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Discussions

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Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements

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Abstract

Concentrations of dissolved organic carbon (DOC) in runoff from catchments are often subject to substantial short term variations. The aim of this study was to identify the spatial sources of DOC and the causes for short term variations in runoff from a forested catchment. Furthermore, we investigated the implication of short term variations for the calculation of annual runoff fluxes. High frequency measurements (30 min intervals) of DOC in runoff, of discharge and groundwater table were conducted for one year in the 4.2 km^2 forested Lehstenbach catchment, Germany. Riparian wetland soils represent about 30 % of the catchment area. The quality of DOC was investigated by three dimensional fluorescence excitation-emission matrices in samples taken from runoff, deep groundwater and shallow groundwater from the riparian wetland soils. The concentrations of DOC in runoff were highly variable at an hourly to daily time scale, ranging from 2.6 mg l^{-1} to 34 mg l^{-1} with an annual average of 9.2 mg l^{-1}. The concentrations were positively related to discharge, with a pronounced, counter clockwise hysteresis. Relations of DOC to discharge were steeper in the summer/fall than in the winter/spring season. Dynamics of groundwater table, discharge, DOC concentrations and DOC quality parameters indicated that DOC in runoff originated mainly from the riparian wetland soils, both under low and high flow conditions. The annual export of DOC from the catchment was 84 kg C ha^{-1} yr^{-1} when calculated from the high frequency measurements. If the annual export was calculated by simulated random fortnightly samplings, the range was 47 to 124 kg C ha^{-1} yr^{-1}. Calculations of DOC export fluxes might result in significant errors when based on infrequent (e.g. fortnightly) sampling intervals. Future changes in the precipitation and discharge patterns will influence the DOC dynamics in this catchment, with largest effects in the summer season.

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1 Introduction

The importance of dissolved organic carbon (DOC) for the functioning of terrestrial and aquatic ecosystems is widely known. DOC plays an important role in the C cycle, in the acid-base chemistry of soils and surface waters, it influences nutrient cycling, and affects the mobility and availability of metals and contaminants (Bolan et al., 2011; Kalbitz et al., 2000). Although numerous studies on DOC in soils and catchments have been published in the last decade, sources and sinks of DOC in soils and the transition of DOC from terrestrial to the aquatic ecosystems are still poorly understood in their quantitative response to driving factors, like climatic conditions, flow paths, vegetation and soil conditions.

DOC in runoff from forested catchments originates mostly from soil organic matter (Degens et al., 1991). Depending on precipitation, flow paths and catchment characteristics, different soil types and soil horizons from different parts of the catchment may feed the runoff with DOC, resulting in temporal variations of DOC quality and quantity in runoff. In general, the DOC export from forested catchments in Skandinavia was found to be positively related to the area of wetland soils (Laudon et al., 2011). To identify the spatial sources of DOC in runoff, quality parameters of DOC can be used, like fluorescence spectroscopy (Ishii and Boyer, 2012; Fellman et al., 2009; Austnes et al., 2010). This is a highly sensitive method to determine changes in DOC quality and can be applied to a large number of samples.

DOC concentrations in runoff from forested catchments are often subjected to temporal variations of one order of magnitude at time scales ranging from hours to seasons. This can be attributed to the large differences in DOC concentrations in the two dominant flow components contributing to individual discharge events, i.e. groundwater (baseflow) versus shallow groundwater and surface runoff from riparian wetland soils (high flow) (McGlynn and McDonnell, 2003; Hood et al., 2006). Ludwig et al. (1996) related the DOC fluxes to drainage intensity, basin slope, and the amount of carbon stored in soils. Interestingly, they found a negative relationship between basin slope and DOC concentrations as steeper slopes may cause a restricted contact between soil and water, and thus lead to lower DOC concentrations in runoff.

Hysteretic relationships between discharge and solute concentrations have been observed by inter alia Hornberger et al. (1994), Evans and Davies (1998), Butturini et al. (2006), Raymond and Saiers (2010), Pellerin et al. (2012), and Jeong et al. (2012). Evans and Davies (1998) proposed the hysteretic concentration/discharge relationship for the analysis of episode hydrochemistry. Using a three component model, they categorized the concentration/discharge relationships into clockwise and counter-clockwise hysteresis with a positive, negative or no trend. This categorization allows the distinction of flow components that are drained during the rising or falling limbs of the hydrograph. Generally, high concentrations during the rising limb of the hydrograph lead to clockwise hysteresis, while high concentrations during the falling limb imply counter-clockwise hysteresis. Clockwise hysteretic patterns have been attributed to early flushing and depletion effects as well as changes in the connectivity of riparian or hillslope flowpaths (Hornberger et al., 1994; Boyer et al., 2000; Ågren et al., 2008; Pacific et al., 2010; McGlynn and McDonnell, 2003).

Only recently, field-deployable automated devices became available to analyze physico-chemical parameters of runoff in high temporal resolution. From such measurements, new insights in the hydrological, chemical and biological controls of runoff chemistry might emerge (Kirchner et al., 2004). Using high frequency measurements of DOC quality parameters, (Spencer et al., 2007) found diurnal patterns which would not have been revealed by discrete sampling strategies, whereas Jeong et al. (2012), for a catchment in monsoonal climate, showed up to 23 % of the annual exports of DOC and 48 % of POC being realized in only a few discrete events.

The DOC export fluxes with runoff might represent a substantial contribution to the net C budget of ecosystems (Kindler et al., 2011). If the DOC concentration varies with discharge, the flux calculation is subjected to potential errors since discharge is in most cases recorded permanently, while DOC concentrations are often measured infrequently in larger time intervals (like fortnightly) with interpolation procedures needed for the calculation of annual fluxes (e.g. Method 5, Walling and Webb, 1985). It is a matter of debate whether the period-weighted interpolation method leads to an underestimation of annual DOC fluxes as the majority of DOC is exported during storm events in a rather short time period which are likely missed by the interpolation method (Clark et al., 2007). The risk of miscalculation depends on catchment properties and the discharge/concentrations relations. Koehler et al. (2009) reported the annual DOC flux with runoff from 30 min measurements to be similar to calculations based on infrequent samplings once a day, once a week and once a month. In case of mineral elements (sulfate, nitrate, chloride), that typically show more of a chemostatic behavior, fortnightly sampling of runoff will be adequate to capture annual fluxes (Alewell et al., 2004).

Overall, the state on knowledge indicates that concentrations and fluxes of DOC in runoff from forested catchments are largely driven by hydrological conditions and that catchment properties, like the occurrence of riparian wetland soils have a major impact.

The objectives of this study were thus (1) to quantify the effect of hydrological conditions on DOC variations in runoff from a forested watershed, (2) to identify the spatial origin of DOC in runoff, and (3) to investigate the implications of the short term variations for the calculation of DOC export fluxes at the annual scale.

To these ends we have studied the relationship between DOC, discharge and groundwater level in a forested headwater catchment based on high temporal resolution techniques.

2 Material and methods

2.1 Study site

The Lehstenbach catchment is located in the Fichtelgebirge region (50° 8′35′′ N, 11° 52′8′′ E) in southeastern Germany (Frei et al., 2010). The catchment area is 4.2 km^2 with elevations ranging from 695 to 877 m a.s.l. Mean annual precipitation is 1150 mm

(1971–2000). The annual temperature averages at 5.3 °C (1971–2000). During winter a substantial snow cover develops regularly.

The bedrock is variscan granite. Most abundant soil types are Dystric Cambisols, Haplic Podsols and Histosols (WRB, 2007). About one third of the catchment area is covered by Histosols, mostly by minerotrophic fens with some bogs in between (in the following referred to as wetland soils). The wetland soils have been drained by ditches established probably in the 19th century and some active ditches still exist.

Norway spruce (*Picea abies* (L.) KARST.) covers approx. 90 % of the catchment area. The wetland soils are covered partly by Norway spruce, but also by Sphagnum mosses with patches of *Vaccinium myrtillus*, *Juncus effusus*, *Carex nigra*, *Carex rostrata*, *Carex canescens*, *Molinia caerulea*, and *Eriophorum vaginatum* (Matzner, 2004).

In the upland areas of the catchment the mean groundwater depth is more than 10 m. Inclination of the catchment averages at 3° and surface runoff is of minor importance (Lischeid et al., 2002). However, based on a modeling approach, Frei et al. (2010) suggested some surface runoff from the wetland soils. Concerning both discharge and solute concentrations, the catchment runoff usually reacts within hours to rain storm events (Lischeid et al., 2004).

The groundwater level was measured in the riparian wetland soils about 2 m away from the stream using a piezometer with an immersed pressure sensor (Solinst Canada Ltd., Georgetown, Ontario, Canada). Discharge of the Lehstenbach stream was measured using a pressure sensor (Solinst Canada Ltd., Georgetown, Ontario, Canada) which was immersed at a discharge flume and weir at the catchment outlet. Precipitation was continuously recorded in the upper part of the catchment by a tipping bucket rain gauge.

DOC concentrations were measured in different compartments of the catchment (Table 1). Concentrations were largest in the wetland soils and in the Oa horizon of the forest floor percolates. Lowest concentrations were observed in the deeper layers of the upland forest soils and in the deeper groundwater.

2.2 Measurements of DOC concentrations in runoff in high temporal resolution

DOC concentrations in runoff were measured in 30 min intervals from 6 August 2010 to 5 August 2011 by a spectrometric device (spectro::lyser, s::can Messtechnik GmbH, Vienna, Austria) which was permanently immersed in the stream at the weir at the catchment outlet. A UV-VIS spectrum with a range from 200 to 732 nm was recorded every 2.5 nm. DOC concentrations were calculated by the spectro::lyser software based on the inclusion of about 80 wavelengths under correction for turbidity. The spectro::lyser device was calibrated by measured DOC concentrations in runoff from the Lehstenbach. Hence, we used a customized calibration instead of a general setting. Although the spectro::lyser could potentially also measure nitrate from absorption in the UV-range, we found that this is not possible in presence of high and variable concentrations of DOC.

For quality control, the spectro::lyser measurements were regularly cross-checked with direct DOC measurements by thermo-catalytic oxidation (TOC-VCPN-Analyzer, Shimadzu, Kyoto, Japan). To do so, runoff samples were obtained by an automated sampling system (ISCO portable sampler, Teledyne Isco, Inc., Lincoln, Nebraska, USA). These cross-checks were done in August, September, and November 2010 and in March, April and June 2011. The R^2 of the linear correlation between the two methods ranged from 0.95 and 0.98 (data not shown). As there was no drift of the DOC concentration due to environmental conditions, we decided against installing an automated cleansing system. The measuring cell was manually cleaned fortnightly.

Due to instrumental failure no measurements of DOC concentrations were available from 25 August 2010 to 2 September 2010, from the 8 to 23 December 2010, and from 13 to 14 January 2011. The missing concentration data (7 % of all measurements) were interpolated by means of an Artificial Neural Network (software SPSS 19, Modeler 14.1, IBM, Armonk, New York, United States) using the high resolution measurements (30 min) that were aggregated to daily mean values and then processed. A multilayer perceptron model with a feed-forward algorithm, one hidden layer and five neurons

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was used to model the daily values of DOC concentration. The model was trained with a back propagation algorithm using 70 % of the data. Validation of the model was done with the remaining 30 % of the data. This resulted in a model efficiency of $R^2 = 0.89$ and a RMSE of 1.63 mg l^{-1}. The best prediction for the daily average DOC concentrations was achieved with four input parameters in the order of (1) the precipitation sum of the 6 days before the gauging, (2) mean discharge on the day of measurement, (3) mean temperature of the 170 days before the measurement and (4) the precipitation at the day of measurement.

A detailed analysis of 24 storm events > 5 mm was done, relating discharge dynamics to dynamics of DOC concentrations and fluxes in runoff. The 24 events represented 61 % of the annual DOC export flux with runoff, and 60 % of the annual rainfall sum.

2.3 DOC fluxes with runoff

Annual fluxes of DOC with runoff were calculated by multiplying the 30 min discharge with the corresponding 30 min DOC concentrations, and then cumulated to the annual flux for the period August 2010 to August 2011. Due to instrumental failure no data were available for 27 days. For these days the fluxes were calculated based on daily average values of concentrations and discharge, with concentrations derived from the artificial neural network interpolation (see above). The interpolated data accounted for 7 % of the annual flux.

To simulate the effect of infrequent sampling strategies on the calculation of annual runoff fluxes, the daily 12.00 h values of the 30 min records of concentrations and discharge were taken for a simulated fortnightly sampling strategy with shifting starting dates from the 6 August 2010 to the 19 August 2010.

The data from these artificially created fortnightly observations were inserted into the Method 5-equation of (Walling and Webb, 1985) Eq. (1) to calculate the annual flux.

$$F = K \cdot Q_r \cdot \left(\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \right) \tag{1}$$

F stands for the annual DOC flux; K stands for the conversion factor (here number of seconds in the corresponding period of time); Q_r stands for the daily mean discharge of the year; Q_i stands for the discharge at the sampling day; C_i stands for the DOC concentration at the sampling day; and n is the number of sampling events.

2.4 DOC quality

To identify the spatial origin of DOC in runoff, the quality of DOC in the potential source areas was compared to the quality of DOC in runoff. Samples from shallow groundwater in the wetland soils (28 samples), from deeper (oxic) groundwater (4 wells, depth 3–15 m, 12 samples), from upstream runoff without riparian wetlands (4 samples), and from downstream runoff (26 samples) were taken on 4 occasions in summer 2011 (27 April, 18 May, 2 June, 16 June).

Shallow groundwater from the riparian wetland soils was sampled using a plastic syringe and silicon tube, deep groundwater was sampled from a well located in the upland forest area using an electric pump (Eijkelkamp, Giesbeek, the Netherlands), and surface water from the wetlands was taken as a grab sample.

For time resolved sampling of runoff, we used an ISCO bottle sampler (ISCO 6712, Teledyne Isco, Inc., Lincoln, Nebraska, USA) programmed in a 2 h time interval. We chose samples according to DOC concentration and discharge measurements, trying to represent the rising limb of the hydrograph, DOC concentration peak and the falling limb with 5–10 samples per event. Samples were stored in 100 ml PE bottles at 2 °C until analysis. In total, 116 runoff samples were analyzed for DOC quality (26 on same dates as groundwater samples, 90 on other occasions).

Three dimensional fluorescence excitation-emission matrices (EEMs) with subsequent evaluation by parallel factor analysis (PARAFAC, Stedmon et al., 2003) were used to characterize DOC quality. DOC samples were filtered (0.45 µm nylon, WICOM, Heppenheim, Germany) and diluted if necessary to an absorption at 254 nm ¡ 0.3 to minimize inner filter effects (ultrapure water, Barnstead Nanopure, Dubuque, Iowa, USA). Inner filter correction was performed following McKnight et al. (2001), as implemented in the MATLAB toolbox by Cory and McKnight (2005). To this end, UV-VIS absorption scans were recorded on a Varian Cary 1E spectrophotometer (range 200–800 nm, 0.5 nm resolution, Varian Inc., purchased by Agilent Technologies, Santa Clara, California, United States). Sample correction according to the toolbox of Cory and McKnight (2005) further includes blank subtraction and normalization of fluorescence intensities to the Raman peak intensity at an Excitation of 350 nm. Raman scans, EEMs for blanks, and sample EEMs were recorded on a Perkin Elmer LS 55 fluorescence spectrometer (Waltham, Massachusetts, USA) at a resolution of 0.5 nm for emission (300–600 nm) and 5 nm for excitation (240–450 nm).

All data evaluation and PARAFAC modeling was done using MATLAB 2008a (MathWorks, Natick, Massachusetts, USA) and following the toolbox by Cory and McKnight (2005). Therefore, EEMs were reshaped to the appropriate resolution and range (excitation 250–400 nm, 5 nm steps; emission 350–440 nm, 2 nm steps). The PARAFAC Model from Cory and McKnight (2005) uses 13 fixed, previously identified components to describe each sample EEM. These components were found to sufficiently explain quality differences in our samples with only small residuals remaining unexplained. As a chemical molecular interpretation of the PARAFAC components identified by Cory and McKnight (2005) has become a matter of discussion (Macalady and Walton-Day, 2009), we used the 13 PARAFAC components to derive statistical fingerprints mainly, omitting a distinct discussion about chemical quality of the DOC of the respective sources.

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2.5 Statistical analysis

Statistical data analysis, data processing, and plotting were done in R-project version 2.13.0 (R Development Core Team, 2011) if not otherwise stated. To aggregate the 30 min data to daily values we used the functions daily from the R project package Animal (Hanninen and Pastell, 2009) and the function ddply from the package plyr (Wickham, 2011).

3 Results

3.1 Discharge, groundwater and precipitation

Precipitation from August 2010 to August 2011 occurred at 232 days and summed up to 1057 mm (Fig. 1). Highest rainfall intensity was observed on the 5 June 2011 with a rainfall of 15 mm within 30 min.

Maximum discharge was 0.89 $m^3 s^{-1}$, observed on the 14 January 2011 (snow melt event), minimum discharge was 0.018 $m^3 s^{-1}$ on the 29 June 2011. Discharge averaged at 0.087 $m^3 s^{-1}$. The discharge responded within minutes to hours to rain fall events, indicating the flashiness of the catchment (Fig. 1).

The groundwater table in the riparian wetland soils showed rapid changes in response to precipitation events (Fig. 1). Groundwater was near surface in August 2010, and in the winter months 2010/2011. Lowest levels were observed on the 31 May 2011 at 0.62 m below surface.

3.2 DOC concentrations

During the one-year period, DOC concentrations in runoff averaged at 9.2 $mg l^{-1}$. The minimum was 2.6 $mg l^{-1}$ in May 2011, and the maximum was 33.8 $mg l^{-1}$ in September 2010 (Fig. 1). The concentrations of DOC changed rapidly within hours and corresponded generally to the dynamics of the groundwater table and discharge with highest

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concentrations observed at shallow groundwater table and high discharge. The maxima of the DOC concentrations in runoff had a time delay of a few hours in relation to the maxima of the groundwater table and discharge (Fig. 2, Table 2). The average time delay of the DOC maxima was 160 min after the discharge peak and the range of delays was from 30 to 390 min (Table 2). No significant correlation between DOC delay and the single co-variables of Table 2 was found.

The response of DOC to discharge followed counter-clockwise hysteretic loops and was seasonally different (Fig. 3). The hysteretic loops for the whole gauging period can be divided into an upper and a lower branch. The branch with shallower slopes in the concentration-discharge relationship represents the winter to spring events whereas the upper branch displays summer and fall events.

To compare the hysteretic relationship between different seasons in more detail, we selected one rainfall event in the winter/spring season and one in the summer/fall season both with a similar amount of discharge of 0.35 to 0.40 $\mathrm{m}^3\,\mathrm{s}^{-1}$ (Fig. 4). The loop of February 2011 had lower DOC concentrations than the loop of November 2010. Also, the hysteresis was more pronounced in November with a larger distance between the rising and falling limb. The larger hysteresis in the summer/fall season than in winter/spring was also found for other events (Fig. 3).

3.3 DOC quality

The DOC fingerprinting by fluorescence excitation-emission matrices with subsequent PARAFAC analysis clearly separated DOC originating from deep groundwater, shallow groundwater from riparian wetland soils and from runoff (Fig. 5). From the 13 fluorescence components of the applied PARAFAC Model (nomenclature according to Cory and McKnight 2005 is given in brackets), components 1 (C1), 5 (SQ1), and 6 (unidentified) were more prominent in wetland samples; components 3 (unidentified), 8 (tryptophan-like), and 12 (Q3) were more prominent in groundwater samples. Exemplarily, we used component 1 (C1, Cory and McKnight, 2005) indicative of samples from riparian wetland soils, and component 12 (Q3) as indicative of groundwater samples (other components not shown). Contribution of component 1 in DOC-fluorescence of runoff samples lined up between deep groundwater and the shallow wetland groundwater samples, suggesting a mixture of both sources, but clearly dominated by wetland-borne DOC. Using both component 1 and component 12 (Cory and McKnight, 2005), a clear separation of samples was possible (Fig. 5), yielding 2 groups of either groundwater dominated samples or DOC-rich samples dominated by wetland-borne DOC. While fluorescence of DOC-rich samples from shallow wetland groundwater was characterized by higher relative contribution of component 1, deeper groundwater samples where characterized by higher contribution of component 12. With respect to these two distinctive components, DOC quality in upstream runoff, with negligible influence from riparian wetland water and closer to a groundwater spring, was similar to deep groundwater samples (Fig. 5, open diamonds). A rise in DOC concentrations with discharge always coincided with an increasing contribution of component 1 and a decrease in component 12 (Fig. 6).

3.4 DOC fluxes with runoff

The cumulative DOC fluxes followed generally the cumulative discharge (Fig. 7). However, during the discharge events in summer and autumn 2010, the curve for DOC was steeper than for discharge. The snow melt in January 2011 resulted in a huge increase of both cumulative discharge and DOC export. The cumulative fluxes increased only slightly after the snowmelt in 2011 due to generally low discharge rates without major discharge peaks (Fig. 1).

The DOC flux calculations based on high frequency measurements (30 min) yielded an annual export of 84 kg C $\mathrm{ha^{-1}\,yr^{-1}}$ with 51.3 kg C $\mathrm{ha^{-1}\,yr^{-1}}$ during rainfall events $>$ 5 mm (Table 2).

43 % of the annual DOC export occurred in the growing season (Mai–October) and 57 % in the dormant season (November–April).

The calculation of DOC fluxes from the artificially created fortnightly sampling sequences with different starting dates (Table 3) resulted in variations of the annual flux from 47 to 124 kg C ha^{-1} yr^{-1}.

4 Discussion

4.1 Range, origin and mobilization of DOC in runoff

The DOC concentrations in runoff from the Lehstenbach catchment were highly variable at hourly to daily time scales, and ranged from 3 to 34 mg l^{-1}. The DOC concentrations in the lower range occurred at baseflow conditions, whereas concentrations increased with discharge. In comparison to other studies in forested watersheds, temporal variations and average concentrations (9.2 mg l^{-1}) of DOC in runoff in our study are quite high (Jeong et al., 2012; Koehler et al., 2009). However, Roulet et al. (2007) reported even higher average DOC concentrations of 47.5 ± 13 mg l^{-1} in a study on a northern ombrotrophic bog. Short term variations of DOC in runoff have been related to changing water flow paths under high-flow, draining different compartments than under baseflow conditions (Hood et al., 2006). In the Lehstenbach catchment the quality of DOC, concentration range and groundwater dynamics, point to the riparian wetland soils as the main source of DOC in runoff under high-flow conditions. The fluorescence spectroscopy of DOC distinguished between deep groundwater and water samples from shallow groundwater in the riparian wetland soils. The decrease of the groundwater component with rising discharge and the increase of the wetland component strongly suggest the riparian soils as the origin of both the fast runoff components (Frei et al., 2010) and high DOC concentration.

Although an interpretation in a molecular sense of PARAFAC derived fluorescence components from Cory and McKnight (2005) seems to be limited (Macalady and Walton-Day, 2009), this approach proved to be suitable for distinguishing DOC sources in our study, when interpreting fluorescence compounds as bulk quality indices or fingerprints. Taking the shallow wetland groundwater samples and deeper groundwater samples as possible end members in DOC quality indices, e.g. component 1 was indicative of wetland soil derived, shallow groundwater, while component 12 dominated fluorescence of DOC originating from deeper groundwater with low DOC contents (Fig. 5). Correspondingly, under groundwater derived base-flow conditions low in DOC, relative contribution of component 12 increased, while under high discharge conditions rich in DOC, component 1 increased (Fig. 6). Following Cory and McKnight (2005), component 1 was correlated to Ketal or Acetal Carbon as analyzed by ^{13}C NMR, and component 12 to % aliphatic carbon content. Due to its refractory character, a higher proportion of aliphatic carbon seems reasonable in groundwater with longer residence times. Fellman et al. (2009) attributed an increase in riparian wetland-borne DOC to increases in tryptophan-like fluorescence, with tryptophan being a rather labile amino acid. However, according to the PARAFAC Model of Cory and McKnight (2005), who assigned component 8 to tryptophane-like fluorescence, in our dataset tryptophane-like fluorescence was higher in deeper groundwater than in shallow riparian wetland groundwater. This indicates that the interpretation of PARAFAC modeling, even if not on a molecular level, is probably not unique and needs to be done with caution.

The conclusion that the primary source for DOC in runoff is located in the wetland soils is also supported by the observed low DOC concentrations in deeper soil layers and groundwater (Table 1). Forested upland soils as a potential source of peaking DOC concentrations can practically be ruled out since direct surface runoff that could rapidly connect the upper soil layers with the streams is not observed in the Lehstenbach catchment, and response times of respective flow paths are too long to explain short term variations. The water percolating the forest floor layers enters deeper groundwater after DOC being removed largely by sorption or decomposition in the soil (Schulze et al., 2011), resulting in DOC concentrations in the groundwater of only about 1–3 mg l^{-1} in our study. Lastly, increasing DOC in runoff always coincided with shallow groundwater levels in the riparian wetland soils, as also observed by Morel et al. (2009) for a catchment in France.

An explanation for the observed short term variations of DOC in runoff is the non-linear increase in catchment discharge with rising riparian groundwater levels. This increase is probably the combined effect of efficient surface flow networks that develop when groundwater levels reach surface depressions (Frei et al., 2010) and a general non-linear decrease of lateral hydraulic conductivity with depth (e.g. Seibert et al., 2009). Both mechanisms result in a rapid, non-linear increase of drainage efficiency of the system when riparian groundwater levels are rising. The latter mechanism has been termed transmissivity feedback (Bishop et al., 2004) and was shown to control the transfer of solutes from the riparian zone to the streams (Seibert et al., 2009). The lateral hydraulic conductivity is typically lower in the deeper layers of wetland soils due to the compacted and more decomposed organic matter than in the porous and less decomposed shallow layers. The differences in hydraulic conductivities between deeper layers and shallow layers of wetland soils can be several orders of magnitude (Jacks and Norrström, 2004), causing shallow layers to drain much more effectively than deep soil layers. The shallow layers of the riparian wetland soils typically contain more DOC than deeper soil layers (Table 1). Rising groundwater levels in the riparian soils progressively engage soil layers with higher hydraulic conductivity and increasing DOC concentrations in the runoff generation process causing the strong response of DOC in runoff. The DOC pool available for mobilization in the riparian wetland soils seems to be large (Worrall et al., 2008) as also in our study there was no decrease in maximum DOC concentrations during subsequent rain events.

4.2 Temporal dynamics of DOC in runoff

The high temporal resolution of the DOC concentrations enabled a number of observations that would have been missed by typically infrequent samplings. The response of the DOC concentrations in runoff to discharge was characterized by counterclockwise hysteretic loops with lower concentrations on the rising limb compared to the falling limb. No flush of DOC at the beginning of the event was observed and the peak of DOC occurred a few hours (160 min on average) after the discharge peak. Furthermore, the hysteretic loops were more pronounced and had a steeper slope in the summer/fall season than in the winter/spring season.

The majority of hysteretic loops described in the literature are clockwise (e.g., Hornberger et al., 1994; Butturini et al., 2006; Jeong et al., 2012). This was also reported in studies where DOC was found to originate mainly from riparian wetland soils (McGlynn and McDonnell, 2003; Hood et al., 2006). Minding the proposed Transmissivity Feedback (Bishop et al., 2004) for DOC exports and highest DOC concentrations in the riparian wetland soils, this would also be expected for our catchment. However, although we could clearly identify the wetlands as DOC source areas based on DOC quality, we found counter-clockwise hysteretic loops, indicating that the peak of DOC concentration occurred on the falling limb of the hydrograph. The relation of DOC to discharge on the falling limb was steady and uniform, whereas the relation during the rising limb seems to depend on the preceding groundwater level in the wetland soils.

Evans and Davies (1998) used hysteretic loops to analyze episode hydrochemistry and hydrologic characteristics of catchments. According to their classification Lehstenbach catchment fall into the category A2: Counter-clockwise and positive. The A2 type requires a near surface hydrological component with lower DOC concentrations than in the shallow groundwater of the wetland riparian soils. Hence, the counterclockwise hysteretic loops in our study are likely caused by a small, short term, but still significant water flux with less DOC than in the shallow groundwater of the wetland soils. Such a bypass in the Lehstenbach catchment might be caused by the still existing ditches in the wetland soils. According to this model, the restricted contact between this runoff component and the DOC-rich soil layers during initial runoff will result in lower DOC concentrations in the rising limb as compared to the falling limb. A possible bypass effect by a surface or surface-near flow component was further suggested by occasional, small peaks in nitrate concentrations at the begin of rain events after longer drought (data not shown), minding that in the riparian wetlands there is usually

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no nitrate present due to anoxic conditions (Goldberg et al., 2010). The effect of the bypass seems short term as indicated by the few hours delay of the DOC peaks in relation to the discharge peaks.

The mobilization of DOC from soil organic matter often follows seasonal patterns with increasing concentrations during the summer season. This has been shown for forest floors in field (Michalzik and Matzner, 1999) and in laboratory studies (Gödde et al., 1996) as well as for wetland soils (Koehler et al., 2011; Clair et al., 2002). The mobilization of DOC from soil organic matter is partly driven by microbial (enzymatic) processes and partly by physicochemical processes (Bolan et al., 2011), both being temperature dependent. Hence, the steeper slope of the hysteretic loops and the more pronounced hysteresis in the summer/fall season than in the winter/spring season seems largely due to a temperature effect on DOC mobilization.

In addition, the flow paths of water in the winter season might be different from the summer/autumn season, since the top layers of the riparian wetland soils – in summer responsible for high DOC concentrations in runoff – might not be drained due to freezing.

4.3 DOC fluxes

The annual export of DOC from the Lehstenbach catchment amounted to 84 kg C ha^{-1} yr^{-1}. The annual export is rather high in comparison to other forested watersheds. Kindler et al. (2011) calculated average DOC losses for 5 Northern European forested catchments to be 35 kg C ha^{-1} yr^{-1}.

The carbon export rates at the Lehstenbach catchment might be relatively high because a substantial part of the catchment is covered by riparian wetland soils. Laudon et al. (2011) defined the ratio of wetlands to upland soils in boreal forested catchments as a driving variable for the DOC export with runoff. However, they suggest that the proportion of DOC in runoff from wetlands decrease with rising discharge as the contribution of water from upland zones increases. In our study we observed the opposite, since the proportion of DOC from wetlands increased with discharge.

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If we assume that the majority of DOC export from the Lehstenbach catchment results from the riparian wetland soils, representing 30 % of the area, the solute C export from these soils is in the range of 240 kg C $\mathrm{ha^{-1}\,yr^{-1}}$. This equals the average C accumulation rates of northern peatlands (Lavoie et al., 2005), emphasizing the huge contribution of DOC to net C exchange in these ecosystems.

Annual DOC exports were calculated both from high frequency measurements and by simulated infrequent sampling intervals with subsequent interpolation (Method 5, Walling and Webb, 1985). The 30 min data yielded a DOC export of 84 kg C $\mathrm{ha^{-1}\,yr^{-1}}$ which is taken here as the "true" reference flux. When the data were aggregated to daily values, the resulting flux was similar (82.4 kg C $\mathrm{ha^{-1}\,yr^{-1}}$). However, applying the widely used interpolation equation from Walling and Webb (1985) on the fortnightly shifted date sequences, a range of 47 and 124 kg C $\mathrm{ha^{-1}\,yr^{-1}}$ resulted, equal to 56 and 148 % of the "true" flux. Hence, massive errors in calculating DOC export by e.g. fortnightly samplings are possible. Our results contradict Koehler et al. (2009) who suggested a weekly or monthly sampling frequency as adequate to calculate the yearly DOC flux with runoff from an Atlantic blanket bog catchment.

5 Conclusions

In the Lehstenbach catchment, DOC concentrations in runoff are subjected to substantial short term variations at an hourly to daily time scale driven by dynamics of the hydrological regime. Concentrations increased with increasing discharge, with strongest response in the summer/fall season. Quality parameters as well as the dynamics of groundwater table in the riparian zone document that the DOC in runoff originates from the riparian wetland soils. The DOC export represents a major contribution to the net C budget of the wetland soils.

Future changes in the hydrological regime, e.g. by changing distribution and intensities of precipitation, will influence the DOC dynamics in this catchment, with largest effects in the summer/fall season.

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The high frequency measurements documented that calculations of DOC export fluxes based on infrequent samplings might be subject to significant errors if steep concentration/discharge relations exist.

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Table 1. Range of DOC concentration in different compartments of the Lehstenbach catchment.

compartment	range (mg l^{-1})	reference
soil solution beneath Oa horizon (upland forest soil)	30–80	Schulze et al. (2011)
soil solution in 90 cm depth (upland forest soil)	3–5	Schulze et al. (2011)
soil solution in 0–30 cm depth (riparian wetland soil)	10–150	this study
soil solution in > 30 cm depth (riparian wetland soil)	10–80	this study
shallow groundwater in 50–100 cm depth (riparian wetland soil)	4–40	this study
deeper groundwater (3–15 m depth)	0.8–3	this study
catchment runoff	3–34	this study

Table 2. Detailed analysis of 24 events with rainfall > 5 mm.

Event	Start	End	Duration (h)	Rain (mm)	Q sum (m^3)	DOC delay (min)	DOC max ($mg\,l^{-1}$)	DOC flux ($kg\,ha^{-1}\,event^{-1}$)
1	6 Aug 2010 00:00	7 Aug 2010 06:00	30	45	24 800	120	31.2	3
2	12 Aug 2010 06:00	12 Aug 2010 19:30	13.5	26	14 226	150	32.2	1.8
3	13 Aug 2010 19:00	13 Aug 2010 23:30	4.5	10	14 453	120	29.8	1.6
4	16 Aug 2010 19:00	18 Aug 2010 05:30	34.5	28	19 881	90	32	2.3
5	26 Aug 2010 20:30	27 Aug 2010 23:30	27	35	14 879	n.d.	21.1	1.3
6	29 Aug 2010 14:00	31 Aug 2010 13:00	47	33	27 327	n.d.	25.1	2.8
7	27 Sep 2010 16:30	29 Sep 2010 00:30	32	35	57 490	n.d.	33.8	6.6
8	5 Nov 2010 20:00	8 Nov 2010 08:30	60.5	30	23 660	120	27.8	1.9
9	11 Nov 2010 20:00	13 Nov 2010 06:30	34.5	35	29 567	360	26.8	2.9
10	15 Nov 2010 16:30	17 Nov 2010 07:00	38.5	33	15 220	90	23.3	1.3
11	18 Nov 2010 06:30	18 Nov 2010 14:30	8	7	18 251	150	21.9	1.5
12	7 Dec 2010 11:00	8 Dec 2010 20:30	33.5	44	27 084	150	22.3	2.3
13	6 Jan 2011 10:30	9 Jan 2011 23:00	84.5	67	128 631	60	19.2	8.5
14	12 Jan 2011 15:30	15 Jan 2011 12:00	68.5	38	120 430	n.d.	15.3	7.1
15	4 Feb 2011 10:00	4 Feb 2011 22:30	12.5	9	30 773	270	12.3	1.3
16	11 Feb 2011 00:00	12 Feb 2011 12:00	36	10	25 846	180	14.8	1.3
17	16 Mar 2011 19:00	18 Mar 2011 19:00	48	9	35 501	120	14.1	1.8
18	4 Apr 2011 06:00	4 Apr 2011 15:00	9	11	7962	390	13.7	0.4
19	31 May 2011 19:00	1 Jun 2011 16:30	21.5	41	7645	150	15.4	0.3
20	5 Jun 2011 16:30	6 Jun 2011 02:30	10	26	4790	150	20.1	0.3
21	20 Jun 2011 17:30	21 Jun 2011 10:30	17	10	2203	120	12.4	0.1
22	7 Jul 2011 22:00	8 Jul 2011 07:30	9.5	6	1464	150	11,1	0.1
23	10 Jul 2011 16:00	11 Jul 2011 05:00	13	19	4755	30	24.2	0.4
24	20 Jul 2011 06:30	20 Jul 2011 19:30	13	23	4874	240	25.7	0.4

Table 3. Effect of shifting starting dates of virtual fortnightly samplings on the annual DOC fluxes with runoff.

Start date	End date	Export (kg C ha^{-1} yr^{-1})
6 Aug 2010	5 Aug 2011	102
7 Aug 2010	23 Jul 2011	121
8 Aug 2010	24 Jul 2011	70
9 Aug 2010	25 Jul 2011	64
10 Aug 2010	26 Jul 2011	55
11 Aug 2010	27 Jul 2011	47
12 Aug 2010	28 Jul 2011	83
13 Aug 2010	29 Jul 2011	92
14 Aug 2010	30 Jul 2011	84
15 Aug 2010	31 Jul 2011	73
16 Aug 2010	1 Aug 2011	73
17 Aug 2010	2 Aug 2011	112
18 Aug 2010	3 Aug 2011	124
19 Aug 2010	4 Aug 2011	70

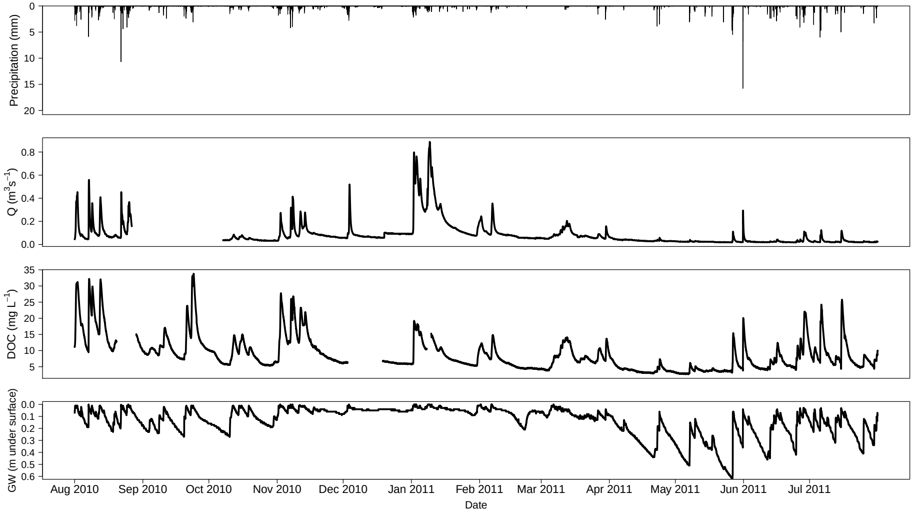

Fig. 1. Precipitation, discharge (Q), DOC concentration and riparian groundwater level in the Lehstenbach catchment.

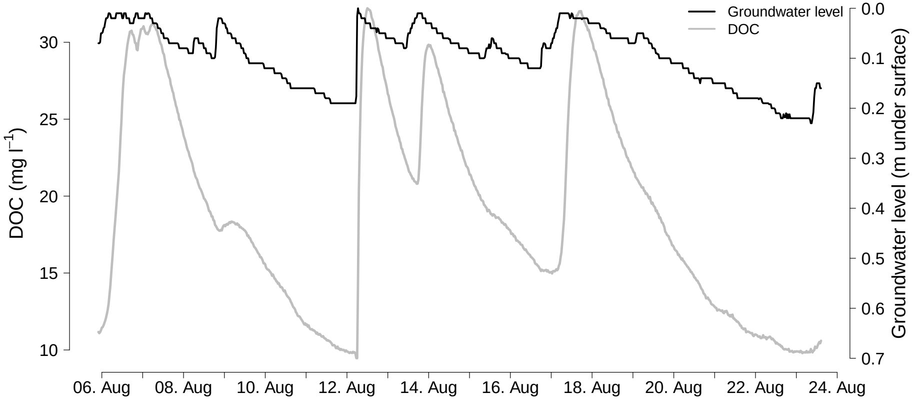

Fig. 2. Dynamics of DOC concentration in runoff and of the riparian groundwater level in August 2010.

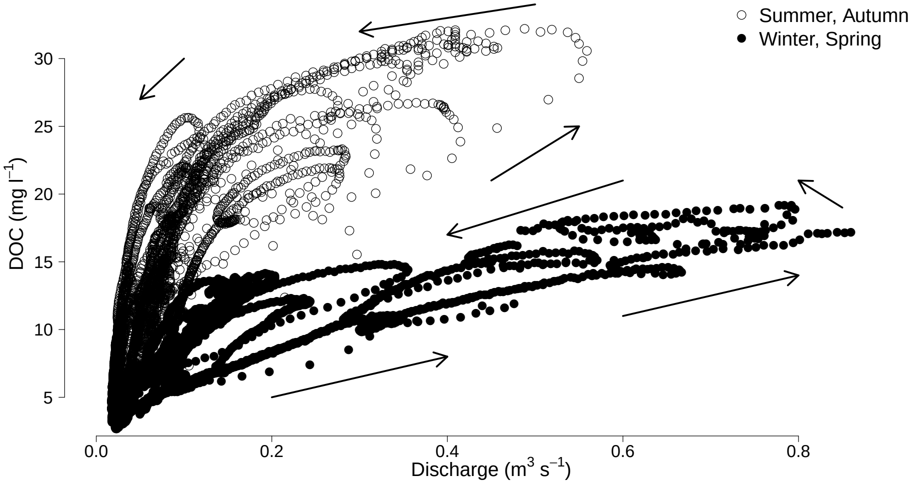

Fig. 3. Hysteretic loops of DOC concentrations in response to discharge.

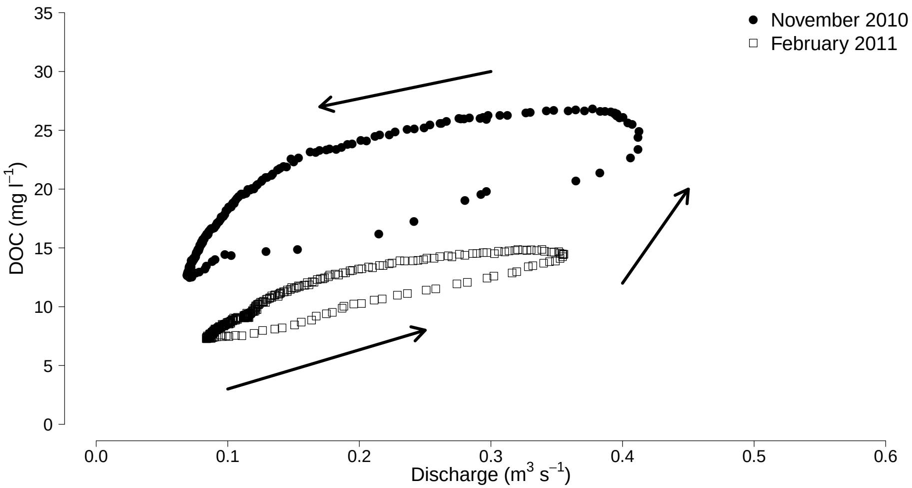

Fig. 4. Hysteretic loops of DOC concentrations in response to discharge for two selected events.

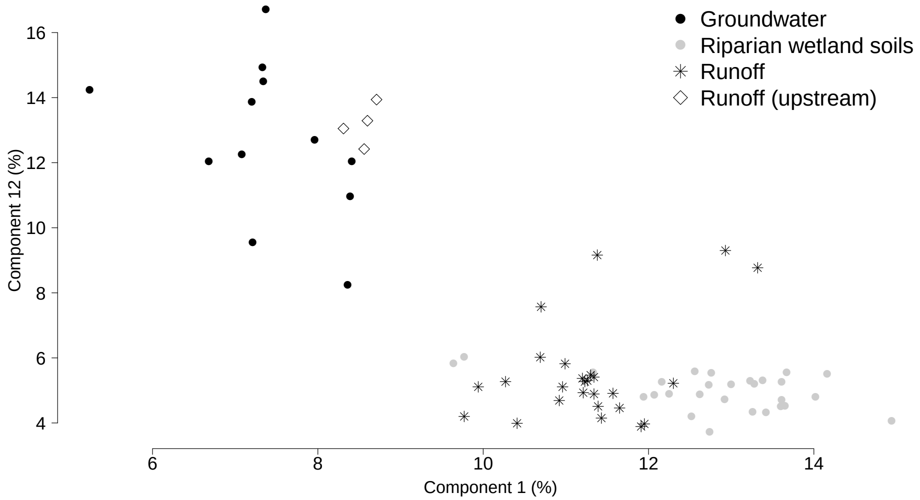

Fig. 5. Quality of DOC from different origins as revealed by fluorescence excitation-emission matrices with subsequent PARAFAC analysis.

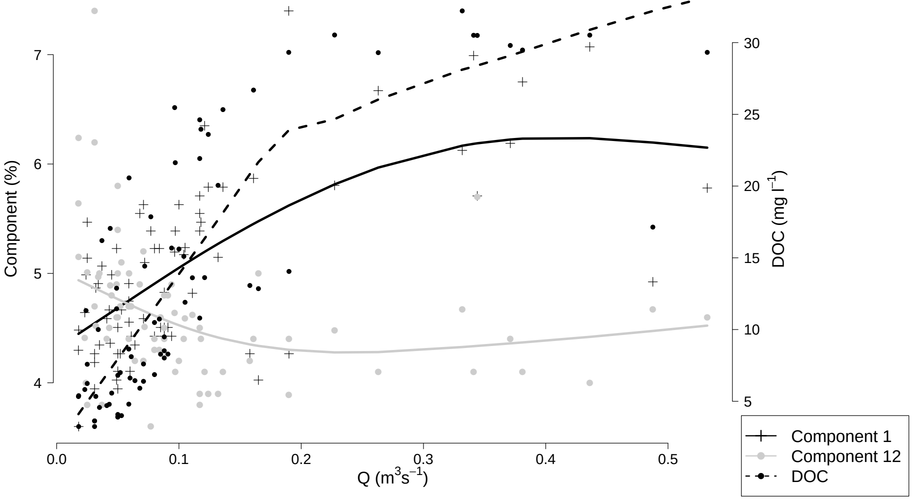

Fig. 6. DOC concentration and quality in response to discharge.

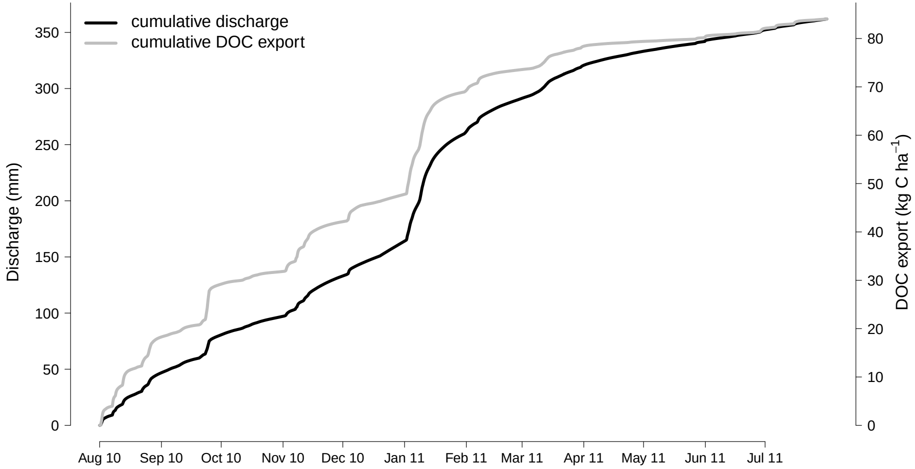

Fig. 7. Cumulative discharge and cumulative DOC export with runoff.

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