Author's Response to Referee's

We would like to thank the two Referees for their helpful and constructive comments, which greatly improved the manuscript. Our detailed responses to the comments are listed below. For Author's changes see the attached revised manuscript with mark ups (track changes in MS Word) below. Page and line numbers of changes in the attached manuscript are given in brackets.

Response to Referee #1

 # The objectives could be improved by a clearer focus and formulation of hypotheses or research questions. The major drawback is the only fair scientific and presentation quality that needs to be improved. My major criticism is the simpified verbal description of the results that lacks quantitative assessments of concentrations/ component levels, seasonality and event behavior. Also, a quantitative statistical analysis on major governing factors such as temperature is needed.

Response: In our revised manuscript we reworked the last section of our introduction to clarify our objectives and research question (p. 3 line 30 – p. 4 line 16). Additionally, we added statistical analysis (descriptive, as well as correlations and tests of significant differences) to our data to strengthen our statements (Table 1 p. 22, Figure 3 and 7 p. 27 and 33). These issues will be addressed in further detail in the specific comments of this response (see below).

 # Specific comments and technical corrections

 # Abstract: For me, it reads a bit to technical and focussed on the results. I would like to see terms and variables like "C2%" to be reduced in favor of a stronger focus on discussion and implications (expanding the messages now in the last sentence).

Response: As suggested by the referee we adjusted the focus of the abstract rather to discussion and conclusions and shortened the result section. We revised the abstract also in view of the comments of referee #2. We included major outcomes of the study like the high variability of DOM quality due to hydrologic conditions, which makes it necessary to cover discharge events during monitoring studies. We outline the differences between both studied catchments (bog/forested riparian zone) and shortly discuss the suitability of spectrofluorometric indices to track DOM origin and dynamics in this headwater stream. (p. 1 line 19 - p. 2 line 3)

 # Introduction: P2Line5: The first sentence need a reference.

Response: We added a reference to that statement (Mulholland 2003). (p. 2 line 13)

 # P2Line 7f: This also needs a reference. Check also for this paper: Ledesma JLJ, Grabs T, Bishop KH, Schiff SL, Kohler SJ (2015) Potential for long-term transfer of dissolved organic carbon from riparian zones to streams in boreal catchments. Global Change Biology, 21, 2963-2979

Response: We included references in the revised version of the manuscript (Fellman et al. 2009, Perdrial et al. 2014 and Wallin et al. 2015: p. 2 line 16-17). We refer to the suggested literature at another point in the introduction (p. 2 line 19).

 # P2L34: Change citation parenthesis.

Response: We changed that in the revised manuscript not only at this particular point (p. 3 line 12), but we thoroughly read through the text and found several more parenthesis errors in the manuscript.

 # P3Line19: Better define what you mean with changes by adding space and time! Do you mean surface water DOM at the catchment outlet or variability within the study site – do you mean seasonal changes, daily fluctuations...: Something like "spatiotemporal dynamic of DOM quality over the course of one year" ...

Response: We rephrased that sentence to avoid misunderstanding. The study aim described here is to elucidate different spatiotemporal dynamics in DOM quality over a year in a headwater stream, as the reviewer suggested. Those dynamics are supposed to be controlled by the bog and forested peaty riparian zone catchment. (p. 3 line 30-33)

P3Line23: Two times starting a sentence with "on the other hand"

Response: The section including this phrase has been reworked (p. 3 line 30 – p. 4 line 30).

 # P3Line31: This last section is not well integrated with the objectives in the section before: I suggest restructuring the objectives a bit starting from P3Line23; there is more or less everything there: What is the general aim? What are specific questions you want to answer/ Hypotheses to follow? Where do you perform this research (references on previous studies) and why there? What are the methods you want to apply? What are discussion/ conclusion and implications aiming at?

Response: We agree with the referee and revised this section of the manuscript in view of the mentioned deficiencies and comments of referee #2. We clarify our objectives/hypothesis in view of these points: I) To test if spectrofluorometric indices can be used to track origin and dynamics of DOM. II) That DOM quality is highly variable in a headwater stream depending on hydrologic conditions and season. We expect short-term DOM quality changes due to high discharge events, which cause changes in hydrologic connectivity of different DOM pools and possible leachate effects of labile DOM during strong rain events. This short-term pattern is expected to be overlain by seasonal DOM changes due to changes of DOM production and consumption over the year. III) We expect general differences in DOM quality between the bog and forested riparian zone catchment. The riparian zone is characterized by accelerated water level fluctuations and a nutrient-richer vegetation than at the bog site, which leads to the hypothesis that DOM quality is strongly affected by changes in hydrologic conditions and is more labile than at the bog site. We point out the suitability of this particular catchment as the stream origins within the bog and enables us to retrieve an exclusively bog derived DOM signal within this headwater stream. We also refer to our previous study at this catchment and the applied spectrofluorometric methods, which are $SUVA_{254}$, S_R, FI, HIX and PARAFAC modeling of excitation emission matrices. (p. 3 line 30– p. 4 line 30)

 # Materials and methods: P4Line1-14: I am not convinced of the study site description in combination with Fig. 1: I suggest to show a soil map or something comparable to better see the position of the bog and the differences between the two sampling locations.

Response: The provided Figure 1 is actually a soil map. We admit that the figure might not sufficiently highlight the information, which is important to this study. To make the figure more comprehensible we extended the figure caption and modified the map by clarifying the declaration of soil type distributions and sampling spots. (Figure 1, p. 23)

 # P4Line15: "Discharge sampling" sounds strange – just water sampling?

Response: We agree with the referee and rephrase that expression. (p. 5 line 15)

 # P4L15ff: Please state the number of different types of samples and the temporal resolution of the discharge measurements..

Response: We include this information now. In short, we took 30 grab samples, 44 water samples by the automated water sampler and 191 samples during high frequency storm event sampling. Discharge was recorded in a 10 minute time interval. (p. 5 line 16 – 23)

 # P4Line27: Unit of absorption?

Response: The missing unit of absorption is m^{-1}. We corrected this. (p. 5 line 30)

 # P4Line29f: Superscript in units!

Response: We edited this mistake. (p. 6 line 1)

 # Results: Fig. 2: What do you mean by "trends during rain events"? I suppose the concentration trends?

Response: We agree that this is a poor expression. We rephraseed it to "trend of concentration" or "trend of quality indices", respectively. (Figure 2, p. 24 line 4)

 # P5Line29f: Please put that statement in numbers (e.g. CV or standard deviation of seasonal concentrations and storm event concentrations).

Response: We picked up the referees comment and strengthened our statements with a table (Table 1, page 22) of descriptive statistics including mean, median, standard deviation and minimum and maximum values for the annual record. For the event data set we present the data more comprehensively in boxplots figures (Figure 3 and 7 p. 25 and 31). Additionally, we provide a table with this event data in the supplement for better comparability of numbers (see supplement, S1). We now refer to specific numbers of the tables in the text if needed (like standard deviations). (p. 7 line 9ff)

 # P5Line30f: You mean the highest recorded concentrations during the entire study period? This is not clear from this sentence.

Response: The referee is right, the statement refers to the entire study period. We rephrased that sentence for clarification. (p. 7 line 12-13)

 # P6Line1: Again – put that into numbers (e.g. mean or median concentrations)

Response: As described to a previous comment we included a new table, which will provide the requested numbers and added necessary information in the text. (Table 1, p. 22 and p. 7 line 16ff)

 # P6Line23ff: I struggle with the interpretation of the components as a "too early" discussion. Maybe a introduction sentence on that?

Response: We included the interpretation of the components in the results after careful consideration and with regard to existing literature to facilitate reading and help the reader understand the common use of these indices. Therefore, we do not consider this as a real "discussion" here. If we include this information only in the discussion section, the result section describing characteristics of different rain events would be more difficult to follow, e.g. as the description of components would remain very technical and abstract. Furthermore the focus of the discussion would be less clear, if we introduce the common interpretation of components only there. From our point of view this interpretation is thus rather a description of the modelled components, in terms of 'results', backed up by literature data (which is admittedly unusual for a normal result section). Such description is found also in the results or method sections in other studies. Nevertheless, to address this unease of an early discussion we included an introducing sentence now. (p. 8 line 9-10)

 # P7Line19ff: Again, I have problems with this type of interpretation in the result section. This more belongs to the discussion chapter.

Response: We shifted the interpreting statements of this sentences (now p. 9 line 7-9) to the discussion section. We now limit the description solely to the components and their contributions (referring to studies identifying similar components) without assigning a source of these components here, but putting this source assignment into the discussion. (p. 12 line 11-13)

 # In general I am not convinced of the discussion of seasonal trends: For a seasonality assessment I would expect a more in depth evaluation of seasonal min and max and potential controls: e.g. Is the seasonality in line with water temperature (which is likely close to soil water temperature), air temperature, light intensity... So, better quantify and describe the seasonality!

Response: We thank the referee for this constructive comment. We agree that statistical indications are helpful to underline our statements in regard to seasonality. We include a description of minimum and maximum values now (Table 1 p. 22 and Fig. 3 and 7 p. 25 and 31). Unfortunately, we did not measure soil temperature and only occasionally water temperature, which limits options to further evaluate seasonality effects as suggested. However, we chose to use air temperature as a proxy for seasonality and included results from Spearman rank correlations in the manuscript (p. 7 line 14-16 and p. 11 line 32 – p. 12 line 1).

 # Discussion: P9Line 6f: This type of statement belongs to the end of discussion/ conclusions!

Response: We agree with the referee and moved this point to the conclusions in the revised manuscript. (p. 11 line 2-3 and p. 16 line 21-22)

Response to Referee #2

 # Specific comments:

 # The study is intended to elucidate the DOM quality and dynamics in two contrasting catchments. The authors expect "water level, temperature and precipitation to be the main controls on stream DOM…". I would acknowledge if the authors provide a more specifically defined working question/hypothesis along which the results and discussion can be organized. How can the DOM of both catchments differ?

Response: Also in line with referee #1 we rephrased our objectives in the introduction to clarify our hypothesis and provide a better readability (p. 3 line 30 – p. 4 line 30). Main objectives/hypotheses were: I) To test if spectrofluorometric indices can be used to track origin and dynamics of DOM. II) That DOM quality is highly variable in a headwater stream depending on hydrologic conditions and season. We expect short-term DOM quality changes due to high discharge events, which cause changes in hydrologic connectivity of different DOM pools and possible leachate effects of labile DOM during strong rain events. This short-term pattern is expected to be overlain by seasonal DOM changes due to changes of DOM production and consumption over the year. III) We expect general differences in DOM quality between the bog and forested riparian zone catchment. The riparian zone is characterized by accelerated water level fluctuations and a nutrient-richer vegetation than at the bog site, which leads to the hypothesis that DOM quality is strongly affected by changes in hydrologic conditions and is more labile than at the bog site. Additionally, we reviewed our result and discussion section in term of hypothesis consistency.

 # Samples were taken by an automated sampler in a six day interval and the filtered samples were stored at 4°C in the dark. How long were the samples stored until analysis? Although filtered, the samples were probably not sterile. Bacteria can degrade organic carbon even at low temperatures. Have the authors tested if the DOC composition remained unchanged?

Response: The storage time of our samples depended upon the type of measurement. DOC concentration and UV-Vis analytics were conducted at the TU Braunschweig. We could therefore measure samples more or less immediately (within a week). Immediate fluorescence measurements were impossible, as those were conducted at the University of Münster, which necessitated measurement campaigns in about three months intervals. To address the problem of conservation we tested UV-VIS changes, which were inconspicuous over that time-period. Furthermore, due to the longtime experience of the ecohydrology group in Münster in fluorescence measurements we came to the conclusion that we produce less analytic artefacts by storing the samples at low temperatures over that time period than freeze them for conservation. We also refer to following literature: Santos et al. 2010, Hudson et al. 2009, Graeber et al. 2012. There it also is recommended that samples should be frozen, if storage time is longer than one year.

 # UV absorption characteristics were used as indicators of DOM composition (absorbance at 254 nm, spectral slope ratio). Besides DOM, however, dissolved iron exhibits significant UV absorption. The dynamics of iron is also related to hydrology, i.e. flood events can be associated with high iron concentrations. Changes in UV absorption may reveal changes in DOM quality but at the same time they can reflect different contributions of dissolved iron. How the authors think about that?

Response: This is an important point. We are aware of biases of UV-VIS and fluorescence DOM characterization by Fe concentration or pH changes. We therefore consulted literature for critical Fe concentration levels, which cause interferences (Weishaar et al 2003; Xiao et al. 2013 and Poulin et al. 2014). We concluded that in our case Fe interference can be neglected as we measured maximum concentrations of 500 µg L^{-1} Fe in our water samples. This results in a Fe_{mg}/C_{mg} ratio of about 0.01, which is very low. Additionally, samples were measured in 6 or 8 fold dilutions resulting in maximum absolute concentrations during measurements of about 60 or 80 µg L^{-1}. Possible biases from pH were assessed by continuous pH measurements, which resulted in a constant pH of about 3.8 over the whole sampling period.

 # The fluorescence index (FI) differentiates between vascular plant derived (FI 1.3 – 1.4) and microbially derived (1.7-2.0) DOM. FI values >1.7 were interpreted as microbial DOM (p. 5 lines 15-20). Can the authors exclude that non-vascular plants (mosses) contributed to DOM generation? Later in the manuscript a contribution of Sphagnum is specifically discussed with respect to SUVA but not to FI (p. 9 lines 15-31).

Response: We are glad that the referee pointed out this apparent limitation of this approach, which also caught our attention before. We do not exclude non-vascular plants, indeed we assume that bog derived DOM does also origin from prevailing Sphagnum vegetation. This fact should not modify assumptions that are made by the fluorescence index. The study of Wickland et al. (2007) published FI values of leachates of plant material. The FI of Sphagnum were around 1.1-1.4, which is similar to vascular plants signatures. We will rephrase the sentence to improve clarity here. (p. 6 line 17)

 # In the results and also in the discussion sections, fluorescence indices and absorption values were often reported to be higher or lower when sites or situations were compared. However, I missed statistics providing a little more confidence if these differences are significant. I recommend including a table/figure, summarizing the main results as well as the levels of significance. This table/figure along with a hypothesis can be used to guide the reader through the results and discussion. I found it less convenient to work through the detailed description of the results. The figures 2, 3, 5, 6, 7 and 8 look more or less similar, which makes it not easy to keep the most important results in mind.

Response: We agree that the former presentation was not easy to follow. We thus extended our study to clear statistical evaluations in the revised version. We prepared descriptive statistic tables (Table 1 p. 22 and S1 in the supplement), which include mean, median, standard deviation and minimum and maximum values of the concentrations and indices. We provide box plots to condense information and acknowledge the formerly unclear presentation (Figure 3 and 7 p. 25 and 31). Differences have now been tested with appropriate statistic tests like Mann-Whitney or Kruskal-Wallis tests and results are included in the boxplots (p. 6 line 23-30 and Figure 3 and 7).

 # Further comments:

 # The title: Please refer more directly to the outcome of the study

Response: We substantiated our title and changed it to "Changes in dissolved organic matter quality in a peatland and forest headwater stream as a function of seasonality and hydrologic conditions" (P.1 line 2-4).

 # p.1 lines 22-24: The concluding sentence of the abstract "Our study demonstrated that DOM export dynamics are not only a passive mixing of different hydrological sources, but…" is unclear. Now the reader expects a statement why it is not a passive mixing or how the process can be characterized instead. However, it is only concluded that "…assessing DOM quality can greatly improve our understanding…". Please include here the most relevant result that improved our understanding. The sources and the quality of DOM appeared to be highly variable within events depending on runoff generation. What are the consequences for sampling/monitoring programs?

Response: We revised the abstract also in view of the comments of referee #1. We now refer stronger to the outcome of this study, which is the mentioned high variability of DOM quality. This implies that monitoring programs have to consider not only changes due to seasonality, but need to cover different hydrologic conditions as well. Furthermore, the study shows that bog DOM quality is less susceptible to changes in hydrologic conditions than the peaty riparian zones. Additionally, the used spectrofluorometric indices proofed to be a useful tool to track DOM origin and dynamics in this headwater stream. (p. 1 line 18 – p. 2 line3)

 # p. 2 line 28: "aromatic or humic", is there a difference?

Response: This is a tricky question. Well for our understanding the term "aromatic" refers to the specific ring structure in an organic molecule, while humic or humic substances rather describes a large fraction of DOM mainly defined as complex, high molecular weight, chromophoric molecules derived from decomposition of plant and animal residues. These

substances comprise an aromatic fraction. We used those terms in account with the general usage in literature, especially in literature reporting fluorescence results (e.g. Inamdar et al. 2012).

 # p. 2 line 33: groundwater DOM is of smaller size and mostly of microbial origin, please include a reference

Response: We now refer to the references Inamdar et al. 2012 and Singh et al. 2012. (p. 3 line 10)

 # p. 4 line 29: The near UV includes light from 300 – 400 nm, 254 nm is in the middle UV range

Response: The referee is right and we changed this. (p. 5 line 31)

 # p. 7 line 9: Figure 5 instead of Figure 6?

Response: The referee is right. We changed this reference to Figure 4 now, due to changes in the Figures. (p. 8 line 28)

 # p. 8 lines 10 and 16-17: I had problems to relate these statements to the figures

Response: We deleted the first statement ("S_R exhibited generally higher values during both spring events indicating smaller DOM molecular size at the forested site") (p. 10 line 2-3), rephrased the second one (now: "Contribution of protein-like component C5% exhibited elevated values during the second spring event with wet preconditions at the bog site (Fig. 6, 7)) and included a new reference to the boxplot figures (p. 10 line 8-9).

 # p. 9 lines 6-9: A confirmation of the suitability of fluorometric indices appears difficult without independent methods (e.g. isotopes, mass spectrometry). It is problematic to conclude that an increase in aromaticity is caused by an increase in apparent molecular size if the latter is not measured.

Response: Regarding the first part of this comment we agree with the referee that this statement might be misleading. This statement was not intended to refer to the suitability of fluorometric indices to represent specific DOM fractions or molecules. We want to express that the spectrofluorometric approach seems an appropriate tool to distinguish relevant hydrological compartments based on DOM quality. We will rephrase that. (p. 11 line 1-2)

Regarding the second part we conclude this from a negative correlation of the SUVA index for aromaticity and S_R which is an index for molecular size as confirmed in available studies (see Helms et al. 2008). This is why we explicitly stated "apparent" molecular size to state that this is a molecular size derived from S_R. Maybe this was unclear. We strengthened this assumption by a significant statistical correlation in the revised manuscript (p.7 line 28-30) and rephrased this conclusion in order of the method limitations. (p. 11 line 2-6)

 # p. 14 line 1: "The export of labile, protein-like DOM was specific…" I suggest being more cautious with characteristics of DOC that have not measured directly (e.g. "labile"). See also P. 9 line 5 "…specific strong microbial DOM signature…".

Response: While in general the suitability of comparable fluorometric indices has been confirmed in existing studies (see e.g. Fellman et al. 2008), we agree that the method has inherent limitations and we adjusted these statements accordingly. (p. 16 line 11-12 and p. 16 line 14-17)

 # In Figures 1, 3, 5 and 6, the individual symbols in highlighted boxes (events) were difficult to distinguish.

Response: We considered this limitation in our revision of the figures. We changed the data point marks and display some results in boxplots now. (Fig. 2 – 7, p. 24 – 33)

References:

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~~DOM quality in a peatland and forest headwater stream: seasonal and event characteristics~~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 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 ~~discharge~~ stream water ~~from~~ 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).

Indices for DOM quality exhibited major changes due to different hydrologic conditions, but patterns were also dependent on season. Stream water at ~~T~~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. ~~During drought a~~A microbial DOM fraction originating from groundwater and deep peat layers was increasing ~~exported~~during drought, while~~, characterized by high FI, high S_R and increasing humic-like fluorophores C1% or C4%. During discharge events this deep-sourced DOM pool was diluted by humic-rich surface-near DOM pools, which were more aromatic, also of microbial origin with high FI and S_R, and an increase in humic-like fluorophores C2% and C3% at the forested site. The FI suggested export of DOM of strong~~ a strongly microbially altered DOM fraction~~alteration~~ was also particularly exported ~~under~~ 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.~~, but assessing DOM quality can greatly improve our understanding of~~

~~DOM sources and their response under different hydrological preconditions.~~ 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.

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 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 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. ~~Especially a~~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 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 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 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 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 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 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 Biester, 2015), the present study ~~is~~ intended to elucidate different spatiotemporal ~~changes~~ dynamics in DOM quality over a year ~~and dynamics comparing~~ comparing a bog and a forested peaty riparian zone, as those landscape types are considered as the main sources of stream DOM ~~in the catchment~~. 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 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 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.

~~These dynamics are expected to be different as the two sub-catchments differ in vegetation, hydrology and soil properties. We expect water level, temperature, and precipitation to be the main controls on stream DOM concentration and quality. On the one hand changes in DOM will depend on season, which is attributed to DOM production and consumption. On the other hand hydrological connectivity of different source areas will also affect stream DOM composition, because shallow groundwater or deeper peat layer versus organic rich upper soil layer or surface near peat layer, can differ in DOM composition. The effects of drought and storm events were particularly considered, as they induce major DOM dynamics due to 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. The characterization of stream DOM is used to track DOM sources and their dynamics under specific hydrologic (pre)conditions to elucidate the role of this specific landscape areas in regulating the stream DOM dynamics.~~

~~For this purpose we chose a headwater stream catchment to compare DOM export from discrete landscape units. Short residence times make in-stream processes negligible and enables landscape type specific studies. For DOM characterization we used spectrofluorometric indices like $SUVA_{254}$, S_R, HIX and FI, as well as PARAFAC modeling.~~

2 Materials and Methods

1.1 Study site

The study site is located within the nature protection area of the Harz Mountains ~~(Fig. 1)~~. The Odersprung bog exhibits an erosion rill, 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 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).

1.2 Sampling and field measurements

~~Discharge~~ 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 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 ~~on~~with a Lambda 25 (Perkin Elmer, USA) in ~~a~~the range of 200-800 nm at ~~a~~ 0.5 nm resolution. 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 ~~near~~ 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 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 ~~vascular~~ plant~~s~~ 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 to 46 mg L^{-1} (SD of 7 mg L^{-1} at the forested site and 8 mg L^{-1} at the bog site) and was greater than during single rain events at both sites, where standard deviations ranged between 1.4 to 1.9 mg L^{-1} at the bog site and 0.6 to 4.2 mg L^{-1} at the forested site ~~ranging between 5 to 45 mg L^{-1}~~ (Fig. 2, 3 and Table 1). However, the rain event~~s~~ in fall was~~ere~~ responsible for the highest recorded DOC concentrations of 37.3 mg L^{-1} and 45.8 mg L^{-1} during ~~a sampled rain event in fall~~the entire study period at both sites. The concentration trend generally followed the vegetation period ~~at both sites~~ 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 and 10 mg L^{-1} were measured during snowmelt at both sites. Concentrations of DOC were significantly higher at the forested site (median of 32 mg L^{-1}) than at the bog outlet (median of 26 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.~~3~~2 at the bog site and between 3.~~4~~5 and ~~6~~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 0.53), but~~and~~ showed a larger variability than at the bog site (mean $SUVA_{254}$ of 4.4, SD of 0.37, see also Table 1). During the summer drought period $SUVA_{254}$ values decreased at both sites, but stronger at the forested site (Fig. 2).

As expected, the S_R as reciprocally proportional index for molecular weight of DOM exhibited an ~~rather~~ 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 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. 34). At the bog and the forested site HIX only varied during snowmelt and spring events with lower values down to 0.75 68 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 similar values at the bog and forested site between 1.5 and 1.75 with significantly higher values at the forested site. At the forested site FI increased during summer 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 in Fig. 54. 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; 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, 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. 54). Fluorescence was elevated during summer and lower values occurred in spring and fall at both sites. Normalizing fDOM to DOC concentrations, i.e. monitoring changes in fDOM composition in percentage of each component, a decrease in the fluorophore fraction in DOM from spring to fall could be observed (Fig. 64). 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, only C4% exhibited a similar seasonal trend as DOC concentrations. 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 forested site showed a greater variability in component contributions over the entire record, but no seasonal trend. T~~The protein-like C5% contributed largely to fDOM during snowmelt and wet spring event~~s~~ (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 ~~more~~ attributed to the bog site (Fig. 6 and 7). ~~Overall, the C4% can 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 attributed to one of the sites.~~

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 - 12 mg L^{-1}), abs_{254nm} (40 - 140 m^{-1}), HIX (0.75 - 0.9), 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 1.95 - 2.2, while S_R at the bog site exhibited mean values of 1.8 - 1.9 (Fig. ~~7~~3), which were still higher than following spring samples, though. $SUVA_{254}$ was significantly lower (4 – 4.5) than in following spring events at the forested site, while at the bog site $SUVA_{254}$ of 4 – 4.5 were similar to values of the rest of the record Table 1, Fig. 2). The protein-like PARAFAC component C5 % was elevated during snowmelt (8 – 16 %) and ~~contributed 8 – 16 % to total fluorescence~~was significantly higher than at the fall event at both sites (Fig. 7~~8~~). 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.~~, while a~~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. ~~8~~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 - 33 mg L^{-1} and 200 – 360 m^{-1}) ~~and much lower~~than after wet preconditions (8 - 24 mg L^{-1} and 80 - 300 m^{-1}) at both sites (Fig. ~~7~~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 ~~also decreasing~~ during spring rain events, but

were still significantly elevated compared to the fall event at the bog site~~kept similar values throughout the rest of the year (3.6 – 4.6)~~. ~~S_R exhibited generally higher values during both spring events indicating smaller DOM molecular size at the forested 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 ~~only~~ 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 ~~spring events at both sites and higher values at~~ the second spring event with wet preconditions at the bog site (Fig. ~~8~~6, 7). The bog derived humic-like C4% ~~was~~ decreased during spring events at both sites (Fig. 6) ~~at both events decreasing~~. 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 ~~both~~ the bog site~~s~~, 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 mg L^{-1} DOC at the forested site and 40 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. ~~7~~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% ~~were decreasing~~decreased during the fall rain event at the forested site, while the forest derived humic-like C2% and C3% increased (Fig. 6~~8~~). The bog derived C4% contributions were significantly higher than during snowmelt and in spring at the bog site (Fig. 7), but ~~with~~ 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 ~~events with slightly decreasing values at both sites~~.

4 Discussion

~~A comparison of the different spectrofluorometric indices confirmed their general suitability to track origin and dynamics of DOM.~~ As expected, the spectroscopic indices for aromaticity ($SUVA_{254}$) and apparent molecular size (S_R) were inversely ~~related~~correlated~~. This~~, which implies that an increase in aromaticity ~~also caused~~ is accompanied by an increase in apparent molecular size. This ~~and~~ suggests that aromatic structures ~~seem to~~ 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 quali~~tiesy should be predicted~~. 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~~during individual discharge events~~ as demonstrated by individual discharge events, also seasonal patterns occurred~~. at both sites, forest and bog. Main overall controls were temperature or vegetation period, respectively and differences in hydrology.~~ 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 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 ~~events and smaller changes by season~~. Thus they were 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. ~~Overall,~~ T~~t~~he C4% ~~can~~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 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 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 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

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 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 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 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

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 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 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

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 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 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, 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 ~~the~~ inherent limitations of the spectrofluorometric approach of DOM characterization.

At the forested site trends of $SUVA_{254}$, HIX and S_R indicated a ~~lower~~ decreasing aromaticity and ~~smaller~~ apparent molecular~~es~~ 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 smaller apparent molecular size and less aromatic during fall event even though trends of the indices were partly reversed ~~in fall~~. 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 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 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.

~~At the bog site~~ U~~u~~nder 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. 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, ~~(~~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 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 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.

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. ~~Overall~~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 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. ~~Main variability in stream DOM concentration and characteristic was thereby generated at the forested site with peaty riparian zones and not at the bog site.~~

The export of ~~labile,~~ 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 limited to deeper peat layer at the bog site and shallow groundwater at the forested site as could be tracked by indices displaying a ~~specific strong~~ 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 ~~strong~~ 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 forested site generated highest DOM concentration peaks under wet preconditions~~.~~

~~A comparison of t~~The different spectrofluorometric indices ~~confirmed their~~were generally suitabi~~lity~~le 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 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

The authors declare that they have no conflict of interest.

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Table 1: General descriptive statistics 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	23.03	30.43	232.82	303.78	4.42	4.56	1.80	1.84	1.58	1.63	0.91	0.92
Median	25.65	32.14	250.41	313.48	4.44	4.59	1.78	1.83	1.58	1.64	0.92	0.92
SD	8.07	7.02	79.29	79.38	0.37	0.53	0.09	0.08	0.04	0.05	0.04	0.02
Min	5.01	11.22	49.33	113.31	3.53	3.43	1.67	1.71	1.52	1.55	0.76	0.86
Max	36.60	45.80	384.14	488.79	5.22	5.93	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	44.03	43.67	25.88	27.70	13.71	16.91	10.25	6.41	6.13	5.31
Median	44.21	43.56	26.19	27.83	13.70	16.78	10.42	6.73	5.18	4.84
SD	1.43	0.93	1.55	1.43	0.88	2.27	2.05	3.62	2.67	1.71
Min	39.95	42.13	22.64	25.04	11.98	13.26	3.77	0.00	4.00	3.28
Max	46.61	45.55	28.66	30.45	15.13	20.96	13.46	11.82	14.47	9.79

* Significant differences between bog and forested site (Mann-Whitney; two-tailed, $\rho < 0.05$)

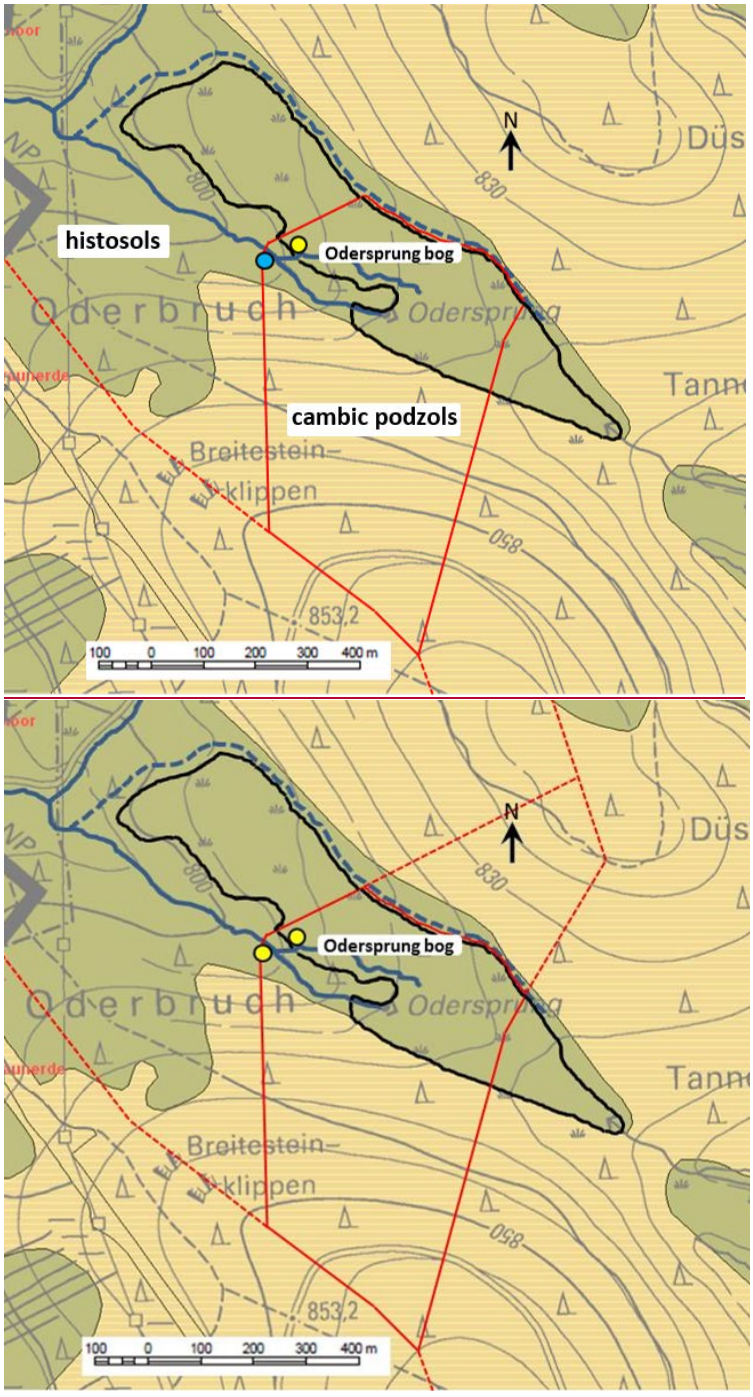


Figure 1: Location of the study area in the Harz Mountains, Germany. Red lines indicate the catchment boundaries, ~~yellow~~ circles represent the discharge monitoring spots (yellow – bog catchment, blue – forest catchment with peaty riparian zone). Green areas indicate ~~peatland or~~ peaty soils, beige-colored 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).

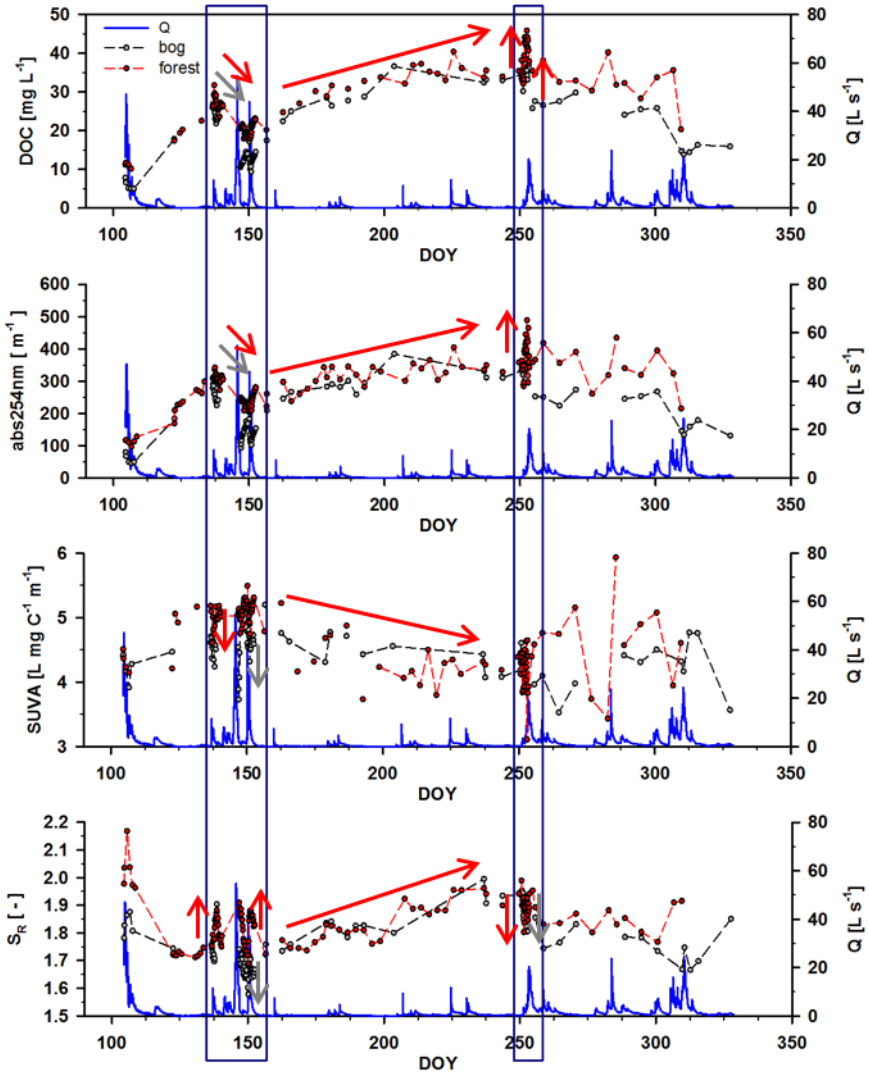


Figure 2: Annual records of DOC concentrations, abs_{254nm}, $SUVA_{254}$, and S_R from top to bottom (DOY - day of the year) in 2013. The blue line represents the bog discharge (Q). Grey circles represent the bog site, red circles the forested site, while arrows indicate concentration or index trends during rain events and summer drought at the different sites. Sampled rain events in spring and fall are highlighted by blue boxes.

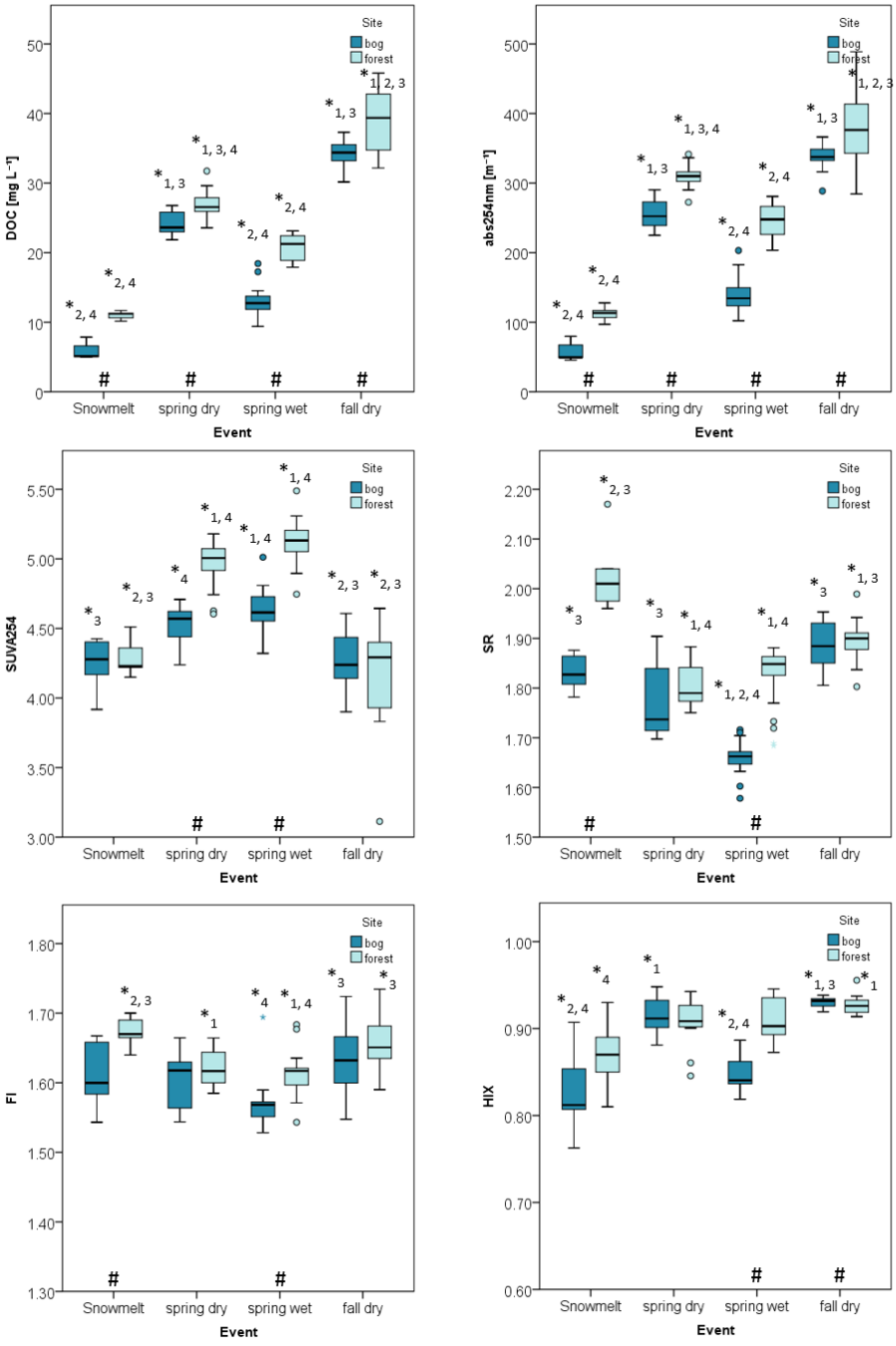
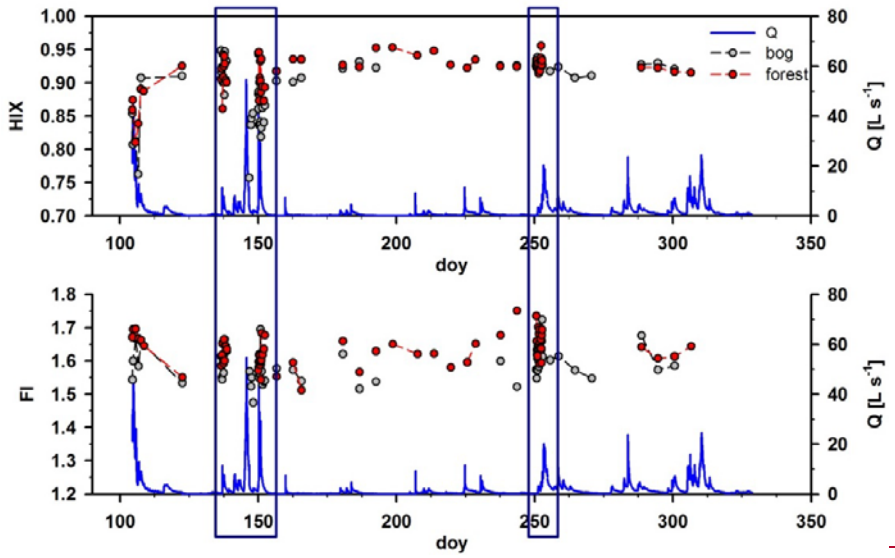


Figure 3: Box plots of SUVA, S_R, HIX, DOC concentrations, abs_{254nm} and FI during events. Dark blue bars indicate the bog site, lighter blue bars the forested site. Asterisks indicate a significant difference between events (Kruskall-Wallis; $\rho < 0.05$), which are indicated by added numbers: 1 – 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.


HIX
FI
Q [L s-1]
doy
Q
bog
forest
1.00
0.95
0.90
0.85
0.80
0.75
0.70
1.8
1.7
1.6
1.5
1.4
1.3
1.2
80
60
40
20
0
100
150
200
250
300
350

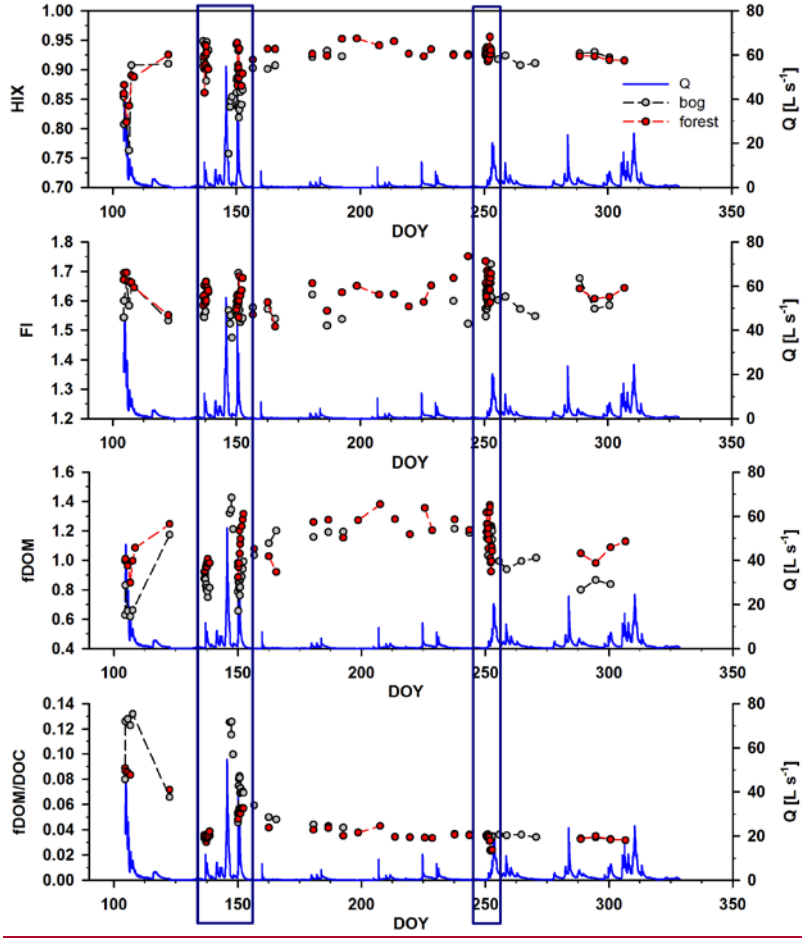


Figure ~~34~~: Annual record of the humification index (HIX), ~~and~~ fluorescence index (FL), sum of all Fmax PARAFAC components values (fDOM) and fDOM to DOC concentration (in mg L^{-1}) ratio against day of the year (DOY) ~~(DOY – day of the year)~~ in 2013. The blue line represents the bog discharge (Q). Grey circles represent the bog site, red circles the forested site. Sampled rain events in spring and fall are highlighted.

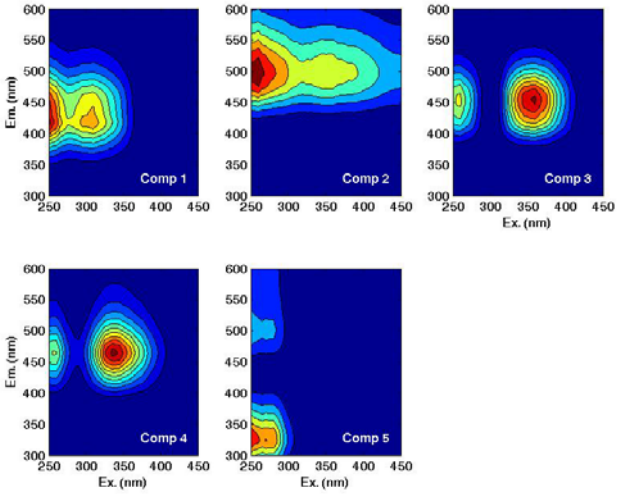
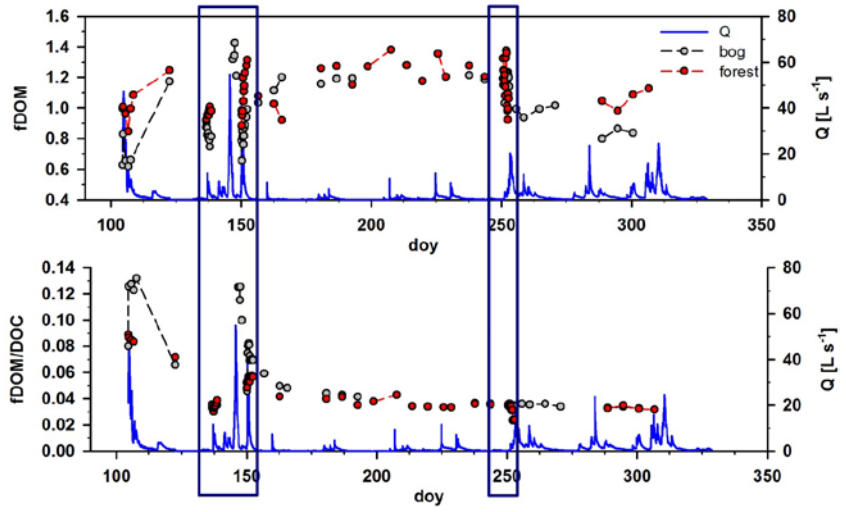
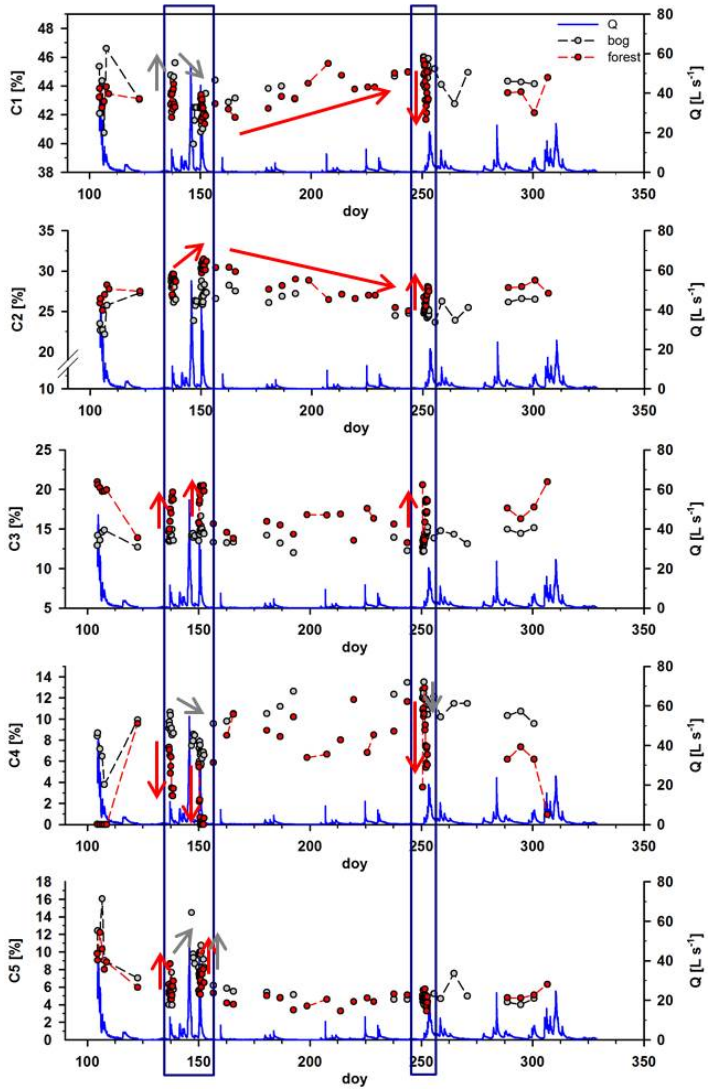


Figure 45: Characteristic EEMs of all five modeled PARAFAC components. For further component description see section 3.1.3.



~~Figure 5:~~


Q
bog
forest
C1 [%]
C2 [%]
C3 [%]
C4 [%]
C5 [%]
Q [L s-1]
doy

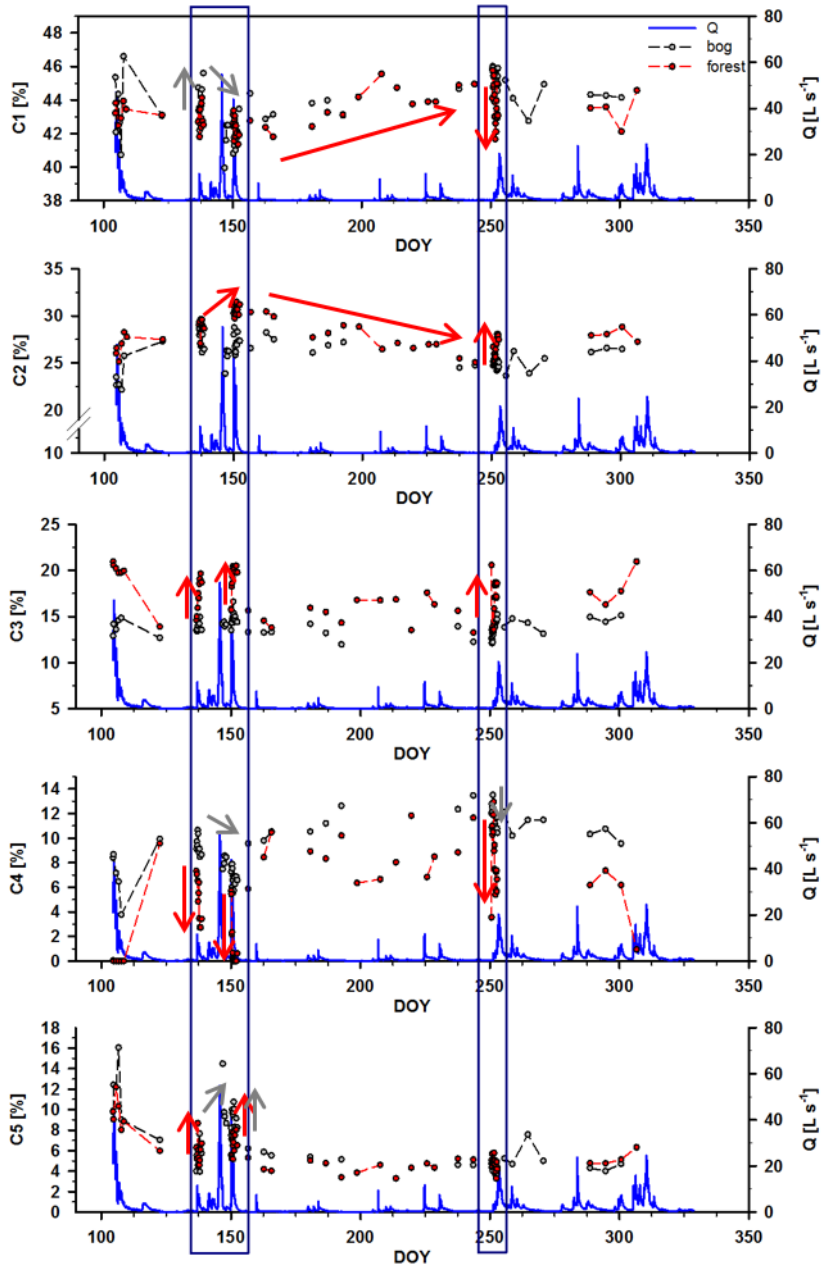


Figure 6: Percentage of PARAFAC components C1-C5. Blue line represents the bog discharge (Q). Grey dots indicate bog site values, red dots forest site values. Sampled rain events in spring and fall are highlighted.

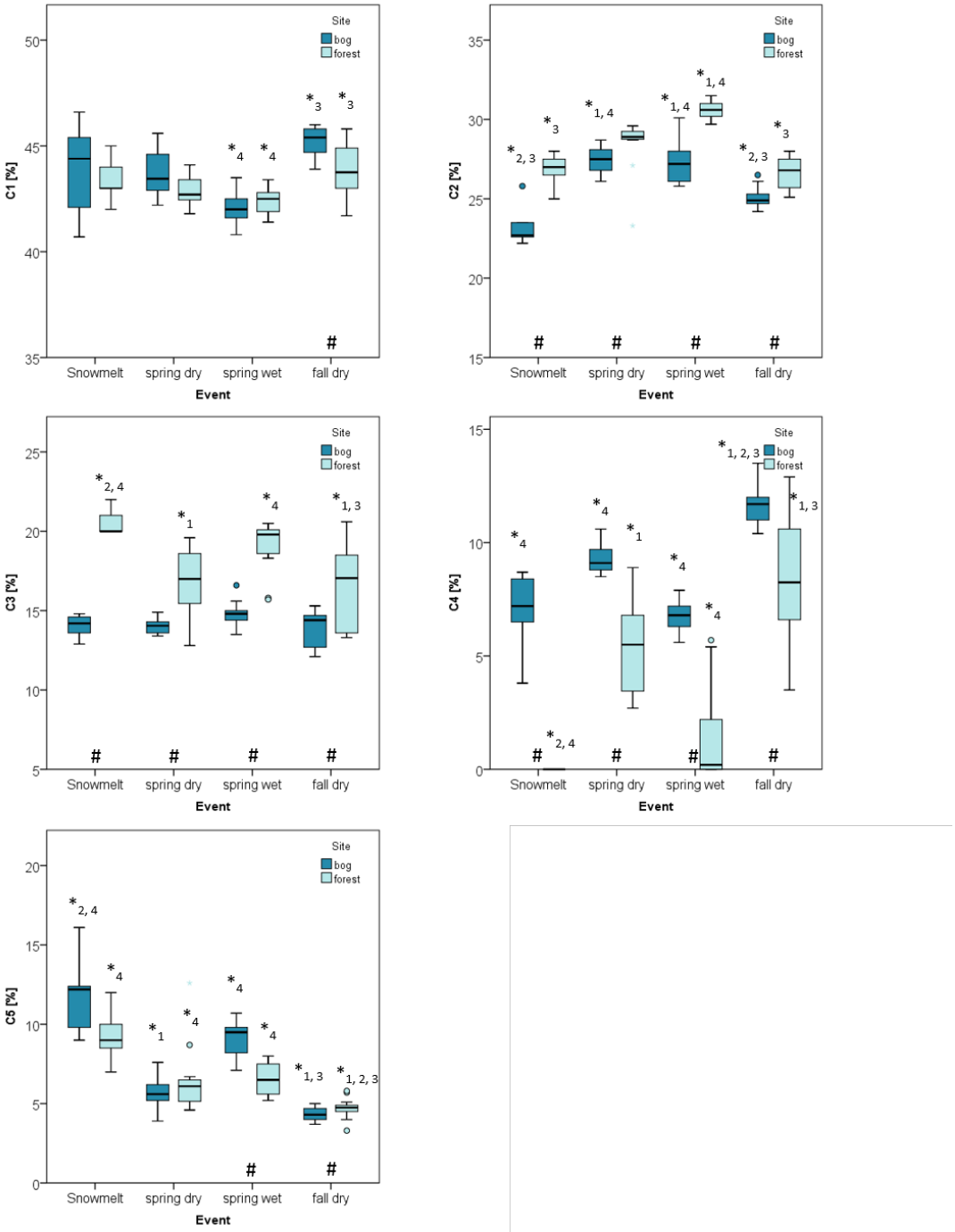
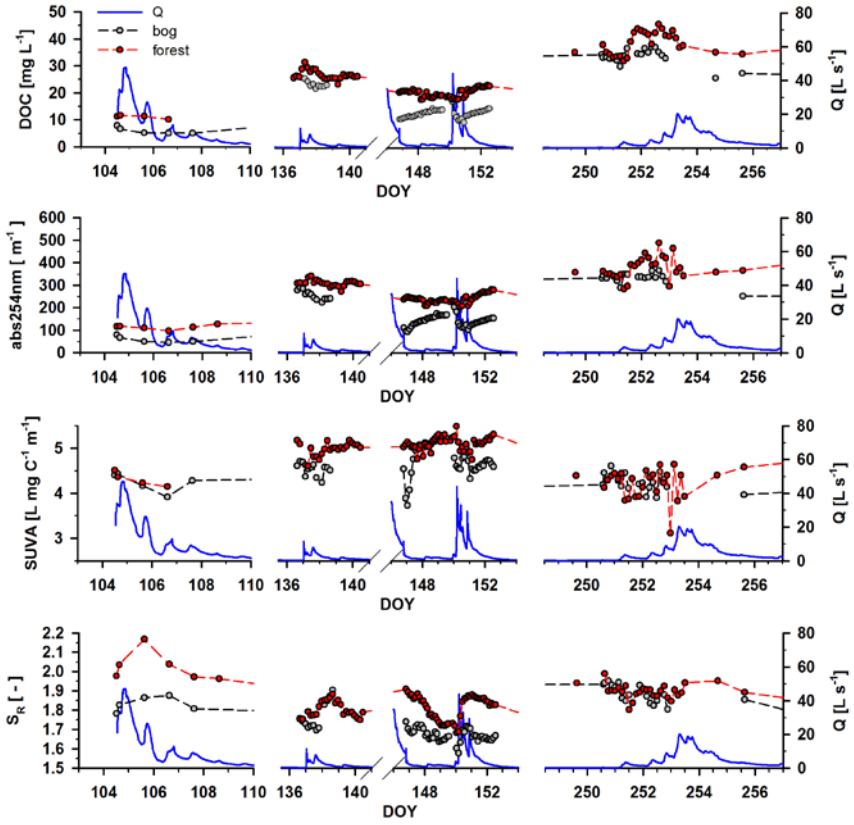


Figure 7: Box plots of PARAFAC components during events. Dark blue bars indicate the bog site, lighter blue bars the forested site. A table of descriptive statistics for each event can be found in the Supplement. Asterisks indicate a significant difference between events (Kruskall-Wallis; $\rho < 0.05$), 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.



~~Figure 7: Event DOC concentrations, abs_{254nm}, $SUVA_{254}$, and S_R from top to bottom during snowmelt (DOY 104-110), spring events (DOY 136-155) and fall event (DOY 247-258). Blue line represents the bog discharge (Q). Grey dots indicate bog site values, red dots forest site values.~~

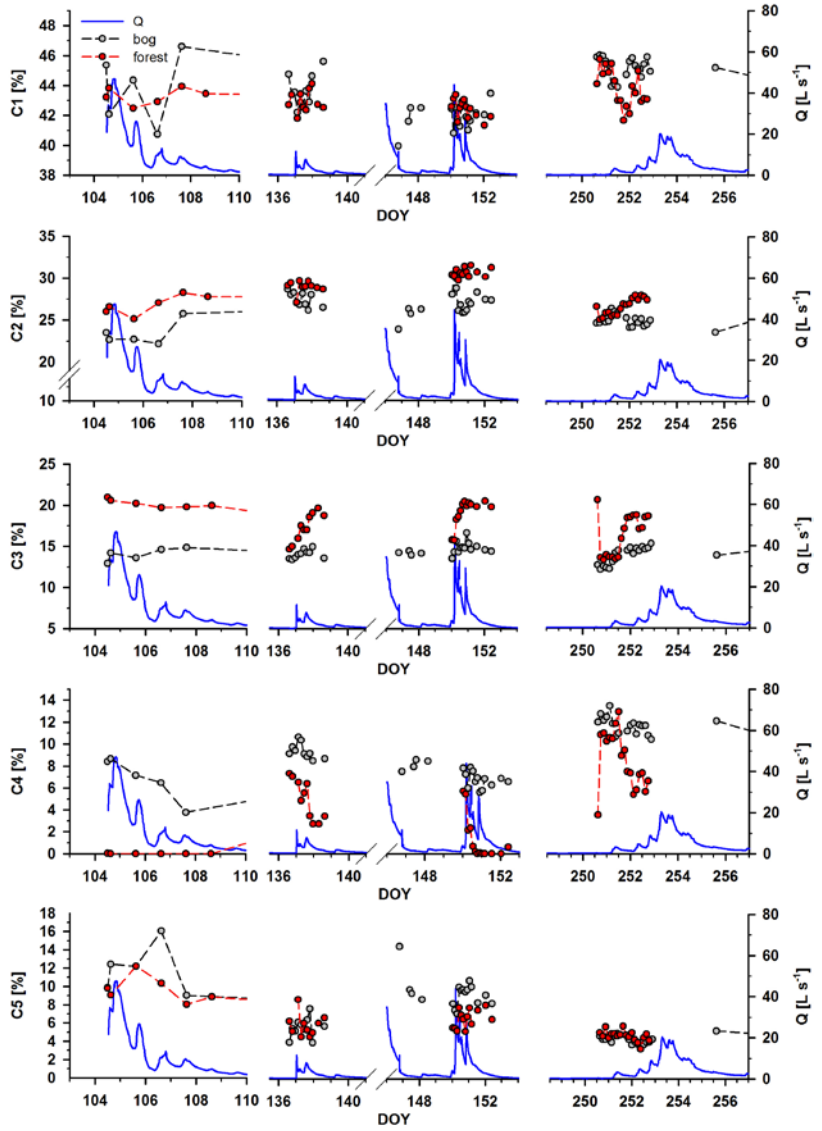
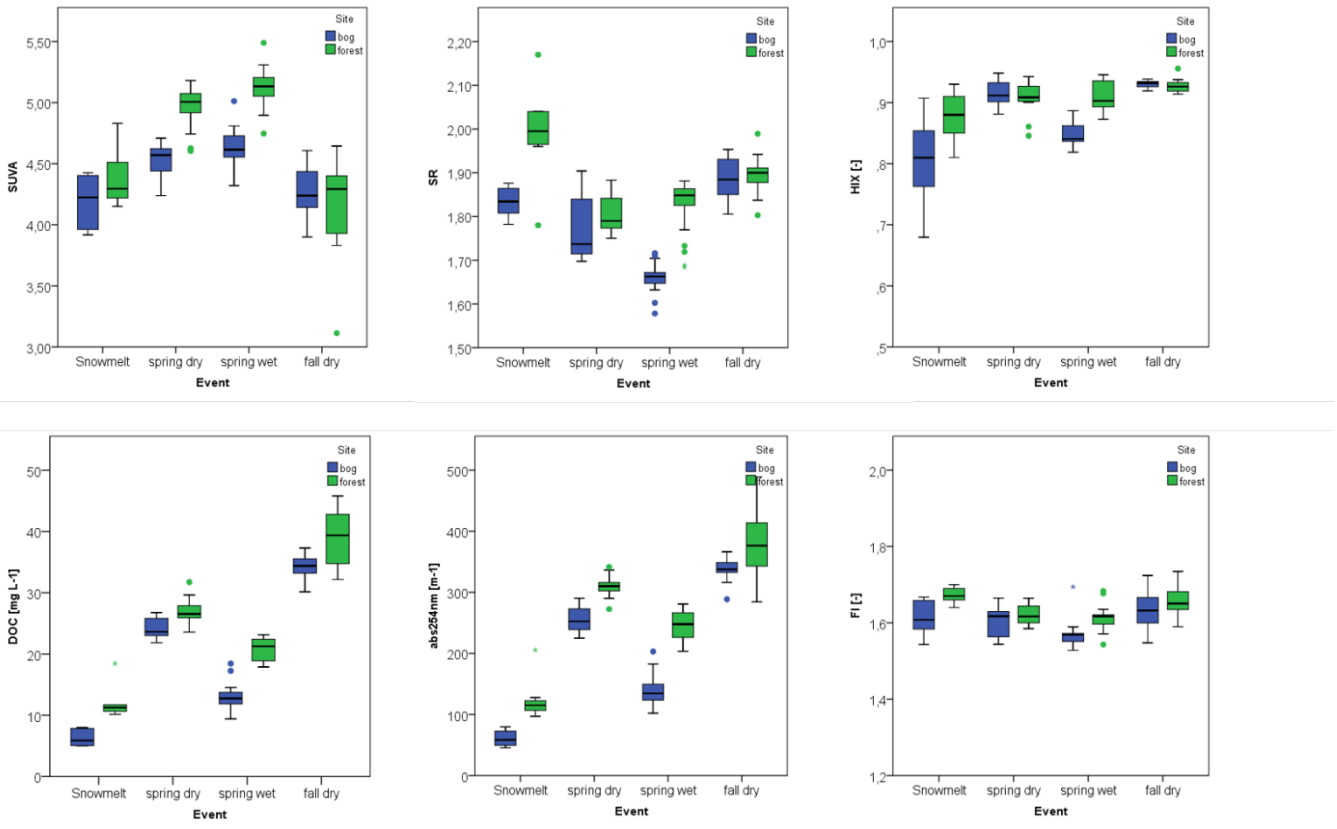
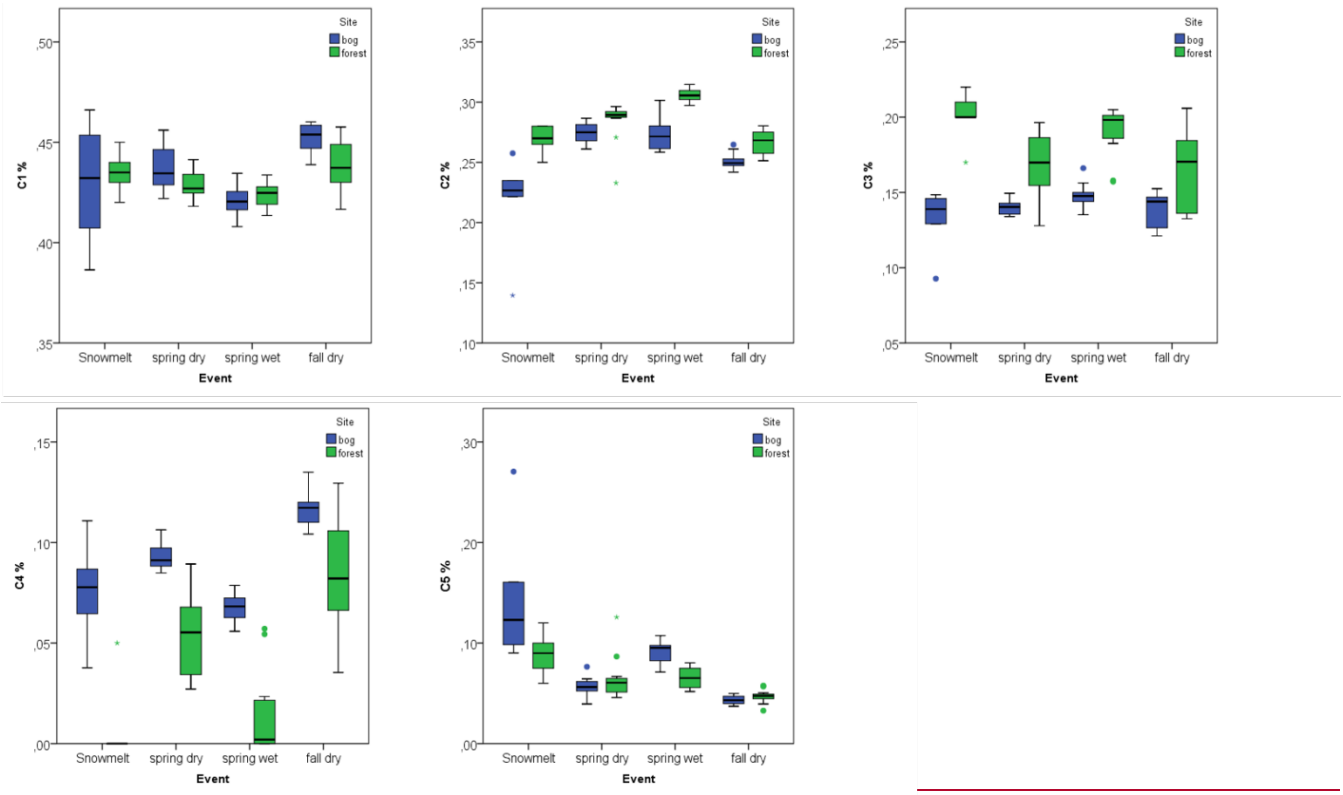


Figure 8: Percentage of PARAFAC components during snowmelt (DOY 104-110), spring events (DOY 136-155) and fall event (DOY 247-258). Blue line represents the bog discharge (Q). Grey dots indicate bog site values, red dots forest site values.



~~Figure S1: Box plots of SUVA, S_R, HIX, DOC concentrations, abs_{254nm} and FI during events. Blue bars indicate the bog site, green bars the forested site.~~



~~**Figure S2: Box plots of PARAFAC components during events. Blue bars indicate the bog site, green bars the forested site.**~~

Table S1: General descriptive statistics for DOC concentrations, and DOM quality parameters (abs_{254nm}, SUVA, S_R, FI, HIX, C1%, C2%, C3%, C4% and C5%) for each sampled event.

DOC	Snowmelt		spring dry		spring wet		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest
N	5	5	13	24	21	23	18	25
mean	5.93	11.00	24.28	27.02	12.93	20.73	34.47	39.09
median	5.14	11.22	23.61	26.54	12.75	21.25	34.39	39.38
STD	1.26	0.61	1.69	1.73	2.14	1.87	1.88	4.19
Minimum	5.01	10.15	21.85	23.57	9.40	17.89	30.15	32.16
Maximum	7.85	11.69	26.77	31.73	18.44	23.13	37.30	45.80

Abs	Snowmelt	spring dry	spring wet	fall dry

	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	12	23	21	23	18	25
mean	58.22	112.22	255.58	309.28	138.22	244.43	337.17	376.84
median	49.33	113.31	252.32	309.94	134.52	247.89	337.50	376.40
STD	14.69	10.05	21.22	14.45	23.37	24.01	17.59	52.04
Minimum	45.46	97.00	224.96	272.49	102.18	203.49	288.66	284.37
Maximum	79.66	127.82	290.32	341.44	203.12	280.87	366.32	488.79

SUVA	Snowmelt		spring dry		spring wet		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest
N	5	5	12	23	21	23	18	25
mean	4.24	4.29	4.53	4.97	4.64	5.12	4.25	4.18
median	4.28	4.23	4.57	5.01	4.61	5.13	4.24	4.29
STD	0.21	0.14	0.14	0.16	0.14	0.16	0.19	0.33
Minimum	3.92	4.15	4.24	4.60	4.32	4.75	3.90	3.11
Maximum	4.43	4.51	4.71	5.18	5.01	5.49	4.61	4.64

SR	Snowmelt		spring dry		spring wet		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	12	23	21	23	18	25
mean	1.83	2.02	1.77	1.80	1.66	1.83	1.89	1.90
median	1.83	2.01	1.74	1.79	1.66	1.85	1.88	1.90
STD	0.04	0.07	0.07	0.04	0.03	0.06	0.05	0.04
Minimum	1.78	1.96	1.70	1.75	1.58	1.68	1.81	1.80
Maximum	1.88	2.17	1.90	1.88	1.72	1.88	1.95	1.99

FI	Snowmelt		spring dry		spring wet		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	17	18
mean	1.61	1.67	1.61	1.62	1.57	1.61	1.63	1.65
median	1.60	1.67	1.62	1.62	1.57	1.62	1.63	1.65
STD	0.05	0.02	0.04	0.03	0.04	0.04	0.05	0.04
Minimum	1.54	1.64	1.54	1.58	1.53	1.54	1.55	1.59
Maximum	1.67	1.70	1.66	1.66	1.69	1.68	1.72	1.73

HIX	Snowmelt		spring dry		spring wet		fall dry	
	Bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	17	18

mean	0.83	0.87	0.92	0.91	0.85	0.91	0.93	0.93
median	0.81	0.87	0.91	0.91	0.84	0.90	0.93	0.93
STD	0.05	0.04	0.02	0.03	0.02	0.03	0.01	0.01
Minimum	0.76	0.81	0.88	0.85	0.82	0.87	0.92	0.91
Maximum	0.91	0.93	0.95	0.94	0.89	0.95	0.94	0.96

C1	Snowmelt		spring dry		spring wet		fall dry	
	Bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	17	18
mean	43.83	43.43	43.61	42.89	42.07	42.39	45.19	43.82
median	44.35	43.00	43.45	42.70	42.04	42.48	45.38	43.72
STD	2.40	0.98	1.07	0.70	0.79	0.62	0.72	1.22
Minimum	40.73	42.00	42.20	41.81	40.80	41.35	43.88	41.66
Maximum	46.61	45.00	45.60	44.13	43.46	43.37	46.02	45.76

C2	Snowmelt		spring dry		spring wet		fall dry	
	Bog	Forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	17	18
mean	23.35	26.86	27.41	28.40	27.28	30.59	25.05	26.67
median	22.69	27.00	27.49	28.94	27.15	30.56	24.94	26.83
STD	1.43	1.07	0.88	1.83	1.27	0.52	0.64	0.98
Minimum	22.16	25.00	26.11	23.29	25.84	29.72	24.19	25.14
Maximum	25.75	28.00	28.66	29.63	30.15	31.47	26.47	28.04

C3	Snowmelt		spring dry		spring wet		drought		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	7	14	17	18
mean	14.03	20.57	14.03	16.89	14.83	19.13	13.00	15.57	13.82	16.32
median	14.19	20.00	14.04	16.99	14.77	19.82	13.00	16.00	14.39	17.04
STD	0.78	0.79	0.52	2.13	0.75	1.64	0.82	1.45	1.08	2.47
Minimum	12.91	20.00	13.40	12.79	13.52	15.72	12.00	13.00	12.11	13.26
Maximum	14.85	22.00	14.95	19.64	16.61	20.5	14.00	18.00	15.25	20.59

C4	Snowmelt		spring dry		spring wet		drought		fall dry	
	Bog	Forest	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	7	14	17	18
mean	6.89	0.00	9.34	5.36	6.75	1.32	11.57	8.57	11.67	8.49
median	7.15	0.00	9.11	5.53	6.83	0.2	11.00	8.00	11.73	8.21

STD	1.96	0.00	0.70	2.09	0.74	2.05	1.13	1.91	0.80	2.59
Minimum	3.77	0.00	8.48	2.72	5.58	0.00	10.00	6.00	10.42	3.54
Maximum	8.67	0.00	10.63	8.93	7.87	5.71	13.00	12.00	13.50	12.95

C5	Snowmelt		spring dry		spring wet		drought		fall dry	
	bog	forest	bog	forest	bog	forest	bog	forest	bog	forest
N	5	7	10	11	13	13	7	14	17	18
mean	11.91	9.29	5.61	6.47	9.07	6.57	5.29	4.36	4.27	4.70
median	12.20	9.00	5.63	6.06	9.52	6.52	5.00	4.50	4.31	4.74
STD	2.74	1.60	1.10	2.33	1.10	1.01	0.49	0.74	0.40	0.57
Minimum	9.02	7.00	3.95	4.58	7.11	5.18	5.00	3.00	3.71	3.28
Maximum	16.05	12.00	7.65	12.57	10.74	8.04	6.00	5.00	4.98	5.77