Changes in dissolved organic matter quality in a peatland and forest headwater stream as a function of seasonality and hydrologic conditions

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Abstract. Peatlands and peaty riparian zones are major sources of dissolved organic matter (DOM), but are poorly understood in terms of export dynamics and controls thereof. Thereby quality of DOM affects function and behavior of DOM in aquatic

10   ecosystems, but DOM quality can also help to track DOM sources and their export dynamics under specific hydrologic preconditions. The objective of this study was to elucidate controls on temporal variability in DOM concentration and quality in stream water draining a bog and a forested peaty riparian zone, particularly considering drought and storm flow events. DOM quality was monitored using spectrofluorometric indices for aromaticity ($SUVA_{254}$), apparent molecular size (S_R) and precursor organic material (FI), as well as PARAFAC modeling of excitation emission matrices (EEMs).

15   Indices for DOM quality exhibited major changes due to different hydrologic conditions, but patterns were also dependent on season. Stream water at the forested site with mineral, peaty soils generally exhibited higher variability in DOM concentrations and quality compared to the outflow of an ombrotrophic bog, where DOM was less susceptible to changes in hydrologic conditions. During snowmelt and spring events surface-near protein-like DOM pools were exported. A microbial DOM fraction originating from groundwater and deep peat layers was increasing during drought, while a strongly microbially altered

20   DOM fraction was also exported by discharge events with dry preconditions at the forested site. This might be due to accelerated microbial activity in the peaty riparian zone of the forested site under these preconditions. Our study demonstrated that DOM export dynamics are not only a passive mixing of different hydrological sources, but monitoring studies have to consider that DOM quality depends on hydrologic preconditions and season. Moreover, the forested peaty riparian zone generated most variability in headwater DOM quantity and quality, as could be tracked by the used spectrofluorometric indices.

Keywords: DOM, PARAFAC, Peatlands, riparian zone, forest soils, fluorescence

1 Introduction

Dissolved organic matter (DOM) is ubiquitous in soils and aqueous ecosystems. It plays a fundamental role in surface water chemistry, e. g. in metal bioavailability and mobility (Tipping et al., 2002), nutrient cycling (Jansson et al., 2012), pH buffering

and ionic balance (Hruška et al., 2003). It affects light penetration (Karlsson et al., 2009), the aquatic food web structure (Jansson et al., 2007), is an energy source for microbial metabolism (Cole et al., 2007; Amon and Benner, 1996) and finally part of the carbon cycle (Cole et al., 2007). But not only DOM quantity is of great interest, as the DOM quality strongly affects function and behavior of DOM in aquatic ecosystems.

5   Main DOM input to aquatic systems is of terrestrial origin (see Mulholland 2003). Concentrations and characteristics of DOM vary strongly among surface waters depending on catchment, climate and hydrology (Ågren et al., 2014; Laudon et al., 2004; Frost et al., 2006; Winterdahl et al., 2014). However, DOM concentrations and characteristics can also vary largely over time due to seasonal changes in production, consumption and transport of DOM (e.g. Fellman et al., 2009; Perdrial et al., 2014; Wallin et al., 2015). Peatlands, which store large amounts of carbon have thereby received attention as a major source of DOM

10   to surface water (Worrall et al., 2002; Aitkenhead et al., 1999). But also wet riparian zones with organic-rich layers are recognized as DOM source (e.g. Bishop et al., 2004; Seibert et al., 2009; Laudon et al., 2004, Ledesma et al., 2015). The annual dissolved organic carbon (DOC) concentration dynamics and long-term DOC concentration increase observed for many catchments (Monteith et al., 2007; Worrall et al., 2004) points out the importance to understand DOM origin and factors controlling DOM export. Storm events have been shown to be quantitatively important for DOM exports to streams in peatland

15   catchments (Clark et al., 2007) and carbon-rich riparian zones, as they generate high DOM concentration peaks. Especially for drinking water production not only DOM quantity, but also DOM quality is important. Aromatic structures of DOM could cause disinfection-by-product (DBPs) generation during drinking water treatment (Korshin et al., 1997). More aromatic, humic DOM also decreases light penetration and DOM photo-degradation potential in surface waters (Cory et al., 2007, Ward and Cory, 2016). The easily biodegradable DOM (BDOM) fraction - mainly fresh, protein-like DOM, derived from root- or leaf

20   exudates, litter decay or leachates - can be readily utilized and serves as important nitrogen and phosphorus source in aquatic systems (Fellman et al., 2009). Microbially processed DOM are residual and recalcitrant substances. Assessing such variability in DOM quality can be a valuable tool to track DOM sources and transport mechanisms (Singh et al., 2014), which is crucial for predicting DOM exports and quality.

Comprehensive studies mainly focused on total DOM concentration and much is known about the DOM export from peatland
25   and forested catchments (e. g. Laudon et al., 2011; Grabs et al., 2012; Clark et al., 2009). Trends of DOM quality during stormflow events or differences depending on catchment type are scarce. Inamdar et al. (2011) and Hood et al. (2006) characterized DOM during storm events in a temperate forest catchment dominated by mineral soils. A high contribution of aromatic structures during storm flow was ascribed to flushing of humic-rich near-surface soil layers and lower contribution of shallow groundwater. Organic soil layer DOM can be highly aromatic or humic, reflecting decomposition of complex plant

30   and soil organic matter. As DOM percolates through the soil sorption to mineral phases preferentially removes larger, aromatic components (e.g. Meier et al., 2004; Kaiser and Zech, 2000) and longer residence times enhance alteration of DOM by microbial processes. Thus groundwater DOM is mostly of microbial origin and of apparently smaller molecular size (e.g. Inamdar et al. 2012, Singh et al. 2014). While Singh et al. (2014) described a strong pulse of protein-like DOM during autumn leaf fall, Perdrial et al. (2014) perceived only modest shifts in DOM quality over seasons in a forested catchment in New

Mexico. Fellman et al. (2009) focused on the bioavailable fraction of DOM from wetland and forest soils, and found a strong biotic control on BDOM interacting with abiotic processes and hydrologic flowpaths. The BDOM fraction was highest during spring due to a low biotic demand and shallow flow paths. Ågren et al. (2008) reported higher aromaticity and apparent molecular size during snowmelt at a wetland catchment compared to a forest catchment. However, a comparison to other high

5   discharge events during the growing season is lacking.

A limitation in DOM quality studies is that determination of DOM structures is elaborate and expensive, while large datasets and high temporal resolution would be desirable (Strohmeier et al., 2013). UV-Vis and fluorescence spectroscopy are limited in data interpretation in terms of specific chemical structures, but due to low cost and rapid analysis enables us to generate a comprehensive dataset covering a wide range of hydrologic and seasonal conditions. It allows distinguishing between different

10   DOM constituents and disentangling their specific export behavior and might also be used to trace different DOM sources (Hood et al., 2006). Several optical indices describe the nature of DOM: Specific Ultra-Violet Absorbance at 254 nm ($SUVA_{254}$) is commonly used as indicator for the proportion of aromatic structures (Weishaar et al., 2003). The spectral slope ratio (S_R) (Helms et al., 2008) is used as a proxy for apparent DOM molecular size. The humification index (HIX) (Ohno, 2002) and fluorescence index (FI) (Cory and McKnight, 2005) are derived from fluorescence-based excitation-emission

15   matrices (EEMs). While HIX describes the degree of humification, FI differentiates between plant derived and microbial or planktonic derived DOM. The fluorescence EEMs can be further analyzed using parallel factor analysis (PARAFAC), decomposing the EEMs into hypothetic fluorophores related to differences in composition of DOM (Stedmon and Bro, 2008; Murphy et al., 2013).

Following up on a previous study describing DOC fluxes and concentration dynamics from a bog catchment (Broder and

20   Biester, 2015), the present study intended to elucidate different spatiotemporal dynamics in DOM quality over a year comparing a bog and a forested peaty riparian zone, as those landscape types are considered as the main sources of stream DOM. We hypothesized that DOM quality is highly variable in a headwater stream depending on hydrologic conditions and season. In addition, we expected that DOM quality at the forested site is more affected by changes in hydrologic conditions than at the bog site. Furthermore, we tested if spectrofluorometric indices can be used to track DOM sources and their dynamics

25   under specific hydrologic (pre)conditions. We expected short-term DOM quality changes due to high discharge events, which cause changes in hydrologic flow paths in the catchment, such as a development of surface flow networks or a connection of organic rich surface layers to discharging waters. Changes in DOM composition in stream water might further reflect DOM sources of shallow groundwater or deeper peat layers versus organic rich upper soil layers or surface-near peat layers. This short-term pattern was expected to be overlain by seasonal DOM changes due to changes of DOM production and consumption

30   over the year. General differences in DOM quality between the bog and forested riparian zone catchments are caused by differences in vegetation, water level fluctuations and an existence of mineral soil layers.

To test our hypotheses, we chose a headwater stream catchment to compare DOM export from discrete landscape units. The Odersprung catchment in the Harz Mountains (Germany) is particularly suitable for our study as the stream originates within a bog and enables us to retrieve an exclusively bog derived DOM signal within this headwater stream. Short residence times

make in-stream processes negligible and allows landscape-type specific studies. The effects of storm events, hypothesized to induce major DOM dynamics, were particularly considered in our sampling design. For DOM characterization and source identification we applied spectrofluorometric indices like $SUVA_{254}$, S_R, HIX and FI, as well as PARAFAC modeling of excitation-emission matrices. Seasonality effect were assessed considering mean daily air temperatures.

2 Materials and Methods

1.1 Study site

The study site is located within the nature protection area of the Harz Mountains. The Odersprung bog exhibits an erosion rill,
10 draining the peatland (Fig. 1). The catchment responds quickly to rainfall events and discharge is mainly fed by surface-near waters. A more detailed hydrologic description is given in Broder and Biester (2015). The bog vegetation is dominated by *Sphagnum magellanicum* and *S. rubellum*, associated with *Eriophorum angustifolium* and *Molina caerulae* (Baumann, 2009). The peatland is surrounded by spruce forest growing on a cambic podzol soil at the hillslopes and peaty soils with deep organic topsoil layer in the riparian zone. One discharge sampling was conducted directly at the rill outflow, where all water originates
15 exclusively from the domed bog. Another sampling spot was established about 20 m further downstream where the small headwater stream increasingly receives water from the surrounding forested, organic rich mineral soils and peaty riparian zone (Fig. 1). The catchment is underlain by granitic bedrock. Bog mean peat thickness is about 3 m, while the mineral soils are shallow at the hillslope (30 cm) and deeper in depressions (100 cm). Organic content of the soil varies between 30 % and 97 % in the organic-rich surface layers (Broder & Biester, unpublished data).

20 ### 1.2 Sampling and field measurements

Stream water sampling at each sampling spot was conducted from snowmelt to begin of snowfall in 2013. Water samples of 500 mL volume were taken by an automated water sampler (Teledyne ISCO, USA) in six-day intervals summing up to 44 samples. Additional grab samples were taken every two to three weeks (30 samples in total) in PE tubes, which were previously rinsed twice with sample water. High frequency storm event sampling was conducted on several occasions in three-hour
25 intervals resulting in 191 samples. A V-notch weir was installed at the bog outlet for discharge quantification. Water stage at the weir as well as at the bog site was recorded at10 minute time resolution by a water level logger (Odyssey dataflow systems, New Zealand) installed in a slotted PVC piezometer tube of 4 cm diameter. Temperature, humidity and precipitation was monitored on site in the same resolution as the water level (using a tipping-bucket rain-gauge and tinytag tgp 4500 and 4810, Gemini, Belgium).

1.3 Laboratory Analysis, indices and PARAFAC modelling

Water samples were vacuum filtered with a 0.45 µm nylon filter (Merck Millipore, Germany) and stored in the dark at 4°C. All water samples were analyzed for DOC by thermo-catalytic oxidation using the NPOC method (non-purgeable organic carbon; multi N/C 2100S, Analytik Jena, Germany). UV-VIS spectra of all samples were recorded with a Lambda 25 (Perkin Elmer, USA) in the range of 200-800 nm at 0.5 nm resolution. A possible iron interference was excluded as the maximum iron concentration of 500 µg L^{-1} (and an iron to carbon ratio of about 0.01) was well below published critical concentration levels (see Weishaar et al. 2003, Xiao et al. 2013, Poulin et al. 2014). For subsequent fluorescence spectroscopy, samples were diluted to absorption <0.3 at 254 nm to reduce inner-filter effects. Absorbance at 254 nm wavelength (abs$_{254nm}$, expressed in m^{-1}) was used as an indicator for the absolute aromaticity of DOM samples as conjugated systems like aromatic molecules have the greatest absorption in the UV range of 200-380 nm (Weishaar et al. 2003). SUVA$_{254}$ was calculated by dividing absorbance at 254 nm (in m^{-1}) by the DOC concentration (in mg L^{-1}) according to Weishaar et al. (2003) with increasing SUVA$_{254}$ values indicating a higher aromaticity. The spectral slope ratio (S$_R$), a proxy inversely related to molecular weight, was calculated after Helms et al. (2008) by dividing the slope in the interval of 275-295 nm by the slope at 350-400 nm. Slopes were determined using linear regression of log-transformed absorption spectra.

Fluorescence spectroscopy was conducted in about three month interval measurement campaigns. During this time filtered samples were stored at 4° C in the dark. Fluorescence excitation-emission matrices (EEMs) were collected with a Cary eclipse fluorescence spectrometer (Agilent, USA) in 5 nm steps over an excitation range of 240-450 nm and 2 nm steps over an emission range of 300-600 nm. Inner filter correction, blank subtraction and Raman normalization was performed using the drEEM 0.2.0 toolbox from Murphy et al. (2013) and MATLAB (Version 2013a, MathWorks, USA). Reshaped EEMs were subjected to parallel factor analysis (PARAFAC) to obtain hypothetical fluorophores for DOM fingerprinting. In total, 435 samples were included in the PARAFAC model, both discharge and pore water samples originating from different sites. Samples examined in this study accounted for 242 samples within this model. A five fluorescence component model could be obtained and split-half validated following the drEEM and N-way toolbox (Murphy et al., 2013 and Stedmon and Bro, 2008). The sum of fluorescence intensities of the modeled components thereby represents the total fluorescence of a sample. The contribution of fluorescent DOM (fDOM) to total DOC was evaluated by normalizing total fluorescence by DOC concentrations (fDOM/DOC ratio).

The FI was calculated by the ratio of fluorescence emission intensities at 470 nm and 520 nm at an excitation wavelength of 370 nm (Cory and McKnight, 2005). The FI differentiates between plant derived (FI: 1.3 - 1.4) and microbial or planktonic derived DOM (FI: 1.7 – 2.0) (McKnight et al., 2001) as the ratio represents the greater decrease in emission with increasing wavelengths of microbial derived DOM. As our study site is a headwater catchment we assume that all DOM is of terrestrial origin and therefore, we interpret an FI > 1.7 as microbial derived or microbial processed DOM. The humification index (HIX) was calculated after the modified equation of Ohno (2002) whereby higher values in a range of 0 to 1 indicate a red-shift of spectral emission and a higher degree of DOM humification.

1.4 Statistical analyses

Statistics were performed using IBM SPSS 24. The dataset was split regarding sampling sites (bog or forest) and was further divided into a seasonal (6 day interval) and an event record (high resolution sampling campaigns). On each subdataset descriptive statistics of mean, median, minimum and maximum value, and standard deviation (SD) were performed. As all datasets were not normal distributed (after Shapiro-Wilk test) nor had a homogeneity of variance (Levene's test). Spearman's rank correlation was used to test correlations of specific parameters. Accordingly, the Mann-Whitney or Kruskall-Wallis test with Bonferroni correction was applied to test significant differences between non-parametric datasets (0.05 level of significance).

3 Results

3.1 Seasonal trends

3.1.1 Hydrologic conditions and DOC concentrations

The DOC concentration record and hydrologic characteristic at the bog site has been described previously in Broder and Biester (2015). In short, bog discharge exhibited a flashy regime with an instantaneous response to rain events. The rain event with the highest recorded discharge peak occurred in spring, while in summer a longer drought period resulted in very low discharge and little response to rain fall due to recovery of water storage within the bog. More frequent rain events in fall at wetter antecedent moisture conditions caused again more flashy discharge and concentration responses.

The variability of DOC concentrations over the year ranged between 5.0 to 45.8 mg L^{-1} (SD of 7.0 mg L^{-1} at the forested site and 8.1 mg L^{-1} at the bog site) and was larger than during single rain events at both sites, where standard deviations ranged between 1.3 to 1.9 mg L^{-1} at the bog site and 0.6 to 4.2 mg L^{-1} at the forested site (Fig. 2, 3 and Table 1). However, the rain event in fall was responsible for the highest recorded DOC concentrations of 37.3 mg L^{-1} and 45.8 mg L^{-1} during the entire study period at both sites. The concentration trend generally followed the vegetation period with highest concentrations in late summer and fall. Spearman's correlation of DOC concentrations with mean daily air temperature was significant and positive at the bog site (coefficient of 0.591; $p < 0.01$, two-tailed), but not at the forested site. Lowest concentrations of 5.0 and 10.2 mg L^{-1} were measured during snowmelt at both sites. Concentrations of DOC were significantly higher at the forested site (median of 32.1 mg L^{-1}) than at the bog outlet (median of 25.7 mg L^{-1}) over the whole sampling period (see Table 1).

3.1.2 DOM quality using spectrofluorometric indices

The abs$_{254nm}$ as index for total aromaticity of the DOM exhibited a similar trend as the DOC concentrations at both sites over the year (Fig. 2). Nonetheless, SUVA$_{254}$ values as index for proportional aromaticity of DOM, varied between 3.5 and 5.2 at the bog site and between 3.4 and 5.9 at the forested site, but with no seasonal trend as observed for DOC concentrations. According to Weishaar et al. (2003) calculated SUVA$_{254}$ values corresponded to a DOM aromaticity of 27 – 38 % for the bog

site and 29 - 42 % for the forested site. Variations were mainly induced by hydrologic conditions with high values during rain events in spring (up to 5.5). Mean $SUVA_{254}$ values were higher at the forested site ($SUVA_{254}$ of 4.6, SD of 0.5), but showed a larger variability than at the bog site (mean $SUVA_{254}$ of 4.4, SD of 0.4, see also Table 1). During the summer drought period $SUVA_{254}$ values decreased at both sites, but stronger at the forested site (Fig. 2).

5   As expected, the S_R as reciprocally proportional index for molecular weight of DOM exhibited an opposite trend than $SUVA_{254}$ (Fig. 2) expressed in a negative correlation on a 0.01 level of significance (Spearman correlation coefficient of -0.616 at the bog site and -0.598 at the forest site). The annual dynamic was similar at both sites, but with higher S_R during snowmelt (S_R up to 2.2) and sampled rain events (S_R 1.7-2.0) at the forested site (Fig. 3), indicating a lower molecular weight than at the bog site. During the summer drought S_R steadily increased from 1.7 to 2.0 indicating decreasing molecular weight. With the onset

10   of fall rain events molecular weight increased again indicated by lower S_R values.

     The humification index (HIX), as well as the fluorescence index (FI) also exhibited no annual trend (Fig. 4). At the bog and the forested site HIX only varied during snowmelt and spring events with lower values down to 0.76 and 0.81, respectively, compared to HIX in summer and fall, where values remained between 0.90 - 0.94 and 0.91 – 0.95, respectively. FI exhibited values between 1.5 and 1.75 with significantly higher values at the forested site. At the forested site FI increased during summer

15   drought (from 1.5 to 1.7).

3.1.3 Hypothetical fluorophores modeled by PARAFAC

     To facilitate a description of the PARAFAC results, the identified components are briefly described here and compared to hypothetical fluorophores typically observed in other studies. PARAFAC modeling resulted in a five component model with four humic-like and one protein-like hypothetic fluorophores. Excitation-Emission regions of each component can be found

20   in Fig. 5. The modeled PARAFAC component C1 can be compared to a terrestrial, humic-like fluorophore originating from forests and wetlands soils, as described by Perdrial et al. (2014) and C2 can again be described as humic-like (see e.g. C3 of Singh et al., 2014), but the excitation-emission region is shifted to higher excitation and emission wavelengths compared to C1 indicating more conjugated and more aromatic fluorescent molecules. A component similar to C3 has previously been described as humic, but also of terrestrial origin, small molecular size, recalcitrant and reduced (Cory and McKnight, 2005;

25   Singh et al., 2014; Fellman et al., 2008; Perdrial et al., 2014). C4 is only slightly shifted compared to the excitation-emission region of C3 and compares to C2 from Fellman et al. (2008) and Ohno and Bro (2006), another humic-like fluorophore. C5 could be described as tryptophan-like, of microbial origin, labile and of recent biological production (described in e. g. Fellman et al. (2008) as C8). It can be used as proxy for BDOM (Fellman et al., 2008). In C1 and C3 also fulvic-like fluorophores might be included, which are more hydrophilic and therefore more mobile than the humic-like DOM (in Fellman et al. (2008): C3,

30   C4), but could not be clearly separated in individual components.

3.1.4 DOM quality using PARAFAC

The fDOM, as the sum of all fluorescent components modeled by PARAFAC, showed changes with discharge events with both minimum and maximum intensities during sampled discharge events (Fig. 4). Fluorescence was elevated during summer and lower values occurred in spring and fall at both sites. Normalizing fDOM to DOC concentrations, a decrease in the fluorophore fraction in DOM from spring to fall could be observed (Fig. 4). This fluorophore fraction decreased also during individual sampled rain events.

The fDOM at the bog site showed little seasonal changes in the contribution of the four components over the year. Greatest changes were perceived during snowmelt with highest protein-like C5% (~10-17%) and variable humic-like C1%, C2% and C4% contributions at the bog site (Fig. 7). The protein-like C5% contributed least to fDOM with about 5% during most of the record. The components C1% and C4% increased during summer drought at the bog site (Fig. 6). The protein-like C5% contributed largely to fDOM during snowmelt and wet spring event (Fig. 6). The humic like C1% increased during summer drought, while C2% deceased at the same time. The components C2% and C3% were significantly elevated at the forested site, while significantly higher contributions of C4% were attributed to the bog site (Fig. 6 and 7).

3.2 Snowmelt, drought and rain events

3.2.1 Snowmelt

Snowmelt samples exhibited a distinct pattern compared to discharge events in other seasons. DOC concentrations (5.0 – 11.7 mg L^{-1}), abs$_{254nm}$ (45 - 128 m^{-1}), HIX (0.76 - 0.93), and fDOM (0.6 - 1.1) were lowest and normalized fDOM/DOC (0.06 – 0.14) was highest during snowmelt at both sites (Fig. 3 and 4). Differences to other events were significant, excluding the wet spring event, though. Values of S$_R$ during snowmelt were high at the forested site with about 1.96 - 2.17, while S$_R$ at the bog site exhibited mean values of 1.78 - 1.88 (Fig. 3), which were still higher than following spring samples, though. SUVA$_{254}$ was significantly lower (4.2 – 4.5) than in following spring events at the forested site, while at the bog site SUVA$_{254}$ of 3.9 – 4.4 were similar to values of the rest of the record (Table 1, Fig. 2). The protein-like PARAFAC component C5 % was elevated during snowmelt (7 – 16 %) and was significantly higher than at the fall event at both sites (Fig. 7). Values of the humic-like C2% (median of 23 %) and C4% (median of 7 %) were low at the bog site compared to median annual values of 26 % and 10 %, respectively. At the forested site the bog derived C4% was almost absent and the humic-like forest-derived C3% was strongly elevated (contributing about 20 % to total fluorescence, Fig. 7). It should be noted though, that the snowmelt event was not entirely covered by our sampling period as the upstream water was still covered with snow.

3.2.2 Spring

The sampled spring rain events could be differentiated by hydrologic preconditions as the first event occurred under dry preconditions, while the second described spring event followed after preceding rain events under wet hydrologic preconditions. DOC concentrations and abs$_{254nm}$ were significantly higher after dry preconditions (21.9 – 31.7 mg L^{-1} and 225

– 341 m^{-1}) than after wet preconditions (9.4 – 23.1 mg L^{-1} and 102 - 281 m^{-1}) at both sites (Fig. 3). SUVA$_{254}$ values at the forested site were persistently high during the whole spring time (4.5 - 5.5), but decreased during each rain events. At the bog site SUVA$_{254}$ values were significantly lower than at the forested site during spring rain events, but were still significantly elevated compared to the fall event at the bog site. High resolution sampling before the wet preconditions spring event during low flow conditions showed a steady decrease in S$_R$ until the onset of the rain event where values momentarily peaked at the forested site. However, at the first spring event with dry precondition the S$_R$ values peaked later at the declining limb of the hydrograph. At the bog site S$_R$ values during spring events were low, but again with increasing values at the declining limb of the hydrograph, which indicates a decrease in apparent molecular size.

Contribution of protein-like component C5% exhibited elevated values during the second spring event with wet preconditions at the bog site (Fig. 6, 7). The bog derived humic-like C4% decreased during spring events at both sites (Fig. 6). This trend was more distinct at the forested site with a quick drop to zero at the second event. The humic-like C1% dropped from the first sampled spring event to the second one at the bog site, while the more aromatic C2% increased at the forested site from the first to second event. The predominantly forest derived humic-like C3% also increased at all storm events and was significantly higher at the forested site.

3.2.3 Drought

The year 2013 was characterized by a strong summer drought, which caused low discharge over the summer months. During the prevailing drought period DOC concentrations, abs$_{254nm}$ and S$_R$ increased, while SUVA$_{254}$ decreased especially at the forested site (from 5.4 to 3.7, Fig. 2). The humic-like C1% increased and the humic-like, but more aromatic C2% decreased at the forested site, while at the bog outlet an increase in the humic-like bog-derived C4% was perceived (Fig.6).

3.2.4 Fall

The fall event following the summer drought generated the highest DOC concentrations of the annual record with 45.8 mg L^{-1} DOC at the forested site and 37.3 mg L^{-1} DOC at the bog site. Even though, abs$_{254nm}$ was high and even increasing during the event at the forested site, SUVA$_{254}$ values were significantly lower than during spring events indicating a lower aromaticity of DOM in fall (Fig. 3). Congruently, S$_R$ values were higher at both sites, indicating smaller DOM during fall event. The humic-like PARAFAC components C1%, C4% and the protein-like C5% decreased during the fall rain event at the forested site, while the forest derived humic-like C2% and C3% increased (Fig. 6). The bog derived C4% contributions were significantly higher than during snowmelt and in spring at the bog site (Fig. 7), but exhibited the same decreasing trend with the ongoing rain event at both sites. The protein-like C5% exhibited lower values during the fall event than at the spring rain.

4 Discussion

As expected, the spectroscopic indices for aromaticity ($SUVA_{254}$) and apparent molecular size (S_R) were inversely correlated, which implies that an increase in aromaticity is accompanied by an increase in apparent molecular size. This suggests that aromatic structures dominate the apparent high molecular size DOM fraction in this study. Fluorometric indices exhibited different trends than UV-VIS indices even though they should reflect similar changes in DOM quality. HIX as fluorometric index for humic components showed less variability than $SUVA_{254}$. A difference between those two indices was also reported by Inamdar et al. (2011). As $SUVA_{254}$ is a proxy exclusively for aromatic DOM, HIX might include other humic or hydrophobic DOM components derived from plant decomposition. Trends of HIX in this study rather indicate that HIX represents all fluorescent humic-like components, which resulted in less variability due to a domination of humic components in all catchment compartments.

The FI values of both sites varied between 1.5 and 1.75. This indicates a domination of microbial or microbial processed DOM over vascular plants derived DOM in the catchment (Cory and McKnight, 2005). As we assume that all DOM is of terrestrial origin it implies that the majority of measured stream DOM is not fresh organic material as would be indicated by high contributions of C5%, nor highly aromatic DOM derived from plant decomposition, but has been strongly modified by microbial processes within the soils. It also indicates long residence times of DOM in the soils, as produced DOM is mainly not immediately transported to surface waters, but gets altered or consumed within the soils of the catchment. This may be supported by the high $SUVA_{254}$ values which indicate a strong aromatic fraction contributing 27 to 42% to DOM, presumably due to residual enrichment.

In contrast to other studies, the forested site exhibited higher $SUVA_{254}$ values for aromaticity most of the time. For example, Ågren et al. (2008) and Wallin et al. (2015) found similar $SUVA_{254}$ values or even higher values at a peatland site, respectively, compared to mineral soils at a forested site. On the one hand this might be due to the dominating *Sphagnum* vegetation and peat at the bog site here, as *Sphagnum* is known to produce less aromatic organic matter than vascular plants, which also occur in peatlands, due to the lack of lignin in *Sphagnum* mosses (Spencer et al., 2008). On the other hand, the domination of peaty soils in the riparian zone and the domination of shallow sub-surface flow over groundwater contribution at the forested site might enhance DOM aromaticity due to release of highly decomposed and modified organic matter. In contrast to the bog, the peaty riparian zone is subjected to great water level changes and accelerated dry-wet cycles, which result in repeated aeration and enhanced decomposition (Singh et al., 2014).

4.1 Seasonal trends in DOM concentrations and quality

Although major changes in DOC quality occurred due to hydrological changes as demonstrated by individual discharge events, also seasonal patterns occurred. DOC concentrations at the bog site were significantly correlated with daily mean air temperatures and generally followed the vegetation period with low concentrations during snowmelt and spring and highest DOC concentrations in early fall. This strong seasonal effect has been observed frequently and was ascribed to DOC production

and solubility, but also enhanced litter decay by leaf fall in early fall (Christ and David, 1996; Singh et al., 2014; Wallin et al., 2015,). Nonetheless, especially at the forested site this seasonal trend was overprinted by hydrological events, which generated high DOC concentration peaks up to 45.8 mg L^{-1} in fall due to rapid mobilization from hydrologically connected source areas. All spectrofluorometric indices and PARAFAC components exhibited major changes during high discharge. Thus they were

5   mainly controlled by hydrologic (pre-)conditions, coinciding with little changes in DOM quality over the year as observed by Perdrial et al. (2014). Due to predominance of Norway spruce, pulses of protein-like DOM from autumn leaf fall (Singh et al., 2014) would not be expected in our catchment Between the two sampling sites specific differences in PARAFAC component contributions were identified. The C4% could be denoted as a bog derived humic-like component, while C2% and C3% were predominantly forest derived humic-like components. The humic-like C1% and the protein-like C5% could not be specifically

10   attributed to one of the sites.

4.2 Event DOM characteristics and DOM sources

4.2.1 DOC concentrations

Organic-rich riparian zones are known to generate high DOC concentrations (Grabs et al., 2012). As a large part of the organic-rich upper soil layer is hydrologically connected and contributes to discharge only during events, high DOC concentrations at

15   the forested site are due to the repeated flushing of peaty soils in the riparian zone. Additionally, upper organic layers of shallow hillslope soils may get connected via surface or surface near flow networks during such events. Therefore, dry preconditions within the catchment facilitated high DOC concentrations during events of a certain magnitude when the upper soil layer gets hydrological connected. The DOC concentrations at the bog site were less sensitive to rain events and not as elevated during those events than at the forested site. Here, partly even decreasing concentrations were observed. Due to the

20   usually high water level, rain events here do not connect additional DOM pools, but lead to dilution by surface flow or an exhaustion effect (Broder and Biester, 2015). We conclude that DOC concentration peaks during rain events were mainly induced by peaty forests soils and not by bogs. Although the latter are strong C sources to the aquatic, they are less susceptible to rain events. DOC concentration trends of the bog site were further disentangled in Broder and Biester (2015).

4.2.2 Snowmelt

25   During snowmelt DOC concentration at both sites were lowest. This has been reported elsewhere (e.g. Laudon et al., 2004; Clark et al., 2008) and can be attributed not only to dilution by snow packs, but also to low microbial and plant activity. The absolute values of chromophore and fluorophore DOM were also lowest. Overall, spectrofluorometric indices point to rather small molecular size, which were less aromatic especially at the forested site. Additionally, PARAFAC components indicate a strong flush of labile, protein-like DOM. This characteristic was also more pronounced at the forested site than at the bog

30   site. The elevated export of a protein-like fraction, i.e. easily biodegradable DOM (Fellman et al., 2009), can be explained by less biotic demand and a domination of shallow flow paths during snowmelt bypassing large, strongly modified and aromatic

DOM pools in the subsurface (Fellman et al., 2009). Also, surface near freeze-thaw cycles during winter provide fresh DOM from microbial cell lysis and root mortality, which is not utilized due to the low productivity (Haei et al., 2012, Fellman et al., 2009). Differences between the two sites were more evident in other PARAFAC components. At the forested site a large fraction of humic-like fluorescence was attributed to C3%, while C4% was absent. C3% only increased strongly at the forested

5   site during rain events, while C3% remained constant at the bog site. This suggests that component C3% is predominantly sourced in the upper, organic layer of the forest soil and is only mobilized during rain events, when these surface near layers get hydrologically connected, even during snowmelt. As this component increases strongest of all identified components, higher DOC concentrations during rain events should be mainly caused by a connection of surface-near organic-rich layers to the streams, irrespective of the season. In our study an increase of C3% coincide with lower $SUVA_{254}$ and higher S_R and FI

10   values. This points to a microbially modified, recalcitrant, but less aromatic DOM fraction of smaller apparent molecular size, confirming previous descriptions of a largely similar fluorophore (e.g Fellman et al., 2008; Singh et al., 2014). Overall, the snowmelt DOM can be described as smaller, less chromophoric, less aromatic and more biodegradable due to a higher protein-like fraction, which is more pronounced at the forested site and has its source in the upper soil layer.

4.2.3 Drought

15   A drought period during summer 2013 caused a strong decrease in the bog water level down to 35 cm depth and exceptionally low discharge representing pronounced baseflow conditions. This dry period induced concomitant changes in DOM quality in stream discharge. While DOC concentrations at both sites continuously increased, aromaticity and apparent molecular size decreased. While FI at the bog site remained constant (around 1.55), FI at the forested site increased during drought up to 1.75 indicating a greater fraction of microbial derived, strongly modified DOM. Under these drought conditions, the indices

20   congruently picture a less aromatic, smaller, and more microbial DOM at the peaty forest soils compared to the bog site and to the rest of the record. This can be explained by a higher contribution of shallow groundwater and decreasing discharge through and DOM contributions from the peaty surface layers of the riparian zone. Due to the adsorption of larger, more aromatic compounds to mineral phases, groundwater DOM is typically of smaller molecular size and less aromatic (Meier et al., 2004; Inamdar et al., 2012). Also for the bog site increasing C1% and bog-derived humic-like C4%, as well as decreasing

25   molecular size hint to a DOM source change toward deeper peat layers. Summarizing the summer drought fingerprint, DOM during this period approaches characteristics observed for shallow groundwater at the forested site and resembles DOM from deeper peat layers at the bog site. This caused a change in DOM quality to smaller, more microbial and less aromatic components.

4.2.4 Rain events

30   The three sampled rain events distributed over spring and fall clearly differed with respect to observed changes in DOM quality. The spring events can be differentiated between dry (first event) and wet (second event) preconditions, while the fall event occurred again under dry preconditions. The main difference between these two preconditions was a significantly higher

DOC concentration under dry preconditions at both sites. While this difference in DOM concentration could be attributed to a dilution effect under wet preconditions at the bog site, also notable differences in DOM quality occurred: The non-fluorescent DOM fraction was clearly elevated following dry preconditions. This indicates that under dry preconditions a specific DOM fraction, which cannot be separated by fluorometric indices, is exported compared to wet preconditions. As non-fluorescent

5   DOM is probably more easily degradable DOM like organic acids or products of biotic activity, this might be a flushing effect, when upper soil layer gets hydrological connected after prolonged aeration, decomposition and concomitant enrichment of potentially mobile DOM, while under wet preconditions this DOM fraction gets exhausted. As this flushing effect also occurred at the dry fall event, the export of this DOM fraction may be mainly attributed to the hydrologic preconditions and not to the low demand of labile DOM in early spring, as has been suggested elsewhere (Fellman et al., 2009). This would

10   further imply that focusing on the protein-like C5% as proxy for BDOM (Fellman et al., 2008) neglects a further labile DOM fraction, which might serve as nutrient source downstream and does not correlate with protein-like fluorescence.

A major seasonal difference between spring and fall event is, that there were no elevated protein-like DOM exports in fall. However, elevated contributions of protein-like fluorescence as described before (Singh et al., 2014) were ascribed to leaf fall at that time of the year. As in our catchment only coniferous trees occurred, this may not be observed in this study. However,

15   the contribution of the non-fluorescent fraction in fall was even higher than in spring. This might be indicative of higher biotic activity, generating small, non-fluorescent molecules, and demonstrates inherent limitations of the spectrofluorometric approach of DOM characterization.

At the forested site trends of $SUVA_{254}$, HIX and S_R indicated a decreasing aromaticity and apparent molecular size during all rain events. This is confirmed by an increasing FI up to 1.74, meaning a shift to more microbial DOM. The DOM was even of

20   smaller apparent molecular size and less aromatic during fall event even though trends of the indices were partly reversed. This reversal was due to the extreme dry preconditions and prevailing baseflow with a high microbial derived DOM fraction, primarily originating from groundwater and deep peat. With the onset of a rain event the organic soil layers get hydrologically connected, leading to a decrease of microbially, shallow groundwater derived compounds and an increase in more aromatic DOM originating from the strongly humified organic matter of the peaty layers. Taking together the trend of the humic-like

25   C1% at the forested site during events and drought period reveals that this component probably represent a rather microbial processed DOM fraction from groundwater, while humic-like C2% and C3% largely contribute to DOM under high discharge conditions and therefore represent a DOM sourced in the upper soil layers. In contrast to other studies (Hood et al., 2006, Inamdar et al., 2011), a general increase of aromatic DOM during rain events at the forested site was not recorded, but an increase in humic and microbial DOM indicating that the humic-like C3% is also microbial derived DOM, but from another

30   source. However, under wet preconditions the decrease in $SUVA_{254}$ was less distinct and C2%, indicative of a shift to rather aromatic structures, contributed stronger to fDOM than under dry preconditions. This indicates a stronger aromatic contribution to DOM export from upper soil layer under wet preconditions at the forested site, while under dry preconditions longer aeration may yield more modified, less aromatic DOM that has pooled up during drought.

Under wet preconditions DOM quantity and quality differed significantly between sites, as expressed by significant differences of all indices except of the PARAFAC component C1%. At the bog site much less DOC was exported than at the forested site indicating an exhaustion, as well as a dilution effect of the surficial DOM pool here (Broder and Biester, 2015). Hydraulic conductivities at greater depths, where high DOM concentrations prevail, are presumably too low for rapid mobilization.

5 Compared to changes at the forested site, aromaticity only moderately shifted during rain events and over seasons. However, even though aromaticity was not elevated at the bog site, S_R indicated DOM of a rather large molecular size being mobilized under wet preconditions. Also the protein-like component was highest at the wet spring event, which is explained by flushing of fresh biotic material in the surface layer. Moreover, during this event overland flow is very likely (Broder and Biester, 2015), which might further leach larger polymers of proteins, cellulose or polysaccharides from the living biomass. Also,

10 Fellman et al., (2009) reported an increase in protein-like DOM export and related this to lower residence times and low biotic demand in a wetland catchment. Unfortunately, S_R was not monitored in that study. The bog specific humic-like C4% component only moderately decreased during rain events and increased over summer drought at the bog site. This dynamic in C4% presumably describes a component from deeper peat layer, which is constantly exported over the year and gets diluted by upper surface or surface-near export during high discharge events. Therefore, this component may be used as tracer for

15 deep bog porewater and the observed dilution effect clearly points out that bogs do not primarily drive variations in DOM loads of streams.

Summarizing dynamics during events, DOM quality changes reflect different contributions of DOM pools depending on hydrologic preconditions and season. Fresh and labile DOM was exported during spring events at both sites, especially under wet preconditions at the bog site. Even though aromaticity of DOM in the studied catchment was high, events showed an

20 increase in microbial or strongly microbially altered DOM. However, PARAFAC components show that this assumed microbial component is not only sourced in shallow groundwater, but that there is an additional microbial DOM pool in the upper soil layer that is especially mobilized under dry preconditions. Comparing the two sites our results demonstrate that not only major dynamics in DOM quantities, but also variability in DOM quality was mainly driven by the forested site, i.e. by shallow peaty soils with stronger variations in water tables and thus hydraulic connectivity of the different layers.

25 **5 Conclusion**

Variability in stream water DOM quantity and quality was primarily generated at the forested site with peaty riparian zones and not at the bog site. Thereby, changes in headwater DOM quality were mainly induced by hydrologic conditions, which points out the importance of high resolution studies and consideration of high discharge events, which not only generate highest DOC concentrations, but export different DOM pools with different chemical properties and fate in aquatic systems. Especially

30 under wet preconditions DOM quantity and quality differed significantly between the bog and the forested site. There was no clear seasonal trend in DOM quality, but DOM concentrations at the bog site generally followed the temperature trend. Nevertheless, the response of DOM quality to changes in hydrologic conditions differed probably also depending on season.

The export of protein-like DOM components was specific for snowmelt and for spring events after wet preconditions at this study site. Those DOM compounds might serve as important nutrient source in the aquatic system. Nevertheless, not only during spring events, but also in fall a non-fluorescent DOM fraction of small apparent molecular size was exported especially during events with dry preconditions that may be of similarly high bioavailability. During drought periods DOM export was

5 limited to deeper peat layer at the bog site and shallow groundwater at the forested site as could be tracked by indices displaying a microbial DOM signature originating from long DOM residence times in the soil and peat. At events with wet preconditions additional surface-near DOM pools were connected due to increasing water levels in the catchment. Next to aromatic DOM compounds, a surface-near microbial DOM fraction was exported during those events, as could be tracked by specific PARAFAC components. While at the bog site a dilution effect of DOM concentration sets in under wet preconditions the

10 forested site generated highest DOM concentration peaks under wet preconditions

The different spectrofluorometric indices were generally suitable to track origin and dynamics of DOM. However, it must be considered that this method could not display apparent dynamics in a non-fluorescent fraction, triggered by hydrologic conditions and season. The PARAFAC modeling of different DOM components proofed a useful tool to track export dynamics of different DOM pools under different seasonal and hydrologic conditions, which could have not been resolved by the

15 spectrofluorometric indices alone. Moreover, our study demonstrates the need for approaches tracking DOM sources to understand DOM export dynamics, while approaches based solely on hypothetic hydrological compartments, such as surface flow, soil water and groundwater, may be too simplistic. This understanding of how different DOM pools gets exported might become even more important in view of future changes in the hydrologic regime due to climate change.

Competing interests

20 The authors declare that they have no conflict of interest.

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References

Ågren, A. M., Buffam, I., Cooper, D. M., Tiwari, T., Evans, C. D., and Laudon, H.: Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements?, Biogeosciences, 11, 1199–1213, doi:10.5194/bg-11-1199-2014, 2014.

5   Ågren, A., Buffam, I., Berggren, M., Bishop, K., Jansson, M., and Laudon, H.: Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer, J Geophys Res, 113, G03031, doi:10.1029/2007JG000674, 2008.

Aitkenhead, J. A., Hope, D., and Billett, M. F.: The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales, Hydrol Process, 13, 1289–1302, doi:10.1002/(SICI)1099-
10   1085(19990615)13:8<1289::AID-HYP766>3.0.CO;2-M, 1999.

Amon, R. and Benner, R.: Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, Geochimica et Cosmochimica Acta, 60, 1783–1792, doi:10.1016/0016-7037(96)00055-5, 1996.

Baumann, K.: Entwicklung der Moorvegetation im Nationalpark Harz, 1.th ed., Schriftenreihe aus dem Nationalpark Harz, 4, 244 pp., 2009.

15   Bishop, K., Seibert, J., Köhler, S., and Laudon, H.: Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry, Hydrol Process, 18, 185–189, doi:10.1002/hyp.5209, 2004.

Broder, T. and Biester, H.: Hydrologic controls on DOC, As and Pb export from a polluted peatland – the importance of heavy rain events, antecedent moisture conditions and hydrological connectivity, Biogeosciences, 12, 4651–4664, doi:10.5194/bg-12-4651-2015, 2015.

20   Christ, M. and David, M.: Temperature and moisture effects on the production of dissolved organic carbon in a Spodosol, Soil Biology and Biochemistry, 28, 1191–1199, doi:10.1016/0038-0717(96)00120-4, 1996.

Clark, J. M., Ashley, D., Wagner, M., Chapman, P. J., Lane, S. N., Evans, C. D., and Heathwaite, A. L.: Increased temperature sensitivity of net DOC production from ombrotrophic peat due to water table draw-down, Global Change Biology, 15, 794–807, doi:10.1111/j.1365-2486.2008.01683.x, 2009.

25   Clark, J. M., Lane, S. N., Chapman, P. J., and Adamson, J. K.: Export of dissolved organic carbon from an upland peatland during storm events: Implications for flux estimates, J Hydrol, 347, 438–447, doi:10.1016/j.jhydrol.2007.09.030, 2007.

Clark, J. M., Lane, S. N., Chapman, P. J., and Adamson, J. K.: Link between DOC in near surface peat and stream water in an upland catchment: Biogeochemistry of forested ecosystem - Selected papers from BIOGEOMON, the 5th International Symposium on Ecosystem Behaviour, held at the University of California, Santa Cruz, on June 25–30, 2006, Sci Total Environ,
30   404, 308–315, doi:10.1016/j.scitotenv.2007.11.002, 2008.

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., Duarte, C. M., Kortelainen, P., Downing, J. A., Middelburg, J. J., and Melack, J.: Plumbing the Global Carbon Cycle: Integrating Inland Waters into the Terrestrial Carbon Budget, Ecosystems, 10, 172–185, doi:10.1007/s10021-006-9013-8, 2007.

Cory, R. M. and McKnight, D. M.: Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter, Environ Sci Technol, 39, 8142–8149, doi:10.1021/es0506962, 2005.

Cory, R. M., McKnight, D. M., Chin, Y.-P., Miller, P., and Jaros, C. L.: Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations, Journal of Geophysical Research: Biogeosciences, 112, G04S51, doi:10.1029/2006JG000343, 2007.

Fellman, J. B., D'Amore, D. V., Hood, E., and Boone, R. D.: Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska, Biogeochemistry, 88, 169–184, doi:10.1007/s10533-008-9203-x, 2008.

Fellman, J. B., Hood, E., D'Amore, D. V., Edwards, R. T., and White, D.: Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds, Biogeochemistry, 95, 277–293, doi:10.1007/s10533-009-9336-6, 2009.

Frost, P. C., Larson, J. H., Johnston, C. A., Young, K. C., Maurice, P. A., Lamberti, G. A., and Bridgham, S. D.: Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed, Aquat Sci, 68, 40–51, doi:10.1007/s00027-005-0802-5, 2006.

Grabs, T., Bishop, K., Laudon, H., Lyon, S. W., and Seibert, J.: Riparian zone hydrology and soil water total organic carbon (TOC): implications for spatial variability and upscaling of lateral riparian TOC exports, Biogeosciences, 9, 3901–3916, doi:10.5194/bg-9-3901-2012, 2012.

Haei, M., Öquist, M. G., Ilstedt, U., and Laudon, H.: The influence of soil frost on the quality of dissolved organic carbon in a boreal forest soil: combining field and laboratory experiments, Biogeochemistry, 107, 95–106, doi:10.1007/s10533-010-9534-2, 2012.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol Oceanogr, 53, 955–969, doi:10.4319/lo.2008.53.3.0955, 2008.

Hood, E., Gooseff, M. N., and Johnson, S. L.: Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon, J Geophys Res, 111, G01007, doi:10.1029/2005JG000082, 2006.

Hruška, J., Köhler, S., Laudon, H., and Bishop, K.: Is a Universal Model of Organic Acidity Possible: Comparison of the Acid/Base Properties of Dissolved Organic Carbon in the Boreal and Temperate Zones, Environ. Sci. Technol., 37, 1726–1730, doi:10.1021/es0201552, 2003.

Inamdar, S., Finger, N., Singh, S., Mitchell, M., Levia, D., Bais, H., Scott, D., and McHale, P.: Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA, Biogeochemistry, 108, 55–76, doi:10.1007/s10533-011-9572-4, 2012.

Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H., and McHale, P.: Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, J Geophys Res, 116, G03043, doi:10.1029/2011JG001735, 2011.

Jansson, M., Berggren, M., Laudon, H., and Jonsson, A.: Bioavailable phosphorus in humic headwater streams in boreal Sweden, Limnol. Oceanogr., 57, 1161–1170, doi:10.4319/lo.2012.57.4.1161, 2012.

Jansson, M., Persson, L., Roos, A. M. de, Jones, R. I., and Tranvik, L. J.: Terrestrial carbon and intraspecific size-variation shape lake ecosystems, Trends in Ecology & Evolution, 22, 316–322, doi:10.1016/j.tree.2007.02.015, 2007.

5 Kaiser, K. and Zech, W.: Dissolved organic matter sorption by mineral constituents of subsoil clay fractions, Journal of Plant Nutrition and Soil Science, 163, 531–535, doi:10.1002/1522-2624(200010)163:5<531:AID-JPLN531>3.0.CO;2-N, 2000.

Karlsson, J., Byström, P., Ask, J., Ask, P., Persson, L., and Jansson, M.: Light limitation of nutrient-poor lake ecosystems, Nature, 460, 506–509, doi:10.1038/nature08179, 2009.

Korshin, G. V., Li, C.-W., and Benjamin, M. M.: Monitoring the properties of natural organic matter through UV spectroscopy:
10 A consistent theory, Water Res, 31, 1787–1795, doi:10.1016/S0043-1354(97)00006-7, 1997.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and Köhler, S.: Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling, Ecosystems, 14, 880–893, doi:10.1007/s10021-011-9452-8, 2011.

Laudon, H., Köhler, S., and Buffam, I.: Seasonal TOC export from seven boreal catchments in northern Sweden, Aquat Sci,
15 66, 223–230, doi:10.1007/s00027-004-0700-2, 2004.

Ledesma, J. L. J., Grabs, T., Futter, M. N., Bishop, K. H., Laudon, H., and Köhler, S. J.: Riparian zone control on base cation concentration in boreal streams, Biogeosciences, 10, 3849–3868, doi:10.5194/bg-10-3849-2013, 2013.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol Oceanogr,
20 46, 38–48, doi:10.4319/lo.2001.46.1.0038, 2001.

Meier, M., Chin, Y.-P., and Maurice, P.: Variations in the composition and adsorption behavior of dissolved organic matter at a small, forested watershed, Biogeochemistry, 67, 39–56, doi:10.1023/B:BIOG.0000015278.23470.f7, 2004.

Monteith, D. T., Stoddard, J. L., Evans, C. D., Wit, H. A. de, Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., and Vesely, J.: Dissolved organic carbon trends resulting from changes in
25 atmospheric deposition chemistry, Nature, 450, 537–540, doi:10.1038/nature06316, 2007.

Mulholland, P. J. (2003): Large-Scale Patterns in Dissolved Organic Carbon Concentration, Flux and Sources. In: S. E. G. Findlay und R. L. Sinsabaugh (Hg.): Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. San Diego, London: Academic Press/Elsevier, S. 139–160.

Murphy, K. R., Stedmon, C. A., Graeber, D., and Bro, R.: Fluorescence spectroscopy and multi-way techniques. PARAFAC,
30 Analytical Methods, 5, 6557–6566, doi:10.1039/c3ay41160e, 2013.

Ohno, T.: Fluorescence Inner-Filtering Correction for Determining the Humification Index of Dissolved Organic Matter, Environ. Sci. Technol., 36, 742–746, doi:10.1021/es0155276, 2002.

Ohno, T. and Bro, R.: Dissolved organic matter characterization using multiway spectral decomposition of fluorescence landscapes, Soil Science Society of America Journal, 70, 2028–2037, doi:10.2136/sssaj2006.0005, 2006.

Perdrial, J. N., McIntosh, J., Harpold, A., Brooks, P. D., Zapata-Rios, X., Ray, J., Meixner, T., Kanduc, T., Litvak, M., Troch, P. A., and Chorover, J.: Stream water carbon controls in seasonally snow-covered mountain catchments: impact of inter-annual variability of water fluxes, catchment aspect and seasonal processes, Biogeochemistry, 118, 273–290, doi:10.1007/s10533-013-9929-y, 2014.

5 Poulin, B. A., Ryan, J. N., and Aiken, G. R.: Effects of Iron on Optical Properties of Dissolved Organic Matter, Environ Sci Technol, 48, 10098–10106, doi:10.1021/es502670r, 2014.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., and Bishop, K.: Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model, Hydrol Earth Syst Sc, 13, 2287–2297, doi:10.5194/hess-13-2287-2009, 2009.

10 Singh, S., Inamdar, S., Mitchell, M., and McHale, P.: Seasonal pattern of dissolved organic matter (DOM) in watershed sources: influence of hydrologic flow paths and autumn leaf fall, Biogeochemistry, 118, 321–337, doi:10.1007/s10533-013-9934-1, 2014.

Spencer, R. G. M., Aiken, G. R., Wickland, K. P., Striegl, R. G., and Hernes, P. J.: Seasonal and spatial variability in dissolved organic matter quantity and composition from the Yukon River basin, Alaska, Global Biogeochemical Cycles, 22, GB4002,
15 doi:10.1029/2008GB003231, 2008.

Stedmon, C. A. and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: A tutorial, Limnol Oceanogr-Meth, 6, 572–579, doi:10.4319/lom.2008.6.572, 2008.

Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J. H., Peiffer, S., and Matzner, E.: Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements, Biogeosciences,
20 10, 905–916, doi:10.5194/bg-10-905-2013, 2013.

Tipping, E., Rey-Castro, C., Bryan, S. E., and Hamilton-Taylor, J.: Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation, Geochim Cosmochim Ac, 66, 3211–3224, doi:10.1016/S0016-7037(02)00930-4, 2002.

Wallin, M. B., Weyhenmeyer, G. A., Bastviken, D., Chmiel, H. E., Peter, S., Sobek, S., and Klemedtsson, L.: Temporal control
25 on concentration, character, and export of dissolved organic carbon in two hemiboreal headwater streams draining contrasting catchments, J. Geophys. Res. Biogeosci., 120, 832–846, doi:10.1002/2014JG002814, 2015.

Ward, C. P. and Cory, R. M.: Complete and Partial Photo-oxidation of Dissolved Organic Matter Draining Permafrost Soils, Environ. Sci. Technol., 50, 3545–3553, doi:10.1021/acs.est.5b05354, 2016.

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and Mopper, K.: Evaluation of Specific Ultraviolet
30 Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon, Environ Sci Technol, 37, 4702–4708, doi:10.1021/es030360x, 2003.

Winterdahl, M., Erlandsson, M., Futter, M. N., Weyhenmeyer, G. A., and Bishop, K.: Intra-annual variability of organic carbon concentrations in running waters: Drivers along a climatic gradient, Global Biogeochem Cy, 28, 451–464, doi:10.1002/2013GB004770, 2014.

Worrall, F., Burt, T. P., Jaeban, R. Y., Warburton, J., and Shedden, R.: Release of dissolved organic carbon from upland peat, Hydrol Process, 16, 3487–3504, doi:10.1002/hyp.1111, 2002.

Worrall, F., Burt, T., and Adamson, J.: Can climate change explain increases in DOC flux from upland peat catchments?, Sci Total Environ, 326, 95–112, doi:10.1016/j.scitotenv.2003.11.022, 2004.

Xiao, Y.-H., Sara-Aho, T., Hartikainen, H., and Vähätalo, A. V.: Contribution of ferric iron to light absorption by chromophoric dissolved organic matter, Limnol Oceanogr-Meth, 653–662, 2013.

Table 1: General descriptive statistics (mean, median, standard deviation (SD), minimum and maximum values) for DOC concentrations, and DOM quality parameters (abs$_{254nm}$, SUVA, S_R, FI, HIX, C1%, C2%, C3%, C4% and C5%) over the whole sampling period. High resolution rain event data is excluded to project seasonal variability.

	DOC		Abs254		SUVA$_{254}$		S_R		FI		HIX	
	Bog*	Forest*	Bog*	Forest*	Bog	Forest	Bog*	Forest*	Bog*	Forest*	Bog	Forest
N	32	37	32	42	32	36	32	42	22	20	22	20
Mean	23.0	30.4	233	304	4.4	4.6	1.80	1.84	1.58	1.63	0.91	0.92
Median	25.7	32.1	250	313	4.4	4.6	1.78	1.83	1.58	1.64	0.92	0.92
SD	8.1	7.0	79	79	0.4	0.5	0.09	0.08	0.04	0.05	0.04	0.02
Min	5.0	11.2	49	113	3.5	3.4	1.67	1.71	1.52	1.55	0.76	0.86
Max	36.6	45.8	384	489	5.2	5.9	2.00	1.98	1.68	1.75	0.95	0.95

	C1%		C2%		C3%		C4%		C5%	
	Bog	Forest	Bog*	Forest*	Bog*	Forest*	Bog*	Forest*	Bog	Forest
N	22	20	22	20	22	20	22	20	22	20
Mean	44	44	26	28	14	17	10	6	6	5
Median	44	44	26	28	14	17	10	7	5	5
SD	1	1	2	1	1	2	2	4	3	2
Min	40	42	23	25	12	13	4	0	4	3
Max	47	46	29	30	15	21	13	12	14	10

* Significant differences between bog and forested site (Mann-Whitney; two-tailed, $\rho < 0.05$)
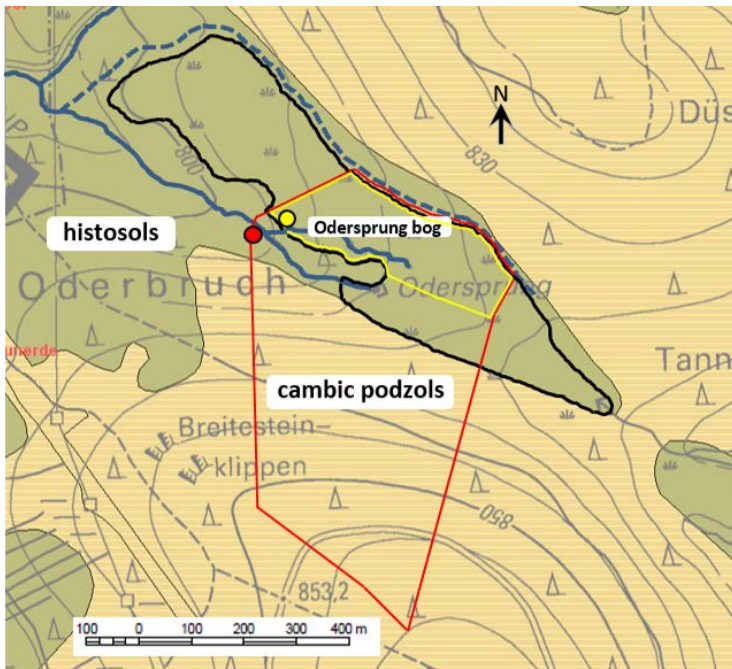
Figure 1: Location of the study area in the Harz Mountains, Germany. Red and yellow lines indicate each catchment boundaries, circles represent the discharge monitoring spots (yellow – bog catchment, red – forest catchment with peaty riparian zone). Green areas indicate peaty soils, beige-colored areas outline mineral cambic podzol soils. The bog area, is confined by the bold black line. Map Source: NIBIS mapserver, Lower Saxony authority for mining, energy and geology (LBEG).
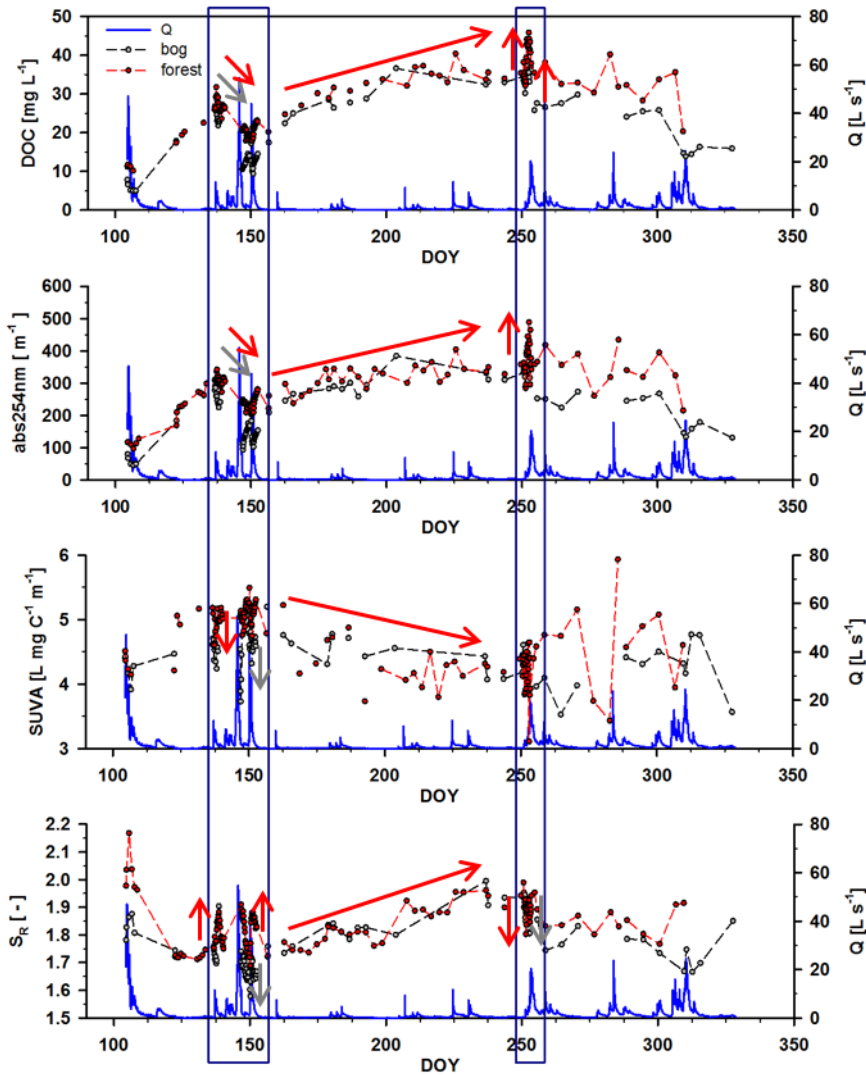
Figure 2: Annual records of DOC concentrations, abs$_{254nm}$, SUVA$_{254}$, and S$_R$ from top to bottom (DOY - day of the year) in 2013. The blue line represents the bog discharge (Q). Grey circles represent the bog site, red circles the forested site, while arrows indicate concentration or index trends during rain events and summer drought at the different sites. Sampled rain events in spring and fall are highlighted by blue boxes.
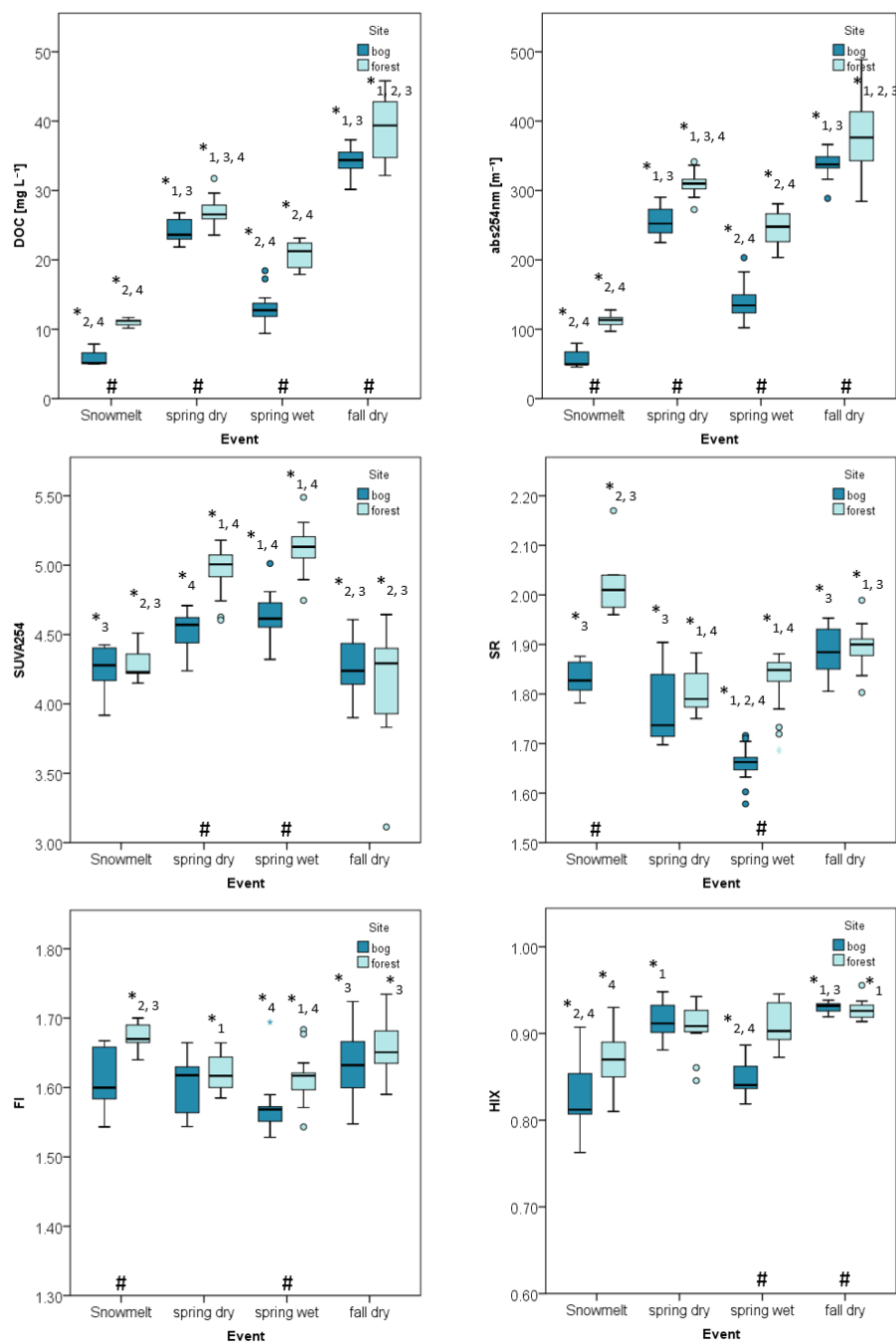
Figure 3: Box plots of SUVA, S_R, HIX, DOC concentrations, abs$_{254nm}$ and FI during events. Dark blue bars indicate the bog site, lighter blue bars the forested site. Asterisks indicate a significant difference between events (Kruskall-Wallis; $\rho < 0.05$), which are indicated by added numbers: 1 – snowmelt, 2 – spring dry, 3 – spring wet, 4 – fall dry. Significant differences between the bog and the forested site at an event (Mann-Whitney; $\rho < 0.05$) are indicated by a hash. A table of descriptive statistics for each event can be found in the Supplement.
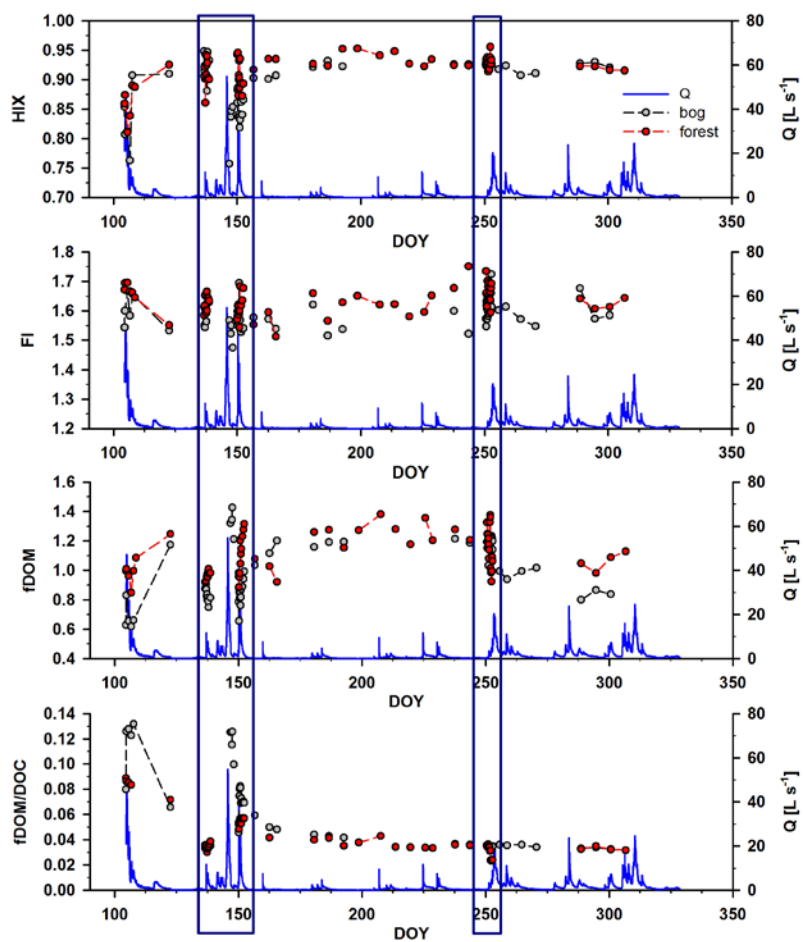
Figure 4: Annual record of the humification index (HIX), fluorescence index (FL), sum of all Fmax PARAFAC components values (fDOM) and fDOM to DOC concentration (in mg L^{-1}) ratio against day of the year (DOY) in 2013. The blue line represents the bog discharge (Q). Grey circles represent the bog site, red circles the forested site. Sampled rain events in spring and fall are highlighted.
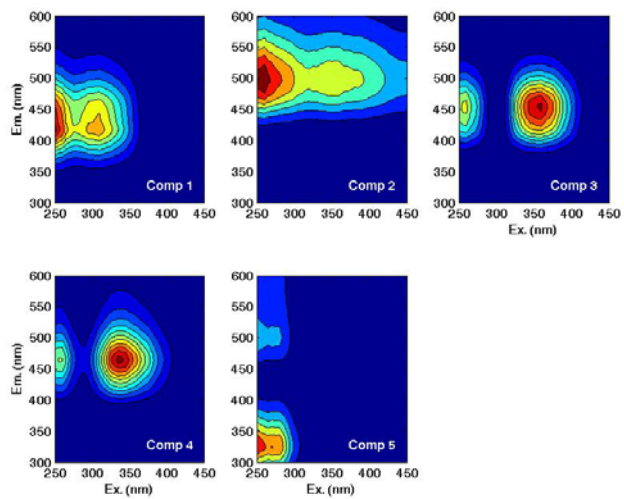
Figure 5: Characteristic EEMs of all five modeled PARAFAC components. For further component description see section 3.1.3.
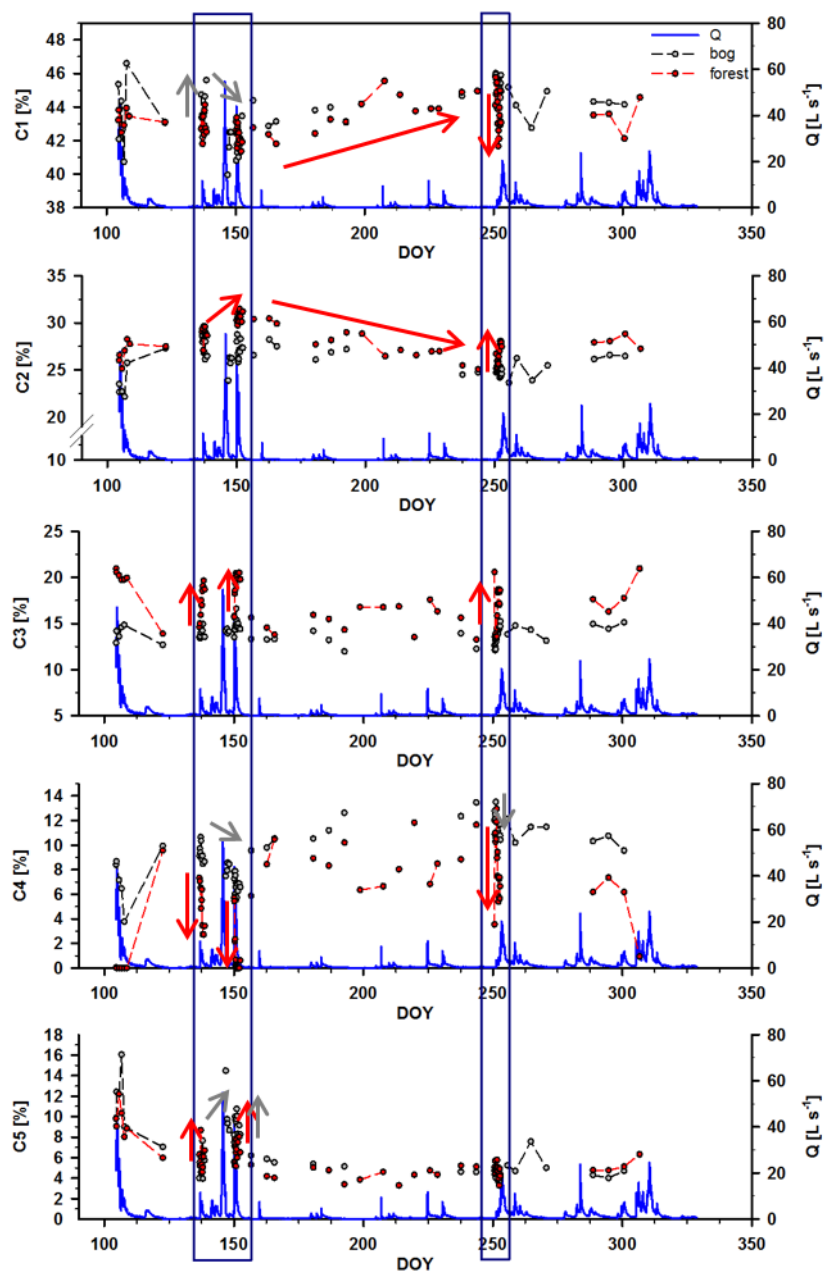
Figure 6: Percentage of PARAFAC components C1-C5. Blue line represents the bog discharge (Q). Grey dots indicate bog site values, red dots forest site values. Sampled rain events in spring and fall are highlighted.
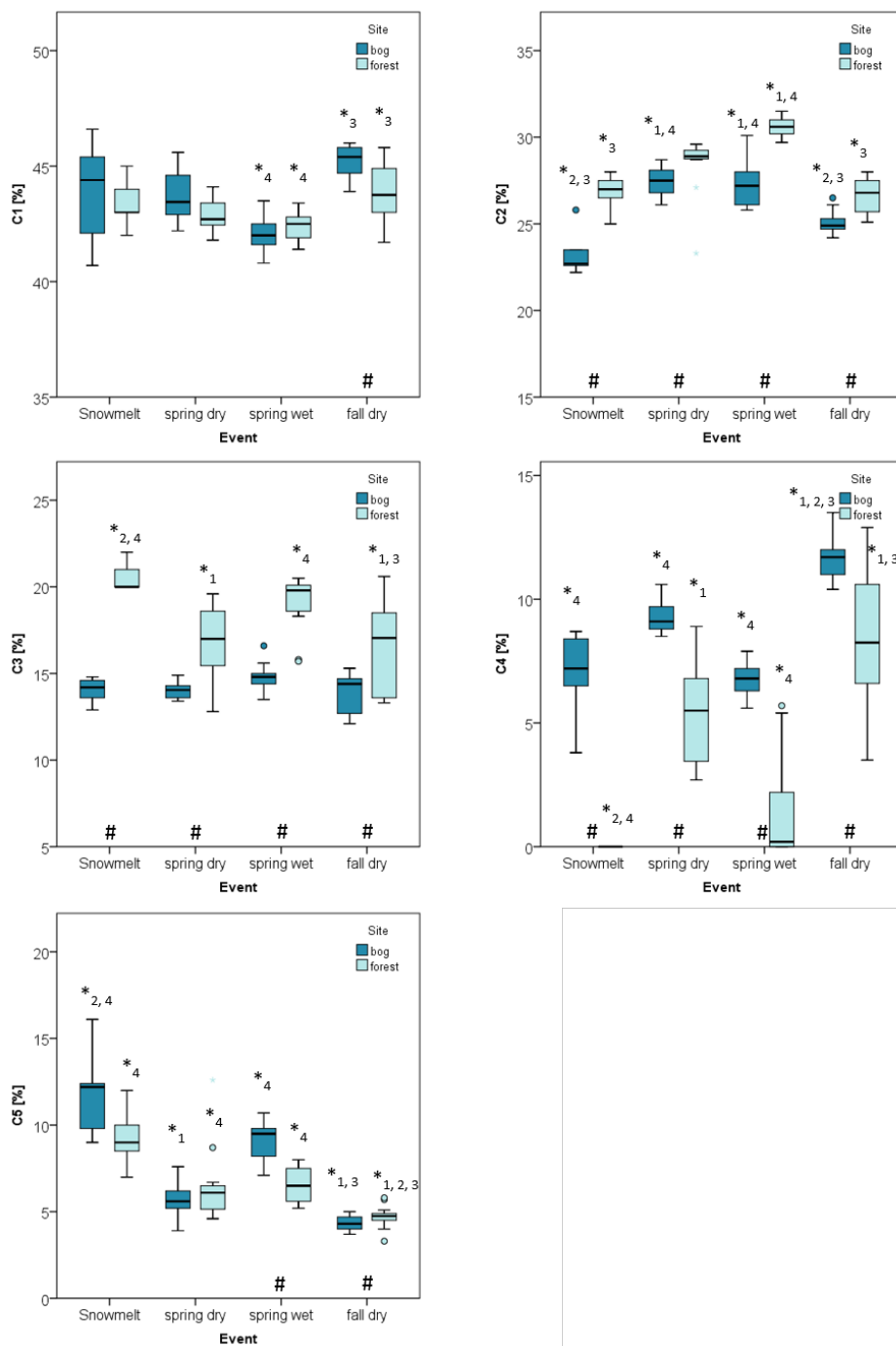
Figure 7: Box plots of PARAFAC components during events. Dark blue bars indicate the bog site, lighter blue bars the forested site. A table of descriptive statistics for each event can be found in the Supplement. Asterisks indicate a significant difference between events (Kruskall-Wallis; $\rho < 0.05$), which are indicated by added numbers: 1 – snowmelt, 2 – spring dry, 3 – spring wet, 4 – fall dry. Significant differences between the bog and the forested site at an event (Mann-Whitney; $\rho < 0.05$) are indicated by a hash. A table of descriptive statistics for each event can be found in the Supplement.