^2 = 0.72*** for DON, n = 30), suggesting that the reductive dissolution of Fe-oxides was the main reason for the low sorption of DOC and DON in the mineral soil.

The proportions of total DOC present as carbohydrates and phenolics were highest in the throughfall (Table 2), while the percentage of hydrophobic DOC and the molar UV absorptivity at 285 nm showed their maximum in the soil solution at 5 cm depth. The molar UV absorptivity is an easily measurable spectroscopic indicator for aromaticity and molecular weight (Chin et al. 1994; McKnight et al. 1997). Across the mineral soil, the relative proportion in DOC of carbohydrates, phenolics, and hydrophobic DOC, and the molar UV absorptivity decreased, which demonstrates that the mineral act as a chromatographic system with the preferential retention of reactive DOC compounds.

DON was the dominant form of the total dissolved N (TDN). Concentrations of NH_4^+ and NO_3^- in the forest floor soil solution were low ($<$ 0.2 mg NH_4^+-N l^{-1}; and $<$ 1 mg NO_3^--N l^{-1}) and decreased from throughfall to the Bg horizon, indicating denitrification as measured by Mohn (1999), or N-immobilisation. The proportion of DON in TDN increased with depth. Below 30 cm depth, all of the TDN was found in the organic form. A large fraction of DON consisted of hydrolysable amino acids. Their proportion of DON decreased from 80% in the throughfall to 20% in the subsoil, indicating a substantial alteration of DON across the soil.

DOC and DON export from catchments

Concentrations and properties of DOC in the runoff were similar to those of the soil solution. Highest DOC concentrations occurred in the runoff from the forest catchment followed by the grassland and the headwater catchment (Figure 5). The runoff from the forested catchment also had the highest phenol concentrations, the largest DOC/DON ratio and the highest molar UV-absorptivity, all of which reflects the properties of DOC mobilised in the

Table 3. Annual fluxes of water, NH_4^+, NO_3^-, DON, and DOC in 1997.

	Water [mm y^{-1}]	NH_4^+-N	NO_3^--N kg ha^{-1} y^{-1}	DON	DOC
Bulk deposition	2036	5.6	5.3	<1	20
Throughfall	1726	8.1	8.6	3.6	71
Forest catchment	1440	0.1	2.8	5.7	185
Grassland catchment	1487	0.2	2.7	6.2	108
Headwater catchment	1740	0.05	3.8	5.5	84

throughfall and the forest floor. This is a first indication that water from the surface was a significant contributor to the runoff.

The average annual DOC export was higher in the sub-catchments than in the headwater catchment (Table 3). Possible reasons for this could be either sorption along pathways from the sub-catchments to the stream, to different water flow paths contributing to the runoff or to in-stream processes as discussed later. Annual DOC export from these catchments were higher than those from upland ecosystems in North Carolina, U.S.A. (4.3 to 25 kg DOC ha^{-1} y^{-1}; Tate & Meyer 1983) and were within the range of exports measured in peatland ecosystems (80 to 400 kg ha^{-1} y^{-1}; McKnight et al. 1985; Urban et al. 1989). However, DOC concentrations in the runoff of the headwater catchment were lower than those in peatland streams, suggesting that the high export from our catchments was partly due to the large discharge (1700 mm) as a consequence of 2000 mm annual rainfall.

As in the soil solution, DON was the major component of N exported from the catchments (Table 3). It accounted for approximately 50% of the ambient wet N deposition and 60% of the TDN export. In contrast to NO_3^- concentrations, which were substantially higher in the winter than in the summer, the seasonal variations of DON were low (data not shown). The ratio of DOC/DON decreased from the soil solution to the runoff of the sub-catchments and finally to the headwater catchment, suggesting that the ecosystem is less retentive for DON than for DOC. This was probably due to the preferential sorption of hydrophobic DOC (Table 2) and of high molecular weight and aromatic DOC as indicated by a decrease of the molar UV absorptivity. These DOC compounds have lower nitrogen contents than hydrophilic and low molecular DOC (McKnight et al. 1985; Qualls et al. 1991).

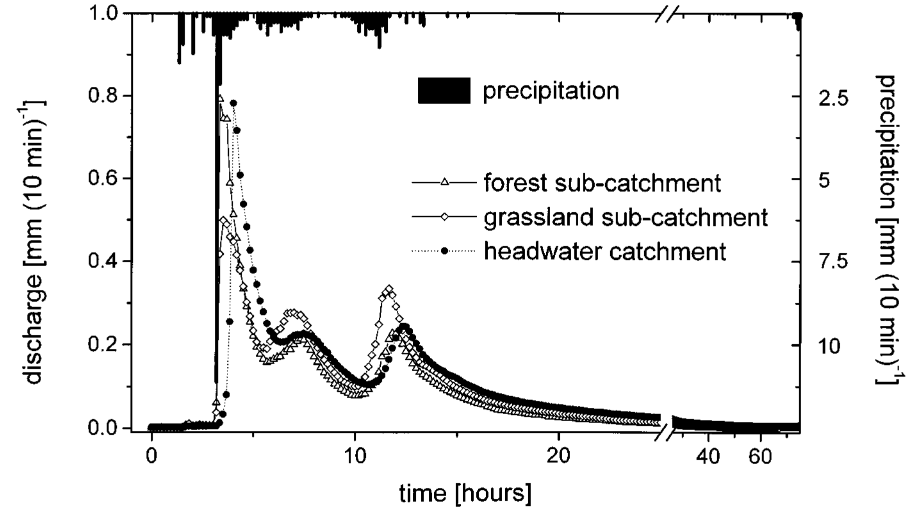

Figure 2. Response of discharge of all catchments to the storm event of 13–16 July 1998.

Runoff generation and end-member mixing analysis during storms

In all catchments, discharge responded rapidly to storm events (Figure 2), which points to a fast water movement through the soil system and/or surface runoff. The runoff peaked within minutes in the sub-catchments and about 30 minutes later in the headwater catchment. Peak discharge of the headwater catchment was as high as that of the sub-catchments, which was probably due to a network of drainage trenches, which rapidly routed the runoff from waterlogged areas to the stream.

We selected the following three end-members: (1) throughfall, (2) the water from the topsoil, and (3) the water from the subsoil (Figure 3). Their water chemistry is shown in Table 4. The choice of throughfall as one end-member violates the assumption of EMMA that the chemistry of end-members are constant in time (Chistophersen et al. 1990), because element concentrations in throughfall change drastically (Burch et al. 1996). However, only throughfall could explain the runoff chemistry at peak discharge with high Cl^- and low Ca^{2+} concentrations (Figure 3). Additional tracer experiments gave evidence for the rapid and preferential transport of throughfall into drainage trenches (Feyen 1999). Figure 2 demonstrates that the storm was short compared to the subsequent runoff. More than 75% of the rain fell within the first 20 minutes. This allowed us to consider throughfall as a short pulse with constant solute concentrations. The subsoil end-member was constrained to explain runoff chemistry during base flow. Since the headwater catchment had higher concentrations of base cations in the base flow than the

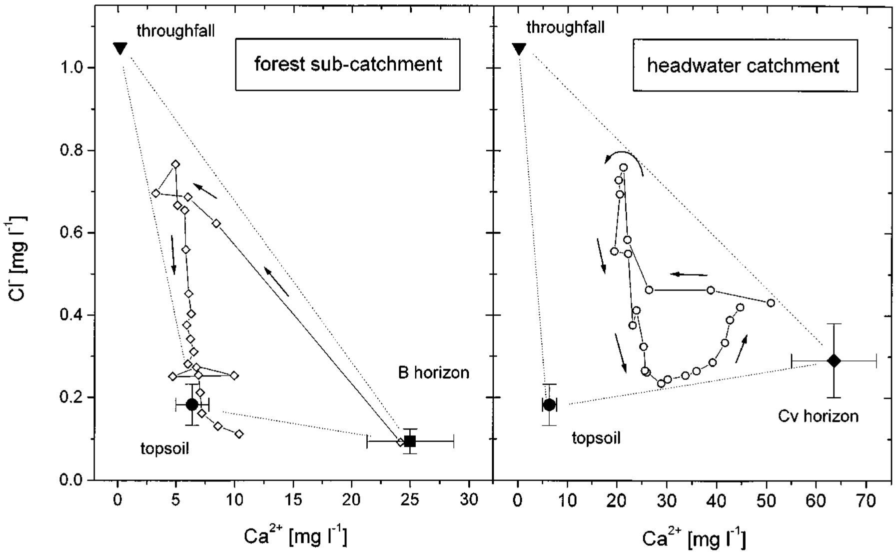

Figure 3. End-member mixing diagram for the forest and the headwater catchment showing concentrations of Ca^{2+} and Cl^- in the runoff and in the proposed water flow paths (water sources) contributing to the runoff. Error bars represent standard deviations. Arrows indicate the progression of time.

sub-catchments (Figure 3), we selected different subsoil end-members for the catchments: the Bg horizon in both sub-catchments and the Cv horizon in the headwater catchment.

The variance of explanation was good for the input parameters used for the EMMA (Table 5), suggesting a conservative mixing of the chosen solutes and a correct selection of end-members. To check the EMMA predictions against independent information, the estimated subsoil contributions were compared with measured water tables. They were all significantly negatively correlated ($r^2 = -0.88$***, $r^2 = -0.82$***, $r^2 = -0.72$*** for the grassland, headwater, and forest catchment, respectively). This strongly supports the findings of EMMA.

EMMA suggested that the largest average contribution of all end-members came from the topsoil water (50%), particularly at later stages of the event (Figure 4). Water from the subsoil contributed substantially only to base flow. Its proportion was largest in the headwater catchment. The estimated proportions of throughfall at peak discharge were approximately 61% in the forest sub-catchment, 57% headwater catchment, and 42% in the grassland sub-catchment (Figure 4). These proportions declined rapidly within the next hours.

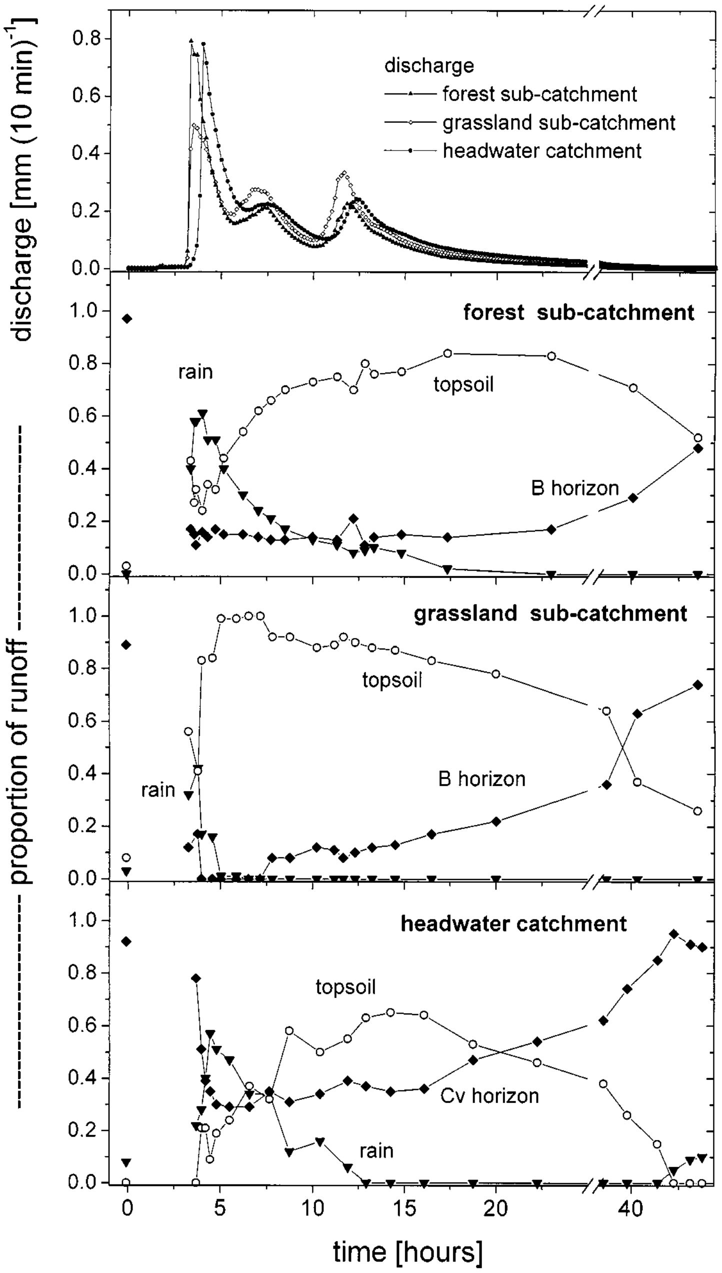

Figure 4. Estimated contribution of water flow paths (end-members) to the catchments runoff during the storm of 13–16 July 1998.

Table 4. Chemical composition of end-members. Mean concentrations and standard deviations of 30 sampling dates.

	Ca^{2+} [mg l^{-1}]	Cl^{-} [mg l^{-1}]	SO_4^{2-} [mg l^{-1}]	EC [μS cm^{-1}]
Throughfall[a]	0.165	1.06	2.52	12
Forest catchment				
Topsoil[b] (5 cm)	6.4 (1.6)	0.22 (0.05)	2.13 (0.68)	37 (9)
B horizon (30 cm)	24.9 (2.8)	0.09 (0.03)	1.07 (0.43)	118 (23)
Grassland catchment				
Topsoil (5 cm)	7.2 (2.1)	0.22 (0.03)	1.41 (0.64)	42 (8.3)
B horizon (30 cm)	30.8 (3.7)	0.10 (0.03)	1.70 (0.39)	132 (18)
Headwater catchment				
Topsoil [c] (5 cm)	6.8 (1.9)	0.22 (0.04)	1.76 (0.64)	39 (9)
Cv horizon (100 cm)	64 (8.5)	0.29 (0.09)	12.5 (3.1)	300 (41)

[a] Concentrations of the storm; 13.07.1998.
[b] Mean of mound ($n = 3$) and depression ($n = 9$).
[c] Mean of forest and grassland catchment topsoil.

Table 5. Prediction of nutrient, DOC, and DON concentrations by the end-member mixing analysis. EMMA was based on electrical conductivity (EC) and concentrations of Ca^{2+}, Cl^{-}, and SO_4^{2-}. Coefficients of determination (r^2) of measured and predicted concentrations ($n = 22$).

	Ca^{2+}	Cl^{-}	SO_4^{2-}	EC	DOC	phenolics	UV absorp.	DON	NO_3^{-}
Forest sub-catchment	0.91	1.00	1.00	0.93	0.32	0.29	0.56	n.s.	0.83
Grassland sub-catchment	0.95	0.91	0.85	0.95	0.75	0.74	0.56	0.65	0.62
Headwater catchment[a]	0.95	0.95	0.90	0.97	0.74	0.85	0.65	0.58	0.52

[a] Without the first sample after the rainfall.

DOC and DON during storms

In weekly samples of stream water, DOC and DON concentrations were positively correlated with discharge ($r^2 = 0.48^{***}$ and $r^2 = 0.51^{***}$, $n = 74$). During all of the 4 monitored runoff events, concentrations of DOC increased compared to base flow in all catchments (Figure 5). This increment reached up to 6–7 mg DOC l^{-1} for all catchments with the highest relative increase in the headwater catchment (+350%). Concentrations of DOC were higher on the descending than on the rising limb of the hydrograph of all catchments, resulting in counterclockwise hysteresis.

As with concentrations, the properties of DOC varied considerably during runoff events (Figure 5). The molar absorptivity at 285 nm, an indicator for aromaticity and molecular weight, first decreased. Then, the absorptivity increased and reached its highest values on the descending limb. The percentage of hydrolysable carbohydrates in DOC was relatively constant in time during high flow (Figure 5). In the headwater catchment, however, carbohydrates increased substantially when discharge dropped back to base flow.

DON concentrations were also considerably higher at high than at low flow (Figure 6). Compared to base flow, DON concentrations increased by 250% in the grassland, by 250% in the forest, and by 1000% in the headwater catchment. The DOC/DON was highest in the later stages of the event. Alkaline hydrolysable amino-acids followed the temporal variations of DON (Figure 6). During storms, however, the proportion of hydrolysable amino acids at DON increased from approximately 60% at base flow up to 80%.

Nitrate concentrations showed a sharp rise immediately at the onset of the event, followed by rapid exponential decline (Figure 6). The first stream water samples after the rain had 5 to 10 time higher NO_3^- concentrations than in the soil solution at 5 cm depth, suggesting that throughfall, which had the highest NO_3^- concentrations in the ecosystem contributed substantially to the runoff. This supports the selection of throughfall as one end-member in the EMMA.

Discussion

Changes in runoff components – an explanation for DOC variations?

DOC and DON concentrations were predicted solely on the basis of the estimated contribution of the three end-members. In the grassland and the headwater catchment, predicted and observed concentrations of dissolved organic compounds were closely correlated (Table 5), suggesting that changes in water flow paths were important determinants for catchment DOC and DON concentrations and properties. For instance, EMMA indicated that the contribution of the DOC and DON-rich topsoil peaked in the later stages of the storm, which explained well the highest DOC and DON concentrations, the highest molar UV absorptivity and the higher proportion of amino-acids in DON as the hydrograph receded (Figure 5). This is consistent with the conceptual model of Hornberger et al. (1994), in which DOC peaks in runoff

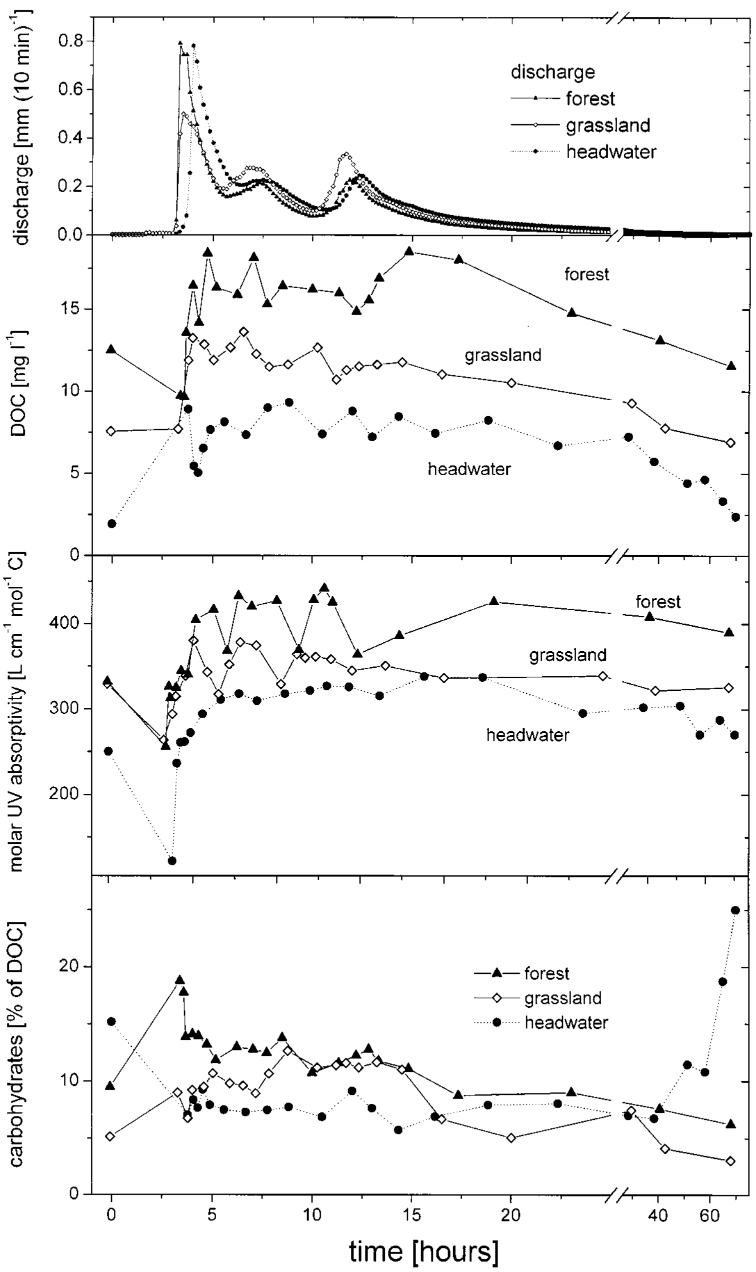

Figure 5. Discharge, DOC concentrations, molar UV absorptivity, and proportions of carbohydrates in the runoff from all catchments during the storm of 13–16 July 1998. Samples were taken proportional to the runoff.

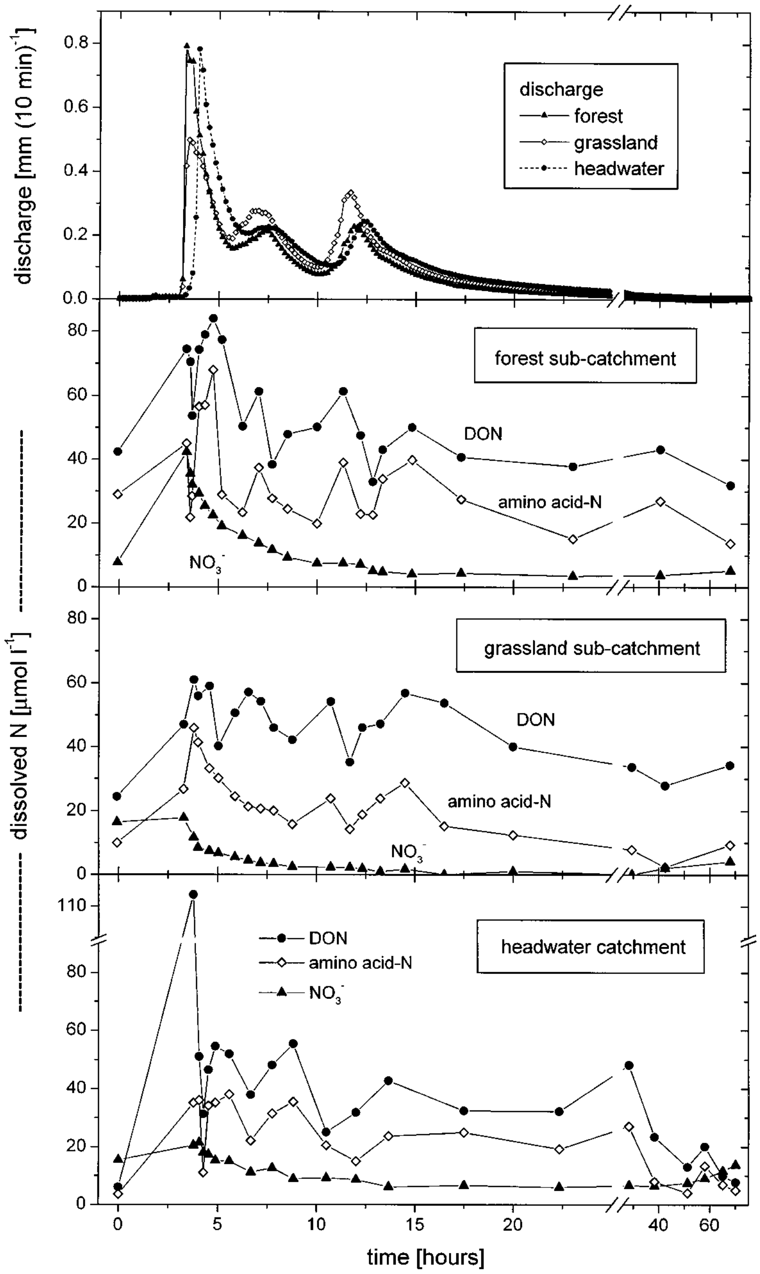

Figure 6. Discharge, and concentrations of DON, hydrolysable amino acid-N, and NO_3^- in the runoff from all catchments during the storm of 13–16 July 1998. Samples were taken proportional to the runoff.

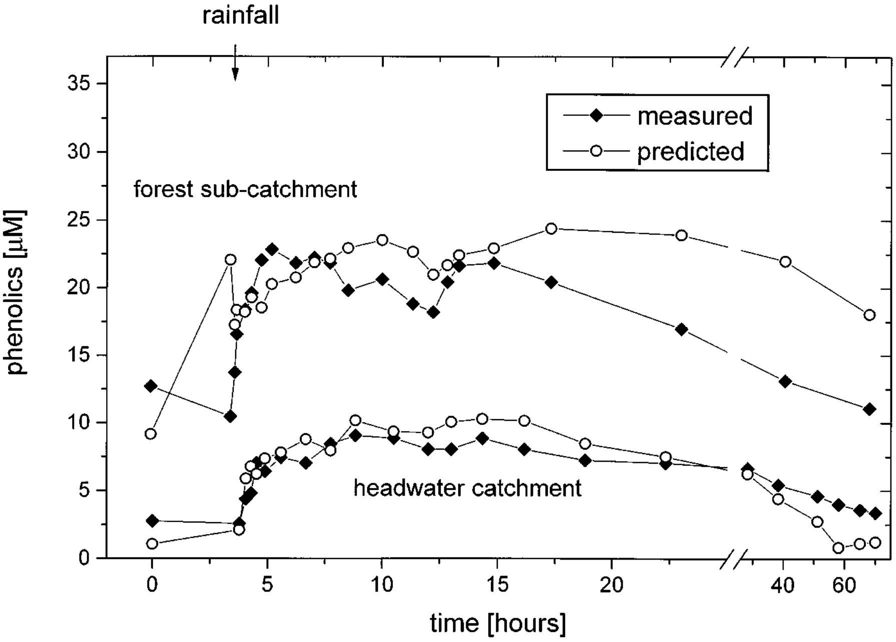

Figure 7. Prediction of phenol concentrations based on estimated water flow paths. Comparison with measured concentrations in the forest and the headwater catchment.

are caused by the flushing of DOC from the upper soil into the stream by a rising water table. In contrast to our results, however, Hornberger et al. (1994) found that highest DOC occurred during rising discharge of the Snake River, Colorado, U.S.A. This was probably due to the different runoff dynamics of the catchments. The runoff of our catchments responded within minutes to rainfalls and EMMA indicated a substantial contribution of throughfall, which was low in DOC. In contrast, discharge of Snake River peaked days later (Hornberger et al. 1994).

EMMA gave a reasonable explanation for the larger relative increases in DOC and DON during storms in the headwater catchment as compared to the sub-catchments. The end-members of the headwater catchment covered a broader range of DOC and DON concentrations than the sub-catchments, which led to the greater temporal variations in DOC and DON.

There were, however, discrepancies between predicted and observed concentration (Table 5). For instance, maximum concentrations of phenolics were well predicted (differences within 7%), but the temporal patterns of observed and predicted concentrations were different (Figure 7).

To estimate, how much of the variation in runoff concentration can be explained by variations in the water flow paths, we calculated ratios of observed and predicted concentrations (Figure 8). Ratios near 1.0 suggest that changes in water flow paths largely explained runoff chemistry, whereas ratios substantially different from 1.0 suggest that other processes were important determinants.

Except for the first sample of the headwater catchment, the temporal variations of the observed/predicted ratio were low for DOC and DON concentrations and the molar UV absorptivity (Figure 8). In contrast, the observed/predicted ratios for carbohydrates, amino acids and NO_3^-, all reactive compounds, were large and showed a distinct temporal pattern. Ratios were generally more variable and above 1.0 in the initial phase of the storm (up to 5 for carbohydrates; Figure 8). In the later stages of the storm, the ratios dropped below 1.0 and increased again at base flow. One reason for the larger variations in the observed/predicted ratios of reactive compounds than in those of total DOC could be the accumulation of DOC during dry periods and the subsequent rapid depletion of this mobilisable DOC (Grieve 1991; Christ & David 1996). An explanation for the pronounced discrepancies in the forest catchment (Table 5) could be the inadequate description of the runoff as a mixture of 3 components. This did not consider a varying contribution from the two topsoil types, muck in the depression and mor on the mounds which showed distinctly different DOC concentrations and properties (Table 2).

In-stream processes?

Another reason for the discrepancies between observed and predicted DOC and DON concentrations may be found in in-stream processes. In-stream processes were indicated by the comparison of the headwater catchment with the sub-catchments, which had no streambed. The carbohydrates in DOC during base flow increased more in the headwater catchment than in the sub-catchments (Figure 5). This increase suggests in-stream production and/or alteration of DOC (Kaplan & Bott 1982; Meyer 1990). Furthermore, in the headwater catchment, DOC and DON concentrations showed two peaks, one directly after the rainfall and one on the descending limb of the hydrograph (Figures 5 and 6). In the sub-catchments, DOC and DON concentrations did not display the initial DOC and DON peaks. The characteristics of the initially exported DOC by the stream was substantially different from soil solution and throughfall samples. It had a very narrow DOC/DON ratio of 6, a low percentage of carbohydrates in DOC (7%) and of phenolics in DOC (2%), and a very low molar UV absorptivity, all of which suggests, that the major source of this stream DOC was not soil or throughfall. This initially exported DOC was probably rather DOC from previously isolated pools of the streambed (Tate & Meyer 1983; Meyer 1990) or DOC from the saturated

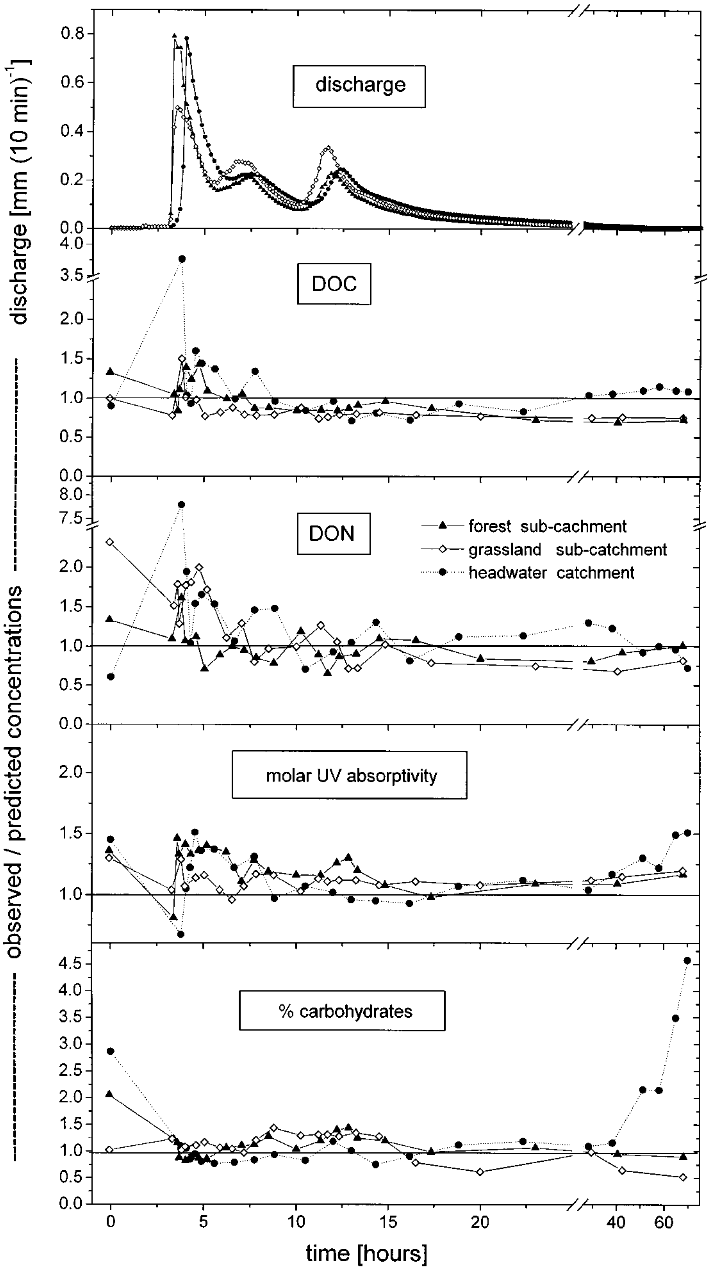

Figure 8. Ratios of observed and predicted concentrations of DOC and DON, of the molar UV absorptivity, and the proportion of carbohydrates during the storm of 13–16 July 1998. Predictions were performed on the basis of estimated contributions of the individual water flow paths.

zone below the stream bottom, which is characterised by a low molar UV absorptivity (Schindler & Krabbenhoft 1998).

Conclusion

DON was the dominant form of dissolved N in the soil water and the major N component exported from the catchments. Concentrations of DOC and DON in weekly samples of stream water were positively correlated with discharge. During individual storms, concentrations and properties of DOC and DON changed drastically. DOC and DON concentrations increased with increasing discharge, reaching their maximum concentrations on the descending limb of the hydrograph. Concentrations of hydrolysable amino acids and phenolics showed comparable increases, whereas the proportion of carbohydrates in DOC decreased at peak flow. End-member mixing analysis based upon inorganic chemistry showed that water flow paths changed substantially during storms. The prediction of DOC and DON concentrations and properties by EMMA indicated that a large part of the variation in DOC and DON was explained by changes in hydrologic pathways. For instance, the highest DOC and DON concentrations in the later stages of the storm were due to the largest contribution of the DOC and DON-rich topsoil water. Discrepancies between observed and predicted concentrations occurred at base flow and in the initial phase of storms. They were largest for the relative reactive DOC compounds, carbohydrates and phenolics. These discrepancies suggest that other mechanisms, such as in-stream processes or a time-variant release of DOC also played an important role.

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