On the mobilization of dissolved organic carbon in a forested headwater catchment

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Linking topography to hydrological connectivity

Dissertation

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Audio Abstract

Der Audio Abstract fasst die vorliegende Arbeit in nicht-wissenschaftlicher, deutscher Sprache zusammen und ist Teil des Podcasts „Das Dilemma“. Die Folge ist über folgende QR-Codes bzw. Links auf verschiedenen Plattformen abrufbar.

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Summary

Dissolved organic carbon (DOC) constitutes an important link between the terrestrial and the aquatic carbon cycle, as terrestrial systems release DOC into aquatic systems. In this context, inland waters play an important role by transporting substantial amounts of DOC from headwater streams towards rivers and finally the oceans. Besides being an important energy source for aquatic organisms, DOC in aquatic systems is partly transformed to carbon dioxide or methane and, therefore, important with regard to climate change. Although not being toxic per se, DOC can transport pollutants and act as a precursor for carcinogenic compounds and, consequently, is important for drinking water quality. Since the 1980s, DOC concentrations have been observed to increase in many freshwater systems of the northern hemisphere. Possible explanations for this increase are a matter of current debate and include temperature increase as well as changes in precipitation patterns and atmospheric nitrogen and sulphur deposition. The majority of DOC export from a catchment occurs during precipitation events. However, event size is not the only factor influencing DOC mobilization and DOC export quantity. Antecedent wetness conditions and catchment topography play an important role as they influence hydrological connectivity between DOC source areas and streams.

This thesis includes four studies investigating the link between hydrological connectivity and topography and how this influences DOC quality, mobilization and export in a small, forested headwater catchment located in the Bavarian Forest National Park (Germany). The focus lies on the analysis of high-frequency in-stream DOC data, which have been collected at three topographically different subcatchments from 2018 until 2021 using ultraviolet-visible spectrometry. In addition to that, shallow and deep groundwater samples as well as soil samples were taken in the catchment. Complementary to DOC concentrations, cation concentrations were analyzed. Moreover, DOC quality was investigated using absorbance and fluorescence spectrometry as well as Fourier transform ion cyclotron resonance mass spectrometry.

Study 1 focused on DOC mobilization processes and DOC export from topographically different subcatchments during four precipitation events, which were characterized by different antecedent wetness conditions and different amounts of precipitation. Generally, DOC load during the events increased with total catchment wetness, which highlighted the importance of antecedent wetness conditions and event size for DOC mobilization. The contribution of the investigated subcatchments to total DOC export from the entire catchment varied between the events. Surprisingly, DOC export of the upper catchment was disproportionally high following drought periods. This observation could be attributed to the low hydrological connectivity in the flat, lower catchment, which inhibited DOC mobilization, rather than an increased DOC export from the upper catchment. This study showed a clear link between antecedent wetness conditions, hydrological connectivity and topography.

Study 2 took up the issue of hydrological connectivity in the flat, lower subcatchment and investigated the influence of microtopographical depressions in the riparian zone for DOC export during events. The shallow groundwater below the microtopographical depressions was characterized by higher DOC concentrations and a higher aromaticity than the shallow groundwater below the typical forest soil. These differences were used to show that water accumulating below and in the microtopographical depressions was exported to the stream during events, thereby altering in-stream DOC quality.

Study 3 shed light on seasonal differences in DOC export from the entire catchment and between the three subcatchments. DOC export was largely influenced by hydrological conditions throughout the one-year investigation period leading to a high DOC export during snowmelt and spring and a low DOC export during summer and winter. The contribution to DOC export from the subcatchments varied seasonally. As seen in Study 1 on an event-scale, the flat, lower subcatchment contributed less than expected in terms of area during and after dry periods due to the low hydrological connectivity. This led to a disproportionally higher contribution of the upper subcatchments on a seasonal scale. The contribution to DOC export was closely linked to the contribution to runoff, which was generally higher in the steep, upper catchments than in the flat, lower catchment.

Study 4 investigated differences in DOC quality along the stream and compared them to potential DOC sources in the riparian zone. DOC quality in the lower stream sections indicated DOC originating from shallow soil layers, whereas DOC quality in the upper stream sections indicated DOC originating from deeper soil layers. These results confirmed the differences in DOC mobilization processes observed in Study 1 and Study 3 and confirmed the importance of upper soil layers in the riparian zone found in Study 2.

In summary, the results of this thesis highlight the importance of topography for hydrological connectivity and its influence on DOC mobilization. As climate change is likely to affect temporal and spatial patterns of hydrological connectivity in the future, changing DOC export patterns and changing DOC quality could have consequences for aquatic organisms, greenhouse gas formation and the management of drinking water reservoirs.

Zusammenfassung

Gelöster organischer Kohlenstoff (DOC) ist ein wichtiges Bindeglied zwischen dem terrestrischen und dem aquatischen Kohlenstoffkreislauf, da terrestrische Systeme DOC in aquatische Systeme abgeben. In diesem Zusammenhang spielen die Binnengewässer eine wichtige Rolle, da sie erhebliche Mengen an DOC aus den Oberläufen in die Flüsse und schließlich in die Ozeane transportieren. DOC ist in aquatischen Systemen nicht nur eine wichtige Energiequelle für Mikroorganismen, sondern wird teilweise auch in Kohlendioxid oder Methan umgewandelt und ist daher im Hinblick auf den Klimawandel von Bedeutung. Obwohl DOC an sich nicht toxisch ist, kann DOC Schadstoffe transportieren und in krebserregende Verbindungen umgewandelt werden. Daher ist DOC für die Trinkwasserqualität von Bedeutung. Seit den 1980er Jahren ist in vielen Binnengewässern der nördlichen Hemisphäre ein Anstieg der DOC-Konzentrationen zu beobachten. Mögliche Erklärungen für diesen Anstieg werden derzeit diskutiert und umfassen den Temperaturanstieg sowie Veränderungen der Niederschlagsverteilung und der atmosphärischen Stickstoff- und Schwefeldeposition. Der größte Teil des DOC-Exports aus einem Einzugsgebiet findet während Niederschlagsereignissen statt. Die Größe des Ereignisses ist jedoch nicht der einzige Faktor, der die DOC-Mobilisierung und die DOC-Exportmenge beeinflusst. Die Vorfeuchte und die Topographie des Einzugsgebiets spielen eine wichtige Rolle, da sie die hydrologische Konnektivität zwischen DOC-Quellgebieten und Fließgewässern beeinflussen.

Diese Arbeit umfasst vier Studien, die den Zusammenhang zwischen hydrologischer Konnektivität und Topographie und deren Einfluss auf die DOC-Qualität, -Mobilisierung und -Export in einem kleinen, bewaldeten Einzugsgebiet im Nationalpark Bayerischer Wald (Deutschland) untersuchen. Der Fokus liegt auf der Analyse von hochaufgelösten DOC-Daten, die von 2018 bis 2021 in drei topographisch unterschiedlichen Teileinzugsgebieten im Bach mittels UV-Vis-Spektrometrie (ultraviolet-visible) erhoben wurden. Darüber hinaus wurden im Einzugsgebiet Proben vom flachen und tiefen Grundwasser sowie Bodenproben entnommen. Ergänzend zu den DOC-Konzentrationen wurden auch die Kationenkonzentrationen analysiert. Außerdem wurde die DOC-Qualität mit Hilfe von Absorptions- und Fluoreszenzspektrometrie sowie von Fourier-Transformations-Ionenzyklotronresonanz-Massenspektrometrie untersucht.

Studie 1 konzentrierte sich auf die DOC-Mobilisierungsprozesse und den DOC-Export aus topographisch unterschiedlichen Teileinzugsgebieten während vier Niederschlagsereignissen, die durch unterschiedliche vorangehende Vorfeuchte-

Bedingungen und unterschiedliche Niederschlagsmengen gekennzeichnet waren. Im Allgemeinen nahm die DOC-Fracht während der Ereignisse mit der Gesamtfeuchte des Einzugsgebiets zu, was die Bedeutung der Vorfeuchte und der Größe des Ereignisses für die DOC-Mobilisierung hervorhebt. Der Beitrag der untersuchten Teileinzugsgebiete zum gesamten DOC-Export variierte zwischen den Ereignissen. Überraschenderweise war der DOC-Export des oberen Einzugsgebiets nach Trockenperioden überproportional hoch. Diese Beobachtung ist eher auf die geringe hydrologische Konnektivität im flachen, unteren Einzugsgebiet zurückzuführen sein, die die DOC-Mobilisierung hemmt, anstatt auf einen erhöhten DOC-Export aus dem oberen Einzugsgebiet. Diese Studie zeigte einen eindeutigen Zusammenhang zwischen der Vorfeuchte, der hydrologischen Konnektivität und der Topographie.

In Studie 2 wurde die Frage der hydrologischen Konnektivität im flachen, unteren Teileinzugsgebiet aufgegriffen und der Einfluss mikrotopographischer Vertiefungen in der Uferzone auf den DOC-Export während Niederschlagsereignissen untersucht. Das flache Grundwasser unterhalb der mikrotopographischen Vertiefungen war durch höhere DOC-Konzentrationen und eine höhere Aromatizität gekennzeichnet als das flache Grundwasser unterhalb des typischen Waldbodens. Diese Unterschiede wurden genutzt, um zu zeigen, dass das Wasser, das sich unter und in den mikrotopographischen Senken ansammelt, bei Ereignissen in den Fluss transportiert wurde, wodurch sich die DOC-Qualität im Fluss veränderte.

Studie 3 beleuchtete die saisonalen Unterschiede des DOC-Exports aus dem gesamten Einzugsgebiet und zwischen den drei Teileinzugsgebieten. Der DOC-Export wurde während des einjährigen Untersuchungszeitraums weitgehend von den hydrologischen Bedingungen beeinflusst, was zu einem hohen DOC-Export während der Schneeschmelze und im Frühjahr und einem niedrigen DOC-Export im Sommer und Winter führte. Der Beitrag zum DOC-Export aus den Teileinzugsgebieten variierte saisonal. Wie in Studie 1 auf der Ereignis-Ebene zu sehen war, trug das flache, untere Teileinzugsgebiet während und nach Trockenperioden aufgrund der geringen hydrologischen Konnektivität weniger bei als flächenmäßig erwartet. Dies führte zu einem überproportional höheren Beitrag der oberen Teileinzugsgebiete auf der saisonalen Skala. Der Beitrag zum DOC-Export stand in engem Zusammenhang mit dem Beitrag zum Abfluss, der in den steilen, oberen Einzugsgebieten im Allgemeinen höher war als im flachen, unteren Einzugsgebiet.

Studie 4 untersuchte Unterschiede in der DOC-Qualität entlang des Baches und verglich sie mit potenziellen DOC-Quellen in der Uferzone. Die DOC-Qualität in den unteren

Bachabschnitten deutete auf DOC aus flachen Bodenschichten hin, während die DOC-Qualität in den oberen Bachabschnitten auf DOC aus tieferen Bodenschichten hindeutete. Diese Ergebnisse bestätigten die in Studie 1 und Studie 3 beobachteten Unterschiede bei den DOC-Mobilisierungsprozessen und bestätigten die in Studie 2 festgestellte Bedeutung der oberen Bodenschichten in der Uferzone.

Zusammenfassend lässt sich sagen, dass die Ergebnisse dieser Arbeit die Bedeutung der Topographie für die hydrologische Konnektivität und ihren Einfluss auf die DOC-Mobilisierung hervorheben. Da sich der Klimawandel in Zukunft wahrscheinlich auf die zeitlichen und räumlichen Muster der hydrologischen Konnektivität auswirken wird, könnten veränderte DOC-Exportmuster und eine veränderte DOC-Qualität Konsequenzen für aquatische Organismen, die Bildung von Treibhausgasen und das Management von Trinkwasserspeichern haben.

1. Introduction

1.1. Dissolved organic carbon – an important link between the terrestrial and the aquatic carbon cycle

Dissolved organic carbon (DOC) is the result of the breakdown of plant and animal tissue and comprises different classes of organic compounds ranging in size from simple amino acids to complex high-molecular-weight DOC (Leenheer & Croué, 2003; Nebbioso & Piccolo, 2013; Neff & Asner, 2001). It is operationally defined as the portion of organic carbon that passes through a 0.45 µm filter in contrast to particular organic carbon (POC), which is defined as the portion not passing a 0.45 µm filter. In forested systems, a large part of the occurring DOC in freshwater systems consists of humic acids, which leads to a typical brown color of the waters in case of high concentrations (Leenheer & Croué, 2003; Roulet & Moore, 2006). Usually, DOC concentrations in freshwater systems vary from 1 to 10 mg L^{-1} but can reach up to 60 mg L^{-1} in swamps and bogs (Thurman, 1985).

DOC represents an important link between the terrestrial and aquatic carbon cycle as terrestrial systems release carbon into aquatic systems. DOC export from inland waters may influence the global carbon cycle more than previously thought (Battin et al., 2009). The global DOC export reaching inland waters annually from the terrestrial environment is estimated at 5.1 Pg C, of which a large part (3.9 Pg C) outgasses to the atmosphere in form of the greenhouse gases carbon dioxide (CO_2) or methane (CH_4) (Drake et al., 2018). Therefore, DOC plays an important role in the context of climate change. DOC is also an important energy source for microorganisms (Marschner & Kalbitz, 2003) and can influence the abundance of aquatic macroinvertebrates (Arzel et al., 2020; Feuchtmeyer et al., 2019). As DOC forms complexes with organic pollutants (Hope et al., 1994) and toxic metals such as mercury (Ravichandran, 2004) or lead (Dörr & Münnich, 1991), it has the potential to influence drinking water quality. Moreover, elevated DOC concentrations can cause problems for drinking water treatment via chlorination as DOC acts as a precursor of trihalomethanes, which have potentially carcinogenic and mutagenic properties (Alarcon-Herrera et al., 1994; Regan et al., 2017; Sadiq & Rodriguez, 2004).

Since the beginning of the 1980s, an increase in DOC concentrations has been observed in a large number of streams, rivers and lakes of the northern hemisphere, where the majority of studies on DOC were conducted (Evans et al., 2005; Monteith et al., 2007; Roulet & Moore, 2006). In addition to the implications of the DOC increase for climate change, aquatic organisms, transport of pollutants and drinking water quality as mentioned above, the increase in DOC concentrations could indicate an increased leaching from soils and peatlands and, therefore, influence terrestrial carbon storage. Rising DOC concentrations could have the potential to deplete the terrestrial carbon pools, which are of global importance for carbon storage (Batjes, 2014; Dixon et al., 1994; Kindler et al., 2011).

Several hypotheses have been proposed in order to explain the increase of DOC in surface waters, including a decline in atmospheric nitrogen deposition (Musolff et al., 2016), temperature increase (Weyhenmeyer & Karlsson, 2009), precipitation increase (Hongve et al., 2004) and a decline in atmospheric sulphur deposition (Evans et al., 2005; Ledesma et al., 2016; Monteith et al., 2007). Roulet and Moore (2006) state that it is difficult to isolate a single factor as there are many different variables influencing DOC production and export. Clark et al. (2010) summarized the research published from 2001 to 2009 about long-term trends in DOC concentrations. The 21 included studies were conducted in North America and Europe and found a positive DOC trend at most study sites during the 1980s and 1990s. The drivers that were most commonly tested were acid deposition, temperature and precipitation and all were found to be responsible for the DOC increase in about half of the studies in which they were tested. Other less frequently tested drivers were sea salt deposition, nitrogen enrichment, atmospheric CO_2 and land management. However, characteristics of the catchment area and sample frequency differed greatly between the different studies. Eimers et al. (2008) also underline the importance of keeping in mind the differences in record lengths, sampling methods and data processing in the numerous studies regarding the topic of DOC increase.

1.2. Influences on DOC production, mobilization and export

Most of the DOC export occurs during precipitation events (Raymond & Saiers, 2010). High DOC export during events is not only a result of increasing discharge but also of increasing DOC concentrations during events, which have been observed in many catchments (Hobbie & Likens, 1973; Meyer & Tate, 1983; Moore, 1989). Large single events can contribute significantly to the annual DOC export in small catchments, whereby the event size is often more important than the event frequency (Raymond et al., 2016). In temperate and boreal catchments, snowmelt plays an important role in DOC mobilization and can substantially contribute to the annual DOC export (Hornberger et al., 1994; Jager et al., 2009; Pacific et al., 2010; Seybold et al., 2019; Wilson et al., 2013). Nevertheless, event size is not the only factor influencing the amount of DOC that is exported during an event. Antecedent wetness conditions can inhibit or enhance the mobilization of DOC during events because wetness conditions largely influence hydrological connectivity of DOC sources to the stream (Detty & McGuire, 2010; McGuire & McDonnell, 2010; Penna et al., 2015).

Many definitions of “hydrological connectivity” have been proposed and the term is often seen as ambiguous (Michaelides & Chappell, 2009). For instance, Blume and van Meerveld (2015) defined hydrological connectivity as the “linkage of separate regions of a catchment via water flow” and Bracken and Croke (2007) defined it as “the passage of water from one part of the landscape to another”. Hydrological connectivity varies over temporal and spatial scales. Temporally, it varies on a large scale over seasons and on a short scale in response to precipitation events (Detty & McGuire, 2010; Zimmer & McGlynn, 2018). It also occurs along many spatial dimensions, which may include hillslopes, the hyporheic zone, groundwater, riparian zones and streams (Covino, 2017). It can vary on a large scale between landscape elements (Laudon et al., 2011) or on a small scale in the vertical soil profile (Ledesma et al., 2018). Numerous studies have shown that patterns and dynamics of hydrological connectivity influence not only discharge but also solute concentrations (e.g. DOC) due to the (dis-) connection of source areas over varying temporal and spatial scales. Therefore, it influences event-based DOC export (Kiewiet et al., 2020; Tunaley et al., 2016) as well as seasonal DOC export (Zimmer & McGlynn, 2018).

However, mobilization is only one side of the coin when investigating DOC export. If a system is lacking DOC, even large precipitation events will not be able to mobilize and export DOC. Therefore, it is necessary to keep in mind DOC production. The predominant locations of DOC production in terrestrial ecosystems are the upper soil layers, from where only a small fraction reaches the stream (Kaiser & Kalbitz, 2012; Kalbitz et al., 2000; Michalzik et al., 2001). Nonetheless, in-stream DOC production can also contribute to DOC export from catchments (Bernal et al., 2019; Lupon et al., 2019) and DOC stored in-stream can contribute to DOC export during events (Wondzell & Ward, 2022). In general, DOC production is strongly influenced by seasonality, as it is linked to temperature (Christ & David, 1996; Neff & Hooper, 2002). DOC production is happening mostly during spring, summer and autumn, when temperatures are higher than during winter (Kalbitz et al., 2000; Tipping et al., 1999; Wen et al., 2020). However, DOC production can even occur in snow-covered soils (Brooks et al., 1999). Soil wetness is another factor influencing DOC production. Dry soils can inhibit decomposition, which is why dry summers can lead to a limited DOC production in spite of warm temperatures (Kalbitz et al., 2000). Nevertheless, several studies have shown that autumnal events following a dry summer export large amounts of DOC due to the accumulation of DOC in disconnected catchment parts during the summer months lacking precipitation events (Biron et al., 1999; van Verseveld et al., 2009; Wen et al., 2020). In forested, temperate ecosystems, autumnal leaf litter constitutes an additional important DOC source (Hongve, 1999; McDowell & Fisher, 1976). The type of vegetation can also influence DOC export. Soil leachates beneath coniferous trees often contain more DOC than soil leachates beneath deciduous trees (Borken et al., 2011; Kalbitz et al., 2000; Schwarze & Beudert, 2009; Thieme et al., 2019).

DOC availability is not only dependent on temperature, soil moisture and vegetation type, but also on the general land cover (Aitkenhead-Peterson et al., 2007; Li et al., 2015; Vaughan et al., 2017). For instance, wetlands are known to contain and export large numbers of DOC (Laudon et al., 2011; Li et al., 2015; Musolff et al., 2018; Zarnetske et al., 2018). In forested catchments, so-called cryptic wetlands, which are hidden beneath the forest canopy, can contribute substantially to DOC export (Creed et al., 2003). Cryptic wetlands are located in topographic depressions, which are known to be an important source zone for DOC (Musolff et al., 2018). Besides antecedent wetness conditions, event size, DOC production and land cover, topography is indeed a key factor for DOC mobilization.

1.3. The role of topography for DOC mobilization and export

Topographic characteristics of a catchment (e.g. slope, hillslope shape) control the occurrence and persistence of hydrological connectivity between different catchment compartments (Inamdar & Mitchell, 2006, 2007; Tetzlaff et al., 2014). This is due to the fact that topography controls soil saturation and the fluctuation of shallow water tables and the formation of flow pathways (Burt & Pinay, 2005; Detty & McGuire, 2010; Rinderer et al., 2014; Rinderer et al., 2016).

By shaping the flow pathways, topography also exerts an influence on DOC mobilization. Flow pathways determine what possible DOC sources are connected to the stream and, therefore, how much and how fast DOC is transported to the stream. Large-scale studies have shown that topography is an important factor for DOC export in many catchments (Li et al., 2015; Zarnetske et al., 2018). In a virtual experiment, Weiler and McDonnell (2006) found that DOC mobilization processes differ with geometrical properties of hillslopes.

McGlynn and McDonnell (2003) observed that hillslopes contributed to runoff at different times during precipitation events in small headwater catchments than riparian zones leading to nonlinear concentration-discharge relationships. Still, topography does not only influence mobilization processes and flow pathways to the stream. For instance, Jankowski and Schindler (2019) have shown that DOC transport and storage in streams differ with catchment morphology, as the temperature sensitivity of respiration depends on geomorphic features.

Several studies have shown that DOC concentrations are correlated to the topographic wetness index (TWI), which represents the propensity of catchment parts for wetness (Andersson & Nyberg, 2009; Beven & Kirkby, 1979; Liu et al., 2014; Musolff et al., 2018; Ogawa et al., 2006). This is due to the abundance of wetlands and riparian zones in flat areas, which both are important DOC sources, especially in temperate catchments. Although not all riparian zones are wetlands, many riparian zones are similar to wetlands especially regarding the biogeochemistry of the saturated soils (Vidon, 2017). Riparian zones are important for DOC export because they are (1) an important DOC source (Blazejewski et al., 2009; Fiebig et al., 1990) and (2) often well connected to the stream (Inamdar & Mitchell, 2006). The riparian zone is often very heterogeneous, varying in width (Ledesma et al., 2018), vegetation (Kuglerová et al., 2014; Park & Kim, 2020), carbon content (Blazejewski et al., 2009), soil composition (Grabs et al., 2012), permeability (Vidon & Hill, 2004) and hydrological connectivity (Ledesma et al., 2018; Ploum et al., 2020). Hydrological connectivity influences which parts of the riparian zone contribute to discharge and DOC export.

Not only topography on the catchment-scale influences flow pathways and DOC mobilization, but also small-scale topographical differences can have an impact on hydrological connectivity, DOC production and export. Surface microtopography can strongly influence hydrological connectivity, as microtopographical depressions fill up with water during precipitation events. The spilling following additional precipitation input can lead to an additional surface water input to streams and can influence runoff generation (Antoine et al., 2009; Frei et al., 2010; Tromp-van Meerveld & McDonnell, 2006). Moreover, microtopographical features have the potential to influence the formation of biogeochemical hot spots in wetland systems (Frei et al., 2012). Several studies found biogeochemical differences in relation to microtopographical heterogeneity in wetlands (Diamond et al., 2021), e.g. regarding redox conditions (Courtwright & Findlay, 2011) and greenhouse gas emissions (Cresto Aleina et al., 2015; Mazzola et al., 2021). Moreover, microtopographical features can affect DOC export. Wet depressions in the riparian zone can strongly contribute to the DOC export from catchments, as shown for both a temperate (Werner et al., 2021) and a boreal catchment (Ploum et al., 2021).

In conclusion, topography, hydrological connectivity and DOC mobilization and export are closely linked. This thesis aims at gaining further insights into the interplay of topography and hydrological connectivity and the influences on DOC mobilization and export.

2. Objectives and Structure

The present thesis was conducted as part of a joint research project with the goal to investigate the influence of natural factors on concentration, quality and effect of dissolved organic carbon (DOC) in the Bavarian Forest National Park (BFNP). The four working packages focused on (1) the impact of topography on the creation of flow paths and the mobilization of DOC (University of Bayreuth), (2) the quality of DOC (Helmholtz Center for Environmental Research Leipzig), (3) the modeling of export and mobilization processes of DOC (Technical University Dresden) and (4) the biological diversity of macro-benthic organisms in relation to DOC (Senckenberg Nature Research Society). The multi-disciplinary project has been developed in close cooperation with the BFNP administration that strongly encourages research in the National Park with the goal to gain further insights into this unique ecosystem and to adjust its management accordingly.

The overall goal of this thesis was to gain insights into DOC mobilization processes and how they are linked to different catchment parts and, therefore, topography. This thesis focuses on the hydrological processes influencing DOC mobilization on different spatial and temporal scales. It also sheds light on chemical DOC composition and biogeochemical processes. This thesis comprises four studies:

Study 1: Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment

Study 2: Microtopographical structures in the riparian zone influence event-based DOC mobilization and quality in a forested headwater catchment

Study 3: High-resolution DOC measurements indicate seasonal differences in the contribution of three nested forested subcatchments to DOC export

Study 4: Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments

The presented studies address several of the “twenty-three unsolved problems in hydrology”, collected by Blöschl et al. (2019), regarding source variability and scaling (e.g. Question 5: “What causes spatial heterogeneity and homogeneity in runoff, evaporation, subsurface water and material fluxes […]?”), interfaces in hydrology (e.g. Question 11: “What are the processes that control hillslope-riparian-stream-groundwater interactions and when do the compartments connect?”) and measurements and data (e.g. Question 16:

"How can we use innovative technologies to measure surface and subsurface properties, states and fluxes at a range of spatial and temporal scale?").

Whereas Study 2 and Study 4 investigated possible DOC sources and their differences in DOC quality, Study 1 and Study 3 highlighted the differences in event based and seasonal DOC mobilization and export between the subcatchments. An asset of Study 1, Study 3 and Study 4 clearly was the high temporal resolution of the collected data. Many studies have shown that weekly or bi-weekly samplings lead to a large uncertainty, when investigating DOC mobilization processes (Schleppi, Waldner, & Fritschi, 2006; Schleppi, Waldner, & Stähli, 2006). As DOC concentrations change in a matter of hours or even minutes as a response to precipitation events, high-frequency data are necessary to capture quick changes in DOC concentrations. In Study 1, Study 3 and Study 4, novel techniques were used allowing the measurements of DOC concentrations at a 15-minutes interval. Therefore, it was possible to investigate the detailed in-stream DOC response to events (Study 1), to observe seasonal changes in DOC export (Study 3) and to examine DOC concentrations and DOC quality during baseflow (Study 4) much more accurately than by using infrequent grab samples.

Study 1 aimed at investigating the influence of event size, antecedent wetness conditions and topography on DOC mobilization and export. The objective was to better understand the interplay between these three factors during precipitation events.

Research questions of Study 1:

- How are DOC mobilization processes influenced by event size and antecedent wetness conditions?
- Are there differences in DOC mobilization and export between subcatchments due to topography?

We hypothesized that hydrological connectivity, which is controlled by the antecedent wetness conditions and precipitation event size, influences DOC mobilization processes and DOC export. We further hypothesized that different topographical positions within the catchment promote different hydrological mobilization and transport processes, and therefore, concentration-discharge relationships and DOC export will differ between the subcatchments.

Study 2 zoomed in on the riparian zone of the lower subcatchment to identify possible DOC source areas and to understand the importance of microtopography for DOC quality and for event-based DOC mobilization.

Research questions of Study 2:

- How does microtopography influence DOC concentrations and DOC quality in the shallow groundwater of the riparian zone?
- Does microtopography have an impact on the quality and quantity of mobilized DOC during precipitation events?

We hypothesized that microtopographical depressions contribute to DOC export to the stream during precipitation events and that the contribution of this DOC can subsequently alter stream DOC quality.

Study 3 shed a light on the seasonal variations in DOC export. The goal was to investigate how DOC exports varied seasonally. A major focus was placed on the differences in DOC export numbers between the subcatchments over the course of one year.

Research questions of Study 3:

- What is the annual DOC export from the entire catchment and how does it vary seasonally?
- Are there seasonal differences between the contributions of subcatchments to DOC export?
- Which factors influence seasonal differences and differences between the subcatchments?

We hypothesized that DOC export is strongly influenced by seasons due to differences in DOC production and hydrological connectivity. We also hypothesized that the contribution of the different subcatchments varies between the seasons as a result of differences in topography and its influence on hydrological connectivity.

Study 4 aimed at characterizing differences in DOC concentration and composition along the topographical gradient of the stream during baseflow conditions. The objective was to investigate in-stream differences in DOC composition and compare the in-stream composition to possible DOC source areas of the catchment.

Research questions of Study 4:

- How do in-stream DOC concentrations and composition vary between the topographically different catchment parts during baseflow conditions?
- Can the in-stream DOC composition be linked to different possible DOC source areas in the catchment?

We hypothesized that the DOC composition in the steep, upper catchment part is driven by groundwater input, whereas the riparian soils influence DOC composition in the lower catchment part. Therefore, we hypothesized that DOC composition would be more variable over the year at the lower catchment part than at the upper catchment part.

3. Materials and Methods

3.1. Study site

3.1.1. Catchment characteristics

All research was conducted from 2018 to 2021 in the Hinterer Schachtenbach catchment (HS_{tot}, 3.5 km^2, Figure 1a), which is part of the Große Ohe catchment (19.2 km^2). The Große Ohe Catchment is part of the Bavarian Forest National Park (BFNP), which is located in southeastern Germany and shares a border with the Czech Republic (Figure 1b). The BFNP covers an area of 243 km^2. HS_{tot} comprises three nested subcatchments (Table 1): The streams of the upper subcatchments Markungsgraben (MG, 1.1 km^2) and Kaltenbrunner Seige (KS, 0.9 km^2) join to form the stream of the lower subcatchment Hinterer Schachtenbach (HS_{sub}, 1.5 km^2).

Table 1: Catchment characteristics of the entire catchment HS_{tot} and the subcatchments KS, MG and HS_{sub}. All data were provided by the BFNP administration.

		HS_{tot}	KS	MG	HS_{sub}
	Area (km^2)	3.5	0.9	1.1	1.5
	Area ratio of HS_{tot} (%)	100	26	31	43
	Elevation (m a.s.l.)	771 - 1373	877 - 1279	876 - 1373	771 – 1085
	Mean slope (°)	12.0	14.5	15.8	7.4
Soil (%)	Cambisol	66	79	55	65
	Podzol	15	16	34	0
	Hydromorphic soil	18	5	5	35
	Other	1	0	6	0
Vegetation (%)	Rejuvenation	34	28	57	21
	Deciduous forest	41	53	29	42
	Coniferous forest	9	1	4	17
	Mixed forest	15	17	8	19
	Other	1	0	3	1

Elevation in the entire catchment ranges from 771 m to 1373 m with a mean slope of 12.0°, whereas MG and KS represent the upper, steep part of the catchment with a slope of 15.8° and 14.5°, respectively, and HS_{sub} represents the lower part of the catchment with a slope of 7.4°. MG has the largest proportion of steep hills with 22.9 % of its area having a slope over 20°. Only 2.2 % of the area of KS and 0.6 % of the area of HS_{sub} have a slope of over 20°. In the large flat riparian zone of HS_{sub}, small ponds of unclear origin are a common feature. The geology of the Große Ohe catchment is dominated by biotite granite and cordierite–sillimanite gneiss. The soils are mainly Cambisols, Podzols and hydromorphic soils, whereby the proportion differs between the subcatchments. KS and MG are dominated by Cambisols and Podzols with a larger proportion of Cambisols at KS. HS is dominated by Cambisols and hydromorphic soils. Almost 40 % of the area of MG are also characterized by rocks, which are interspersed in the soils. Pleistocene solifluction processes created deeper soil layers in the lower catchment parts than in the upper catchment parts. The entire catchment is almost entirely covered by forest. Dominant tree species are Norway spruce (*Picea abies*, 70 %) and European beech (*Fagus sylvatica*) but large parts of the catchment are in a stage of rejuvenation due to bark beetle outbreaks in the mid-1990s and 2000s, especially in the subcatchment MG (Beudert et al., 2015).

Mean annual precipitation was 1557 mm at MG and 1341 mm at HS_{tot} (1988 – 2017) and mean annual temperature was 6.4 °C (1988 – 2017) at Waldhäuser, a station located 3.8 km east of HS_{tot}, outside of the Große Ohe catchment (Table 2).

Table 2: Annual precipitation at MG and HS_{tot} and mean annual temperature at Waldhäuser for the years 2018, 2019, 2020 and 2021 as well as the long-term annual mean precipitation and temperature (1988 - 2017). Waldhäuser is a station located outside of the Große Ohe catchment, ca. 3.8 km east of HS_{tot}. All data were provided by the BFNP administration.

	1988 – 2017 (mean)	**2018**	**2019**	**2020**	**2021**
Annual precipitation at MG (mm)	1557	1274	1380	1293	1438
Annual precipitation at HS_{tot} (mm)	1341	1126	1125	1072	1212
Mean annual temperature (°C)	6.4	7.8	7.7	7.6	6.5

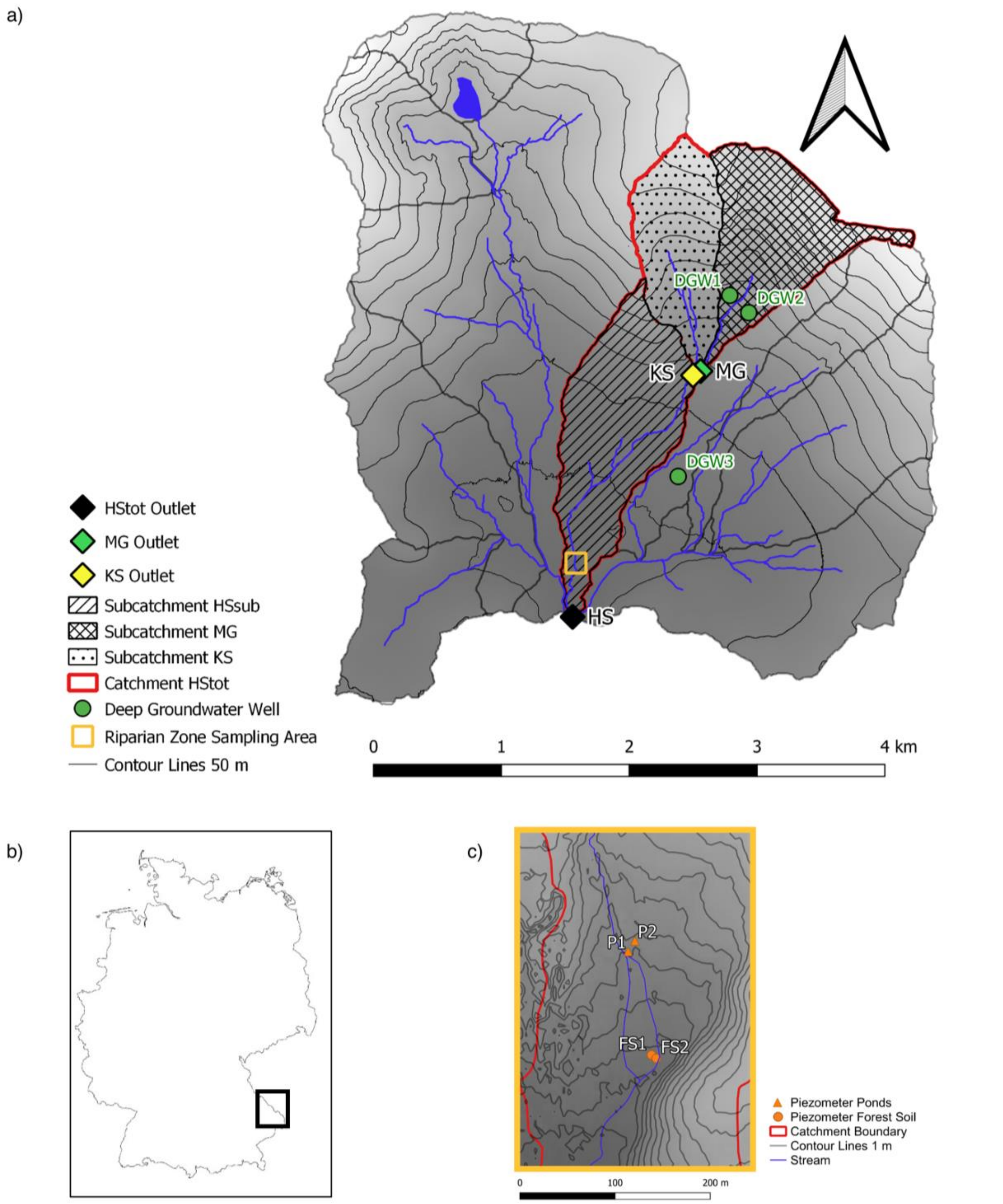

Figure 1: a) The Hinterer Schachtenbach catchment (HS_{tot}, red outline) is part of the Große Ohe catchment and comprises the three subcatchments Kaltenbrunner Seige (dotted), Markungsgraben (checked) and Hinterer Schachtenbach (hatched). The main in-stream sampling sites were located at the corresponding outlets KS (yellow diamond), MG (green diamond) and HS_{tot} (black diamond). Study 4 refers to MG as MGL and to HS_{tot} as HSL. Study 4 includes the additional sampling location HSU (blue diamond). The deep groundwater wells (green dots) are located in the subcatchment Markungsgraben and in a neighboring subcatchment. Shallow groundwater was sampled in piezometers located in the riparian zone sampling area (orange square), which is shown in more detail in Figure 1c. Both the location of the stream network and the digital elevation model were provided by the Bavarian State Office for Environment. b) The BFNP is located in southeastern Germany. The map was derived from Vemaps (2022). c) The riparian zone sampling area with the locations of the two piezometers located in the forest soil (FS1 and FS2; orange circles) and the two piezometers located in the ponds (P1 and P2; orange

triangles, also see Figure 3). Later in the text, site FS refers to FS1 and FS2 and site P refers to P1 and P2.

3.1.2. Previous work in the Große Ohe catchment

Since the creation of the BFNP, great emphasis has been placed not only on nature conservation but also on research. A special focus has been placed on the impact of large bark beetle outbreaks in the 1990s on the forest ecosystem and, consequently, the water regime and water quality. Over 50 % of the area and 75 % of mature Norway spruce (*Picea abies*) were affected (Beudert et al., 2015), which led to a wide public debate if the BFNP should intervene. In the end, the BFNP decided to stick to its policy “Let nature be nature” (Nationalparkverwaltung Bayerischer Wald, 2022). Following the bark beetle disturbances, earlier and intensified snowmelt as well as an increased groundwater recharge in summer and a rise in low flows in autumn were observed in the Große Ohe catchment (Bernsteinová et al., 2015). Schwarze and Beudert (2009) showed that a decrease of evapotranspiration led to a rise in discharge during high flood events, especially as a result of the increase of fast flow components. Public concerns about the possibility of a deteriorating drinking water quality could not be confirmed as in-stream nitrate concentrations increased only temporarily and stayed well below the recommended limit for drinking water (Beudert et al., 2015). However, biodiversity increased significantly following the bark beetle outbreaks leading to the conclusion that the policy of not intervening was the right decision (Beudert et al., 2015).

3.2. Data collection

3.2.1. Sampling locations

High-frequency data was collected at the subcatchment outlets HS_{tot}, MG and KS and shortly at HSU (Figure 1, Figure 2, Table 3). All data that refer to HS_{sub} have not been directly measured but were derived from the difference of HS_{tot} and the upper subcatchments (MG and KS). In Study 1, in-stream data from the outlets of MG and HS_{tot} were used. Study 2 focused on the riparian zone of the subcatchment HS_{sub}, where possible DOC source areas were sampled. In-stream data from the outlet HS_{tot} were used. In Study 3, in-stream data from all three outlets HS_{tot}, MG and KS were used and data for HS_{sub} were derived as explained above. In Study 4, in-stream data from the outlet of HS_{tot} (called HSL in Study 4) and MG (called MGL in Study 4) were used and possible DOC source areas in the riparian zone of the subcatchment HS_{sub} were sampled. Additional in-stream data were collected from several sampling points along the stream in subcatchment HS_{sub} and MG.

Figure 2: The sampling locations of the high-frequency DOC measurements at the outlets of a) HS_{tot}, b) KS and c) MG.

3.2.2. High-frequency measurements of DOC concentrations

High-frequency DOC concentrations were measured in situ using three UV-Vis (ultraviolet-visible) spectrophotometers (spectro::lyser, s::can GmbH, Vienna, Austria) during different periods between 2018 and 2021 (Devices D1, D2 and D3; Table 3). Study 1 used the data of D1 and D2 during the years 2018, 2019 and 2020. Study 2 used no high-frequency data. Study 3 used the data of D1, D2 and D3 during the years 2020 and 2021. Study 4 used the data of D1, D2 and D3 during the years 2018 and 2019.

The spectrometric devices recorded the absorption spectrum of stream water from 200 to 750 nm with a resolution of 2.5 nm every 15 minutes. DOC concentrations were quantified using the internal calibration based on the absorption values by means of the software ana::pro. In order to refine the internal calibration, the DOC concentrations measured by the three UV-Vis spectrophotometers were calibrated using grab stream samples taken over the course of the sampling period at various discharge conditions (n_{D1} = 52, n_{D2}= 22,

n_{D3} = 45). Samples were filtered in the field using polyethersulfone membrane filters (0.45 µm) or polycarbonate track etched membrane filters (0.45 µm). All samples were stored until further analysis at 4 °C. DOC concentrations of the grab samples were analyzed by thermo-catalytic oxidation (TOC-L analyzer; Shimadzu, Kyoto, Japan). For further analysis, the calibrated values were used (R^2_{D1} = 0.98, R^2_{D2} = 0.87 and R^2_{D3} = 0.97). As no drift of the DOC concentration could be identified in the measured signal, we decided against a correction for biofouling as done by Werner et al. (2019). However, the sensor optics were manually cleaned in the field every 2 weeks using cotton swabs.

Table 3: Periods during which the three spectro::lysers (Devices D1, D2, D3) were installed at the catchment outlets of HS_{tot}, MG and KS. Due to technical failures, there are data gaps of several hours to days at all locations. These data gaps were either not of importance for the investigated time periods or they are specified in the respective studies. *In 2018 and 2019, D3 was not installed at the outlet of HS_{tot}, but 1.2 km upstream at HSU (see Figure 1).

Device number (serial number)	HS_{tot}	MG	KS
D1 (12150159)	12.06.18 – 19.11.18 12.03.19 – 19.11.19 01.04.20 – 22.09.21		
D2 (16430001)		12.06.18 – 20.11.18 09.04.19 – 31.05.19 15.04.20 – 23.06.20	09.10.20 – 22.09.21
D3 (09210079)	11.06.18 – 20.11.18* 09.04.19 – 18.11.19*	09.07.20 – 22.06.21	04.04.20 – 09.07.20

3.2.3. Discharge measurements

Starting in June 2018, the water level at HS_{tot} was measured every 15 minutes using a pressure transducer (Solinst Canada Ltd., Georgetown, ON, Canada; SEBA Hydrometrie GmbH & Co. KG, Kaufbeuren, Germany). Flow velocities were measured periodically at the same location with an electromagnetic current meter (FlowSens; SEBA Hydrometrie GmbH & Co. KG, Kaufbeuren Germany) and via tracer dilution (TQ-S; Sommer Messtechnik, Koblach, Austria). Corresponding discharge was calculated following Kreps (1975). For MG, the discharge data for the complete sampling period were taken from the database of the Bavarian State Office for Environment (2021) at a 15-minutes interval. The discharge at KS was measured via tracer dilution (TQ-S; Sommer Messtechnik, Koblach, Austria) at eight occasions and continuous discharge was derived using a relationship between the highly resolved discharge data of MG and the measured discharge at KS (R^2=0.93).

3.2.4. Additional data

This thesis focuses on the collected in-stream DOC data. However, additional data have been gathered. During an event from 25th to 27th of September (63 mm of precipitation), stream water was sampled hourly using a portable water sampler (ISCO Sampler, Teledyne, Thousand Oaks, United States) at HS_{tot} (black diamond, Figure 1a). In 2020, two piezometers (P1 and P2) were installed in two different vegetation-free ponds (Figure 3) and two piezometers (FS1 and FS2) were installed in the grass-covered, flat forest soil. The shallow groundwater level was measured in FS1, FS2 and P1 (but not in P2) at a 15-minutes interval starting in June 2020 using pressure transducers (Solinst Canada Ltd., Georgetown, Canada). Additionally, a time lapse camera took pictures of the pond P1 at an interval of 30 minutes.

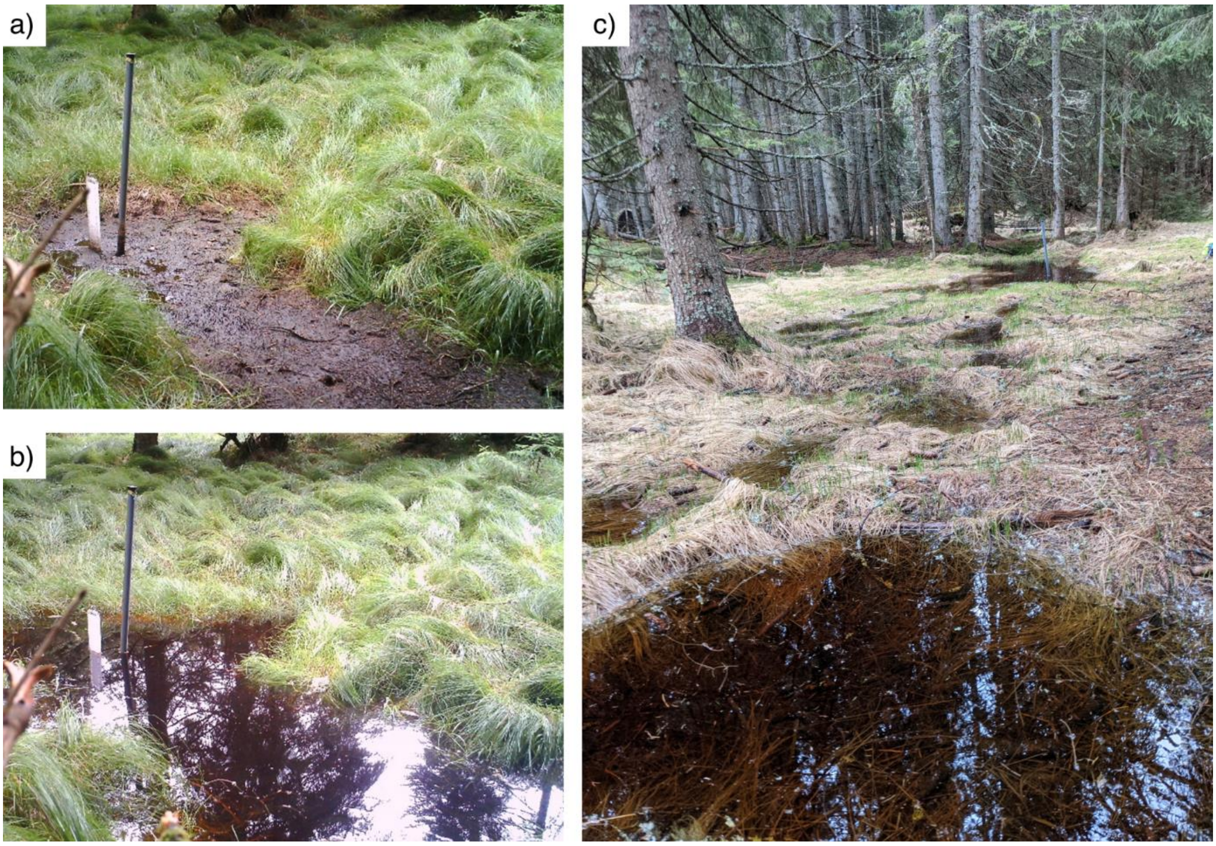

Figure 3: The riparian zone sampling area with a) an empty pond during dry conditions and b) the same pond during wet conditions. c) The ponds became connected via overland flow during wet conditions.

To test for temporal concentration changes, shallow groundwater was sampled from all four piezometers manually using a bailer approximately every three weeks from May until October 2020 resulting in a total of eleven samples per piezometer. Additionally, the pond water itself was sampled at P1 and P2 at five dates. One sample each of three deep groundwater wells (Figure 1) was taken in March 2021: DGW1 (969 m a.s.l., 16. 5 m depth), DGW2 (964 m a.s.l., 17.5 m depth) and DGW3 (819 m a.s.l., 10.3 m depth). The soil profile at FS1 was sampled once by taking six samples using a soil corer over the depth of 5 to 65 cm in October 2020. Furthermore, one grab sample of the topmost 5 cm at P1 was taken in June 2020. Pore water was sampled at P1 and P2 with a resolution of 2 cm to a depth of 20 cm using peepers filled with deionized water which were left to equilibrate with soil water between 16 and 22 days. Precipitation was measured both close to the outlet of HS_{tot} and of MG and data were provided by the BFNP administration for the entire sampling period.

3.3. Laboratory analyses

3.3.1. Spectrometric measurements for the characterization of DOC quality

Absorbance measurements of all samples were performed using UV-Vis spectrophotometry (Cary 100, Varian, Palo Alto, United States), which recorded the absorption spectrum of water samples from 200 to 800 nm with a resolution of 0.5 nm. Two commonly used absorbance metrics were determined: The ratio between the absorbance at 254 and 365 nm (A_{254}/A_{365}), which is negatively correlated to the molecular weight of DOC (Dahlén et al., 1996), and the specific UV absorbance defined as the DOC concentration normalized absorbance at 254 nm ($SUVA_{254}$), which is positively correlated to DOC aromaticity (Weishaar et al., 2003).

A fluorescence spectrometer (LS-55, PerkinElmer, Waltham, United States) recorded fluorescence Excitation-Emission Matrices (EEMs) in 5 nm steps over an excitation range of 240 to 450 nm and in 0.5 nm steps over an emission range of 300 to 600 nm. Prior to analysis, samples were diluted to absorption at 254 nm < 0.3 cm^{-1} to reduce inner-filter effects, if necessary. No Raman normalization was conducted, as ratios were used for further analysis instead of the absolute values. The Fluorescence Index was calculated as the ratio between emission at wavelengths of 570 and 520 nm at an excitation wavelength of 370 nm (McKnight et al., 2001). The Freshness Index was calculated as the ratio between emission at 380 nm and the emission maxima between 420 and 435 nm at an excitation of 310 nm (Parlanti et al., 2000). The Humification Index (HIX) was calculated by dividing the emission intensity in the 435 to 480 nm region by the sum of emission intensities in the 300 to 345 nm region and in the 435 to 480 nm region at an excitation of 255 nm (Ohno, 2002). The spectral slope ratio (S_R) was calculated by dividing the slope in the interval of 275 to 295 nm by the slope at 350 to 400 nm (Helms et al., 2008). In the following, we refer to the calculated absorbance and fluorescence metrics as "DOC quality parameters". We use the DOC quality parameters to highlight qualitative differences between DOC sources, as the characterization of the DOC itself is difficult and the indices need to be interpreted with caution (see Study 2).

3.3.2. Cation concentrations

All water samples for cation analysis were filtered using polycarbonate track etched membrane filters (0.45 µm) or polyethersulfone membrane filters (0.45 µm). All samples were stabilized with 1 vol% 1M HNO_3 and stored until further analyses at 4°C. Concentrations of Al, Ca, Fe, Mg and Mn were determined using inductively coupled plasma optical emission spectrometry (ICP-OES XL 3200, PerkinElmer, Waltham, United States).

3.3.3. Additional laboratory analyses

In addition to the mentioned analyses, Fe(II) and Fe(III) were determined photometrically in some water samples (Tamura et al., 1974). Moreover, reactive iron and pedogenic iron and aluminum oxides in the solid phase were extracted and analyzed (Mehra & Jackson, 1958). C and N content of the solid phase were determined using an elemental analyzer (FlashEA1112, Thermo Fisher Scientific, Waltham, USA). To identify individual molecular formulas of DOC, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) was conducted (Herzsprung et al., 2014; Lechtenfeld et al., 2014; Nebbioso & Piccolo, 2013).

3.4. Data analyses

3.4.1. Analysis of event characteristics and DOC export

P_{tot} is the total amount of precipitation during the event. The antecedent precipitation (AP_{14}) is the cumulative precipitation 14 days prior to the start of the event, following van Verseveld et al. (2009). The sum of P_{tot} and AP_{14} represents the total catchment wetness. In Study 1, DOC concentrations were plotted for each event as a function of discharge at a 15-minutes interval. To describe this non-linear relation, the hysteresis index (h), was calculated as proposed by Zuecco et al. (2016). A positive hysteresis index indicates a clockwise hysteresis, whereas a negative hysteresis index indicates a counterclockwise hysteresis. The larger the absolute value of *h*, the wider the hysteretic loop. Additionally, DOC fluxes were calculated by multiplying the 15 minutes discharge value with the corresponding 15 minutes DOC concentration. These were cumulated to a total DOC export per event or season. Runoff ratios were calculated as the ratio of cumulative area normalized discharge to the amount of precipitation during each event (Study 1) or season (Study 3). For KS and MG, the precipitation measured close to their outlet was used. For HS_{tot} and HS_{sub}, the precipitation measured close to the outlet of HS_{tot} was used. Cumulative discharge for HS_{sub} was calculated as the difference of the discharge of HS_{tot} and the discharge of KS and MG. When comparing the contribution of different subcatchments to total discharge and DOC export in Study 1 and Study 3, we used the ratio of the areas (Table 1) of the subcatchments (0.31 for MG/HS_{tot}, 0.26 for KS/HS_{tot} and 0.43 for HS_{sub}/HS_{tot}) as a benchmark.

3.4.2. Analysis of differences in groundwater level dynamics

In Study 2, the 0.9 quantile ($Q_{0.9}$) of all discharge values during the sampling period was calculated as a measure of event flow. For all data points with discharge values above $Q_{0.9}$, the mean shallow groundwater level for each location was calculated, representing the mean groundwater level during event flow. Additionally, we used the metric t_R, which was defined as the time (in minutes) needed for the water level to recede by 2 cm from the water level maximum during an event.

3.4.3. Statistical analysis of potential DOC source areas

The sampled locations FS1, FS2, P1, P2 and DGW were interpreted as representing different source areas of DOC. The sampled locations were grouped according to their physiographic characteristics: 1) FS1 and FS2 as representatives for sites with a typical forest soil (called FS, hereafter), 2) P1 and P2 as representatifves for sites with ponds (called P, hereafter) and 3) DGW1, DGW2 and DGW3 as representatives for the deep groundwater. In order to verify the similarity of the grouped locations, a cluster analysis was performed. Following the cluster analysis, a Wilcoxon ranksum test for all analyzed parameters was performed to test the similarity between sites P and FS. All statistical analyses were performed using MATLAB (MATLAB R2019b).

4. Results and Discussion

4.1. Study 1: Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment

The comparison of four precipitation events with contrasting antecedent wetness conditions as well as a contrasting amount of precipitation revealed differences in DOC mobilization processes as well as DOC export numbers between the events. Moreover, the comparison showed differences in DOC mobilization and export between the topographic positions MG and HS. In order to stay consistent regarding the wording used in the study, in this section, the name HS is used instead of HS_{tot}. The events in June 2018, October 2018 and May 2019 were of similar size. However, the antecedent conditions were different for all three events: The event in October 2018 had the lowest AP_{14} values, followed by the event in May 2019 with intermediate AP_{14} values and the event in June 2018 with the largest AP_{14} values. The event in September 2020 was unusually large for the sampling period and followed a very dry summer leading to a similarly low AP_{14} as in October 2018.

The comparison of the peak discharge values during the events showed that event size is not the only factor influencing discharge generation, but that the topographic position as well as antecedent wetness conditions also played a role. At HS, peak discharge values were correlated with the total catchment wetness indicating a high dependency on hydrological connectivity for runoff generation. At MG, peak discharge was in a similar range for all events. Moreover, runoff ratios were higher at MG than at HS during all events except in June 2018 and the discharge response was faster at MG than at HS. These observations confirmed that the lower, flat catchment parts need to be rewetted in order to activate flow pathways towards the stream, whereas the steep slopes at MG facilitate a fast delivery of water towards the stream, even following drought periods.

Study 1 revealed not only differences between the events and between the locations regarding runoff generation, but also regarding DOC mobilization and export. During all events, in-stream DOC concentrations increased (up to 19 mg L^{-1}) in comparison to baseflow concentrations (2 – 3 mg L^{-1}). At HS, the DOC-Q hysteresis patterns were counterclockwise for all events. At MG, the events in May 2019 and October 2018 showed counterclockwise hysteresis patterns, whereas the hysteresis patterns in June 2018 and September 2020 showed no clear loop form. Moreover, the hysteretic loops were generally wider at HS than at MG indicating a slower mobilization of DOC at HS than at MG. This finding can be attributed to the slow saturation of the flat soils and, therefore, the slow establishment of hydrological connectivity at HS. Another factor could be the connection of small ponds in the riparian zone, which get connected to the streams during wet conditions (see Study 2). At both locations, the precipitation specific DOC load was increasing with increasing total catchment wetness, which highlights the importance of the antecedent wetness conditions and event size for DOC mobilization. Although one would expect the flat lower catchment to be more important for DOC export for several reasons (e.g. larger riparian zone), the study showed that this is not always the case. The contribution of MG to total DOC export increased with decreasing total catchment wetness leading to a disproportionally high contribution to DOC export after dry periods. This observation can be attributed to the inhibition of DOC mobilization due to the missing hydrological connectivity in the lower catchment following dry periods rather than an increased DOC export of the upper catchment. A similar effect could be seen when looking closer at one singular event. During events following dry conditions, the contribution from MG to total DOC export decreased over the course of the event as a result of an increasing hydrological connectivity in the flat riparian zone of HS.

To conclude, Study 1 showed that event size is important for DOC mobilization, if the antecedent wetness conditions are similar. However, if the events are of similar size, total catchment wetness becomes important leading to a faster and higher DOC export during events following wet conditions. This effect can offset seasonal effects, which would lead to an increased DOC production and, therefore, export during events following warm summer months. Topography is another important factor influencing DOC mobilization, as it influences the establishment of hydrological connectivity and development of flow pathways. In the lower subcatchment with its flat and large riparian zone, the establishment of hydrological connectivity needs more time than in the upper catchment with its steep slopes. Therefore, DOC export is inhibited in the lower catchment during events following dry antecedent conditions, which leads to a disproportionally high contribution of the upper catchment.

4.2. Study 2: Microtopographical structures in the riparian zone influence event-based DOC mobilization and quality in a forested headwater catchment

Study 2 focused on the riparian zone of the lower catchment HS_{sub} and the microtopographical structures within it, which were observed during the work for Study 1. The comparison of the shallow groundwater below microtopographical depressions (called ponds hereafter) and below the typical flat forest soil in the riparian zone revealed differences in groundwater level dynamics, DOC concentrations and DOC quality. Regarding DOC quality, this study pointed out difficulties in the interpretation of DOC quality parameters, such as the Humification Index, Freshness Index and Fluorescence Index, which are widely used to characterize organic matter. Therefore, in this study, these parameters were used primarily to highlight qualitative differences between the possible DOC sources and not to characterize the DOC itself.

The shallow groundwater levels at the sites with ponds (site P) were characterized by larger level fluctuations and a slower receding time than at the forest soil sites (site FS). Therefore, the upper soil layers at site P were regularly rewetted. The resulting higher microbial activity and decomposition rates could lead to higher DOC concentrations and a higher aromaticity in the shallow groundwater at site P than at site FS. Additionally, the convergence of DOC-rich subsurface and surface water flow paths due to the microtopographic characteristics could lead to the accumulation of DOC at the ponds.

The chemical differences between the two sites were used to investigate the influence of the sites on DOC export during a precipitation event. During the event, several measured parameters in the stream approached the values found at site P indicating a contribution of the shallow groundwater at site P to event stream flow. During events, the water level at the sites with the ponds regularly rose above the surface leading to the connection of the ponds to the stream via overland flow in addition to subsurface flow paths. The mean water level during high discharge conditions was clearly above ground at site P, whereas it was below ground at site FS.

Looking at the cation concentrations, it is striking that both iron (Fe) and aluminum (Al) in-stream concentrations increased over the course of the event. Fe concentrations were high in the shallow groundwater at site FS and site P. Therefore, an in-stream increase of Fe concentrations indicated a coupled export of DOC and Fe but not a specific contribution of the ponds to DOC export. However, Al concentrations were much higher at site P and increasing Al concentrations in the stream were, therefore, a clear sign of the ponds' contribution and indicative of a coupled export of Al and DOC.

In summary, the comparison of the shallow groundwater at the site with microtopographical depressions and without microtopographical depressions revealed clear chemical differences in DOC concentrations, cation concentrations and DOC quality parameters. In general, the DOC quality parameters need to be interpreted carefully in terms of DOC characterization. They were, however, useful to highlight qualitative differences between DOC sources. The observed differences in concentrations and quality could be attributed to differences in groundwater level dynamics. During the investigated precipitation event, the ponds likely contributed to DOC export as in-stream parameters approached values found in the ponds over the course of the event.

4.3. Study 3: High-resolution DOC measurements indicate seasonal differences in the contribution of three nested forested subcatchments to DOC export

The annual DOC export of HS_{tot} was 13760 kg or 3931 kg km^{-2}, which is in the range of other European forested catchments. Interestingly, large variations in DOC export numbers could be observed between the five seasons, which were delineated according to precipitation patterns (snowmelt, spring, summer, autumn, winter). Snowmelt was most important for DOC export (40.5 % of annual DOC export, 55 kg d^{-1}), which is due to the availability of large quantities of water and the reconnection of flow pathways to the stream. Additionally, the flushing of accumulated DOC from the topsoil could add to the high DOC export. Moreover, DOC export was linked to daily freeze-thaw cycles highlighting the importance of hydrological flow pathways for DOC export. Spring was also important for DOC export (24.5 %, 56.4 kg d^{-1}). Frequent precipitation events and the saturated soils led to the establishment of a high hydrological connectivity between DOC sources and the stream. DOC production was probably also increasing in spring and summer due to increasing temperatures. However, low hydrological connectivity due to less precipitation events led to a much lower DOC export in summer (10.4 %, 16.7 kg d^{-1}). In autumn, large precipitation events and the additional input of leaf litter led to the export of larger DOC quantities than in summer (20.3 %, 48.8 kg d^{-1}). In winter, DOC export was limited (4.2 %, 9.5 kg d^{-1}) due to the limited DOC production and limited transport via flow pathways as a consequence of snowfall.

In addition to seasonal DOC export variations, differences in the contribution of the three subcatchments to DOC export were observed throughout the investigated period. Runoff ratios, area normalized discharge and DOC export rates were highest during snowmelt and lowest during winter. During winter, all subcatchments contributed equally to DOC export, which meant that KS contributed more than expected and HS_{sub} less than expected, when taking into account the respective areas of the subcatchments. KS showed the highest runoff ratio of all subcatchments during winter. An additional reason for the higher contribution of KS to DOC export in winter could be the high proportion of deciduous trees in this subcatchment, which led to an additional carbon input with litter fall. During snowmelt and spring, HS_{sub} contributed most and KS contributed least to DOC export. The main reason for this distribution, which reflects the area proportions of the subcatchments, is the high hydrological connectivity between the DOC sources and the stream, facilitating DOC export from HS_{sub}. Moreover, the lower elevation of HS_{sub} could lead to an earlier snowmelt than at the higher elevated subcatchments MG and KS, leading to a higher contribution of HS_{sub} to DOC export during snowmelt in comparison to spring, when MG becomes more important. Due to data gaps, the contribution of the subcatchments could not be compared during summer. During autumn, HS_{sub} contributed less and MG contributed more than expected and also most of all three subcatchments. In contrast to the wet snowmelt period, DOC export from the flat riparian zone in HS_{sub} was limited due to the low hydrological connectivity. The results show that the steeper, upper subcatchments are not much affected by the dry summer and are able to establish fast flow pathways already during the first large precipitation events after the drought period.

This effect was most pronounced in autumn but influenced DOC export during the entire year as MG contributed more to DOC export than expected throughout the year, whereas HS_{sub} contributed less than expected during all seasons except during snowmelt. When looking at the contribution to runoff, a similar picture emerged. MG contributed more to runoff and showed higher runoff ratios than HS_{sub}. As explained above, topography is an important factor. The steep hillslopes in the upper catchments, which are interspersed by large rocks, facilitate a fast runoff during events. In contrast, the flat riparian zone of the lower catchment is dependent on the the establishment of hydrological connectivity following the saturation of the deep soils and rising groundwater tables. Over the year, the contribution of HS_{sub} to DOC export exceeded the contribution to runoff. This indicates that the high amounts of DOC being exported during the wet periods offset the limited DOC export during dry periods in the lower catchment. In contrast, the contribution to DOC export from KS and MG was lower than the contribution to runoff indicating a limited DOC pool in comparison to the lower catchment. DOC export in the lower catchment is clearly transport limited, which led to the disproportionally higher contributions of the upper catchments to DOC export during periods of low hydrological connectivity.

To summarize, DOC export clearly varies seasonally and is mainly influenced by the establishment of hydrological connectivity between DOC sources and the stream. Nevertheless, DOC availability also plays a role and is linked to DOC production and vegetation. The contribution of the subcatchments to DOC export also varies seasonally. The disproportional contribution of the upper subcatchments is closely linked to the steep topography, which facilitates DOC mobilization via fast flow pathways. In contrast, DOC export of the lower subcatchment is often limited by low hydrological connectivity as it is dependent on the saturation of the soils. These findings confirm the findings of Study 1 on a seasonal scale.

4.4. Study 4: Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments

This study refers to dissolved organic matter (DOM). DOM is a heterogeneous mixture composed of different compounds (as nitrogen and sulfur) but mainly carbon. DOC corresponds to ca. 90 % of DOM and, therefore, is used as a proxy for DOM concentration. DOC concentrations during baseflow were similar at all three investigated sampling sites HSL, HSU, MG (average of 2.6 mg L^{-1}) but the mean specific discharge was higher at MGL than at HSL. Throughout the seasons, baseflow DOC concentrations were also similar with the exception of spring, which showed slightly higher DOC concentrations indicating the connection of additional DOC sources. The variability of DOC concentrations and discharge was higher at the lowest sampling site HSL. In contrast to the similar DOC concentrations along the stream, clear spatial patterns of DOM quality could be observed.

At the lower part of the catchment (HSL), DOM was characterized by a higher aromaticity, a lower molecular weight and a higher O/C ratio than at the upper part of the catchment (HSU and MGL). All these characteristics indicated the input of fresh plant-derived material and led to the conclusion that the DOC originated from superficial soil layers of the hydromorphic soils in the large riparian zone. In contrast to that, the more microbially processed DOM characteristics at the upper catchment part indicated that DOC originated from deeper soil layers.

The sampling of three potential DOC sources in the lower catchment part also revealed some differences. The riparian zone surface water refers to a pond similar to the ones studied in Study 2. It was characterized by high DOC concentrations, a low O/C ratio, a low H/C ratio and a high aromaticity indicating a less biologically processed DOC. The riparian soil groundwater (sampled in piezometer FS1, which was also sampled in Study 2) was also characterized by high DOC concentrations and a high aromaticity but showed a more variable H/C and a high O/C ratio indicating a more biologically processed DOC. Shallow groundwater was sampled from a spring close to the stream and showed low DOC concentrations, high nitrogen content and mostly aliphatic compounds, which is typical for groundwater samples.

Finally, differences in the in-stream DOC composition could be observed between periods of low and high DOC concentrations. When DOC concentrations were low, DOM was characterized by a high nitrogen content and aliphatic concentrations indicating the higher contribution of groundwater. When DOC concentrations were high, DOM was characterized by a higher O/C ratio, a variable H/C ratio and a higher aromaticity indicating the contribution of water from the superficial soil layers.

In this study, the combination of high-frequency DOC data and FT-ICR-MS data of additional samples proved useful. While the high-frequency data captured the seasonal trends of in-stream DOC concentration and quality, the FT-ICR-MS data provided the link between the stream and possible DOC sources regarding molecular composition. To conclude, in-stream DOM in the lower catchment part was likely to be influenced by DOC derived from upper soil layers, whereas in the upper catchment deeper soil layers were more important. Moreover, with increasing in-stream DOC concentrations the influence of the upper soil layers was increasing.

5. Conclusions

5.1. Main findings on DOC mobilization in the Hinterer Schachtenbach catchment

This thesis brought together the interplay of various natural factors, which influence DOC mobilization and export in the Hinterer Schachtenbach catchment.

First, DOC mobilization depends on the availability of DOC at the source areas and, therefore on seasonal DOC production patterns. This explains at least partly the low DOC export during winter. However, Study 1 and Study 3 have shown that hydrological effects are often more important than seasonal effects, which are linked to temperature. This explains the low DOC export during summer, a time that should lead to a very high DOC export if temperature was the most important factor. Nevertheless, DOC export is low during the summer months as well as during autumnal events following the dry summer months. Study 1 shows that available DOC cannot be transported to the stream due to a low hydrological connectivity in the lower, flat catchment parts. There, the antecedent wetness conditions are crucial for the establishment of hydrological connectivity and runoff generation. Hydrological connectivity is especially high during snowmelt and spring, which leads to a high contribution of the lower catchment during these times (Study 3) and differences in DOC quality (Study 4). Study 1 has also confirmed that event size is a controlling factor of DOC mobilization, which has the potential to offset the limiting effect of dry antecedent conditions and establish hydrological connectivity quickly. A high hydrological connectivity does not only refer to subsurface flow paths, but also to surface flow. Study 2 confirmed the assumption made in Study 1 that the microtopographical depressions in the riparian zone of the lower catchment can become of importance for DOC export during events. Moreover, the results showed that the connection of the microtopographical depressions to the stream can influence the quality of in-stream DOC by exporting more aromatic DOC.

Not only microtopographical patterns play a role in DOC mobilization processes. As seen in Study 1, topography also influences DOC mobilization and is closely linked to antecedent wetness conditions. In the lower catchment parts, hydrological connectivity is established more slowly and is highly dependent on a rising groundwater level and soil saturation. A low hydrological connectivity inhibits the connection of flow pathways from potential DOC sources to the stream. Therefore, the upper catchment parts become proportionally more important for DOC export following drought periods as here, the steep hillslopes facilitate runoff generation. Study 3 confirms differences in DOC export between the subcatchments on a larger temporal scale and reveals that the lower catchment often contributes less to total DOC export than expected in terms of its area. In contrast, the upper catchments contribute more to DOC export than expected in terms of their area, especially during periods when hydrological connectivity is limited in the lower catchment. The higher variability of DOC concentrations and of discharge at the lower catchment during baseflow (Study 4) also suggest that the connectivity of the stream to DOC sources varies more than at the upper catchments. These differences can be attributed to topographic differences, which influence runoff generation. The steep slopes of the upper catchments facilitate the rapid connection of flow paths to the stream, whereas the flat topography of the lower catchment depends on the slow saturation of the upper soil layers and rising groundwater tables in order to establish hydrological connectivity.

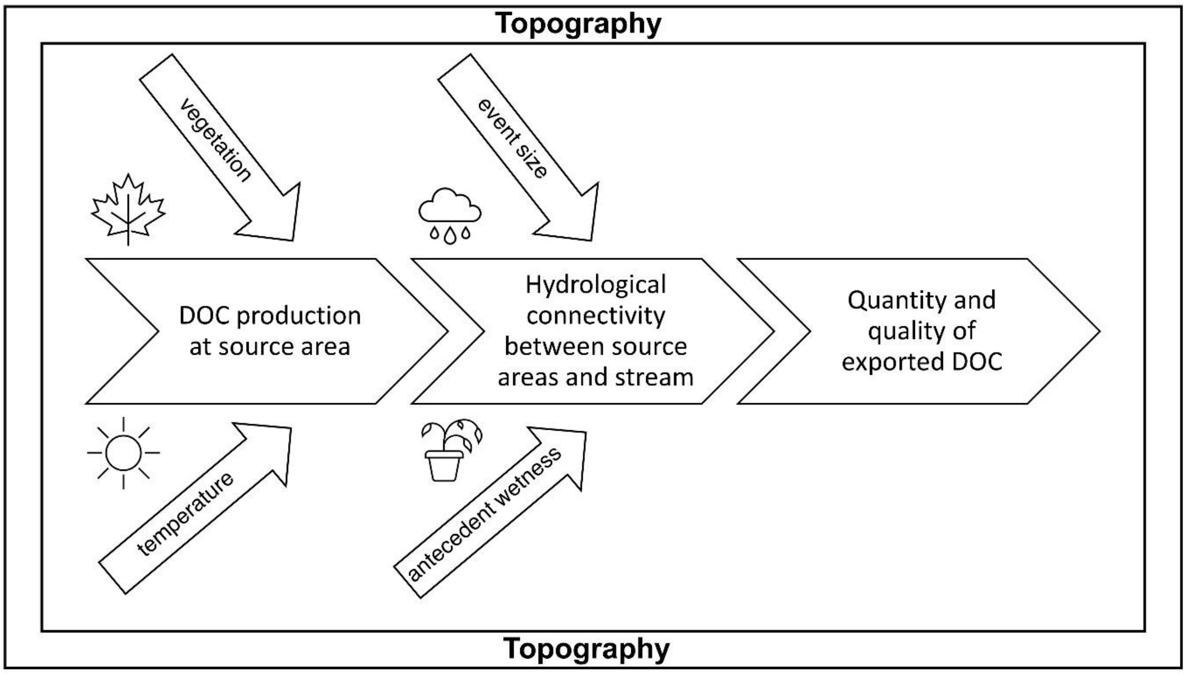

Figure 4: Conceptual figure of the interplay of the factors, which are influencing the quantity and quality of the exported DOC.

This is confirmed by the results of Study 4, which have shown that the DOC quality in the lower catchment parts indicate that the DOC originates from upper soil layers, whereas the DOC in the upper catchment parts originates from deeper soil layers. These effects are visible on the event-scale (Study 1), as DOC mobilization happens faster in the upper catchment part than in the lower catchment part, and on a seasonal scale (Study 3), as DOC export from the lower catchment is limited during drought periods due to a low hydrological connectivity. Moreover, differences in vegetation seem to influence DOC export as the contribution to total DOC export from KS increases in autumn. It is likely that the high percentage of deciduous trees in this subcatchment leads to a high additional input of leaf litter. Additionally, elevation might play a role for seasonal DOC export influencing the extent and timing of the snowpack.

In summary, topography has a large impact on hydrological connectivity and therefore influences DOC mobilization, export and quality (Figure 4).

5.2. Implications for DOC mobilization and export under a changing climate

According to the newest report of the Intergovernmental Panel on Climate Change (2021), our planet will be influenced strongly by climate change in the next decades. Western and Central Europe will be affected by rising temperatures and changing precipitation patterns. On the one hand, the frequency of extreme precipitation events and pluvial flooding is expected to increase. On the other hand, the frequency and intensity of droughts is also expected to increase. Moreover, snow cover extent and seasonal snow duration will probably decline as a result of warming temperatures. All of these aspects are likely to affect DOC mobilization processes and DOC export from headwater catchments. As headwater catchments make up an important part of the global stream length (Downing, 2012), these changes would affect large downstream areas (Gomi et al., 2002; Wohl, 2017).

Generally, rising temperatures could lead to an increased DOC production and a larger potential DOC pool. Changes in snow cover extent and duration could influence DOC mobilization. As more precipitation falls as rain during winter, DOC export during winter could increase. In contrast, the importance of snowmelt-induced DOC export would decline as also suggested by Meingast et al. (2020). Therefore, DOC export could be more evenly distributed over the winter and spring months. Longer warm periods and less snow cover even at high altitudes could also lead to an increasing importance of DOC export from higher elevated catchments. At the Hinterer Schachtenbach catchment, this could lead to a higher DOC export from all subcatchments during winter and a lower DOC export during the snowmelt period. The contribution to DOC export during winter from the upper subcatchments could increase as they are currently affected by a larger and longer lasting snowpack than the lower subcatchment.

As precipitation events are a key driver of DOC mobilization and export, more extreme precipitation events could lead to an increased DOC export. However, this effect could be limited in some catchments by source depletion. In the Hinterer Schachtenbach catchment, DOC mobilization was clearly transport limited. This was also the case for more than 1000 investigated catchments in the U.S. (Zarnetske et al., 2018). Nevertheless, with the frequency and intensity of precipitation events rising, some catchments might switch from a transport limitation to a source limitation as DOC pools become depleted. In the Hinterer Schachtenbach catchment, this would rather be the case for the upper subcatchments as the DOC pool is probably smaller than at the lower subcatchments. The contribution of the lower subcatchment to DOC export during extreme precipitation events could increase as hydrological connectivity is established faster than usual during precipitation events.

As the results of the presented studies show, hydrological connectivity is crucial for DOC mobilization and export. Therefore, a higher frequency and intensity of droughts could inhibit DOC mobilization more often and over longer periods than currently. This could lead to a general decrease in DOC export from drought-affected catchments. Long drought periods could lead to the disconnection of upper catchment parts (Bernal & Sabater, 2012) or even to a change from perennial to intermittent stream systems and a fragmentation of streams, especially in headwater catchments (Jaeger et al., 2014; Messager et al., 2021; Reynolds et al., 2015). The fragmentation of Mediterranean streams following drought has been shown to lead to DOC accumulation in the remaining water pools and a subsequent increase in DOC concentrations following precipitation events (Granados et al., 2020). However, it is likely that more drought periods would decrease DOC export in general as DOC export is closely linked to precipitation events. This decrease in DOC export could potentially slow down the current trend of rising DOC concentrations in freshwater systems. Moreover, several studies in Mediterranean catchments have shown that droughts can alter DOC quality in the stream (Ejarque et al., 2017; Granados et al., 2020; Romaní et al., 2006).

As the results of Study 1 and 3 show, flat, lower catchment parts with a large riparian zone are strongly dependent on soil saturation for DOC mobilization and export. During summer and during events following drought, DOC export from the flat catchment parts is clearly limited. More droughts could therefore lead to a decreasing importance of riparian zones for DOC export as hydrological connectivity is established less frequently.

On the contrary, upper catchments with steep slopes could contribute more to DOC export. These changes could result in a different chemical composition of the exported DOC, as Study 4 has shown that there are differences between the upper and the lower catchment parts. Microtopographical depressions, as the ponds investigated in Study 2, could also be affected by droughts, as they would probably be connected to the stream less frequently. Less rewetting of the upper soil layers in the ponds could also alter DOC quality. The combination of more droughts and more extreme precipitation events could lead to a less evenly distributed DOC export during summer and autumn, in contrast to winter and spring, when DOC export could become more evenly distributed as explained above. Large amounts of DOC could be exported in pulses during events, whereas DOC export could be limited during drought periods. Wen et al. (2020) have shown that increasing hydrological extremes lead to an asynchrony between DOC production and DOC export with DOC production occurring during warm periods but DOC export being limited to few precipitation events.

A changing temporal and spatial in-stream availability of DOC could influence the formation of greenhouse gases and could affect aquatic organisms, which use DOC as an energy source. Moreover, these changes could have an impact on the management of drinking water reservoirs, as the treatment of surface water might need to be adapted according to changing DOC export patterns and changes in the quality of the exported DOC. As mentioned above, these changes would not only affect the headwaters itself but could have a large impact on downstream reaches.

5.3. Outlook

In research, more data are (almost) always better: One could sample more locations, analyze more parameters or extend studies over a longer time period. On the other hand, research – especially if fieldwork is included – comes with challenges: the expected precipitation event is not happening or technical failures render data collection impossible or even result in data loss. As this thesis was not exempt from certain setbacks and limited to a period of four summers of fieldwork, there is still a lot to discover in the investigated catchment.

The high-frequency measurements are certainly a very important and useful tool in order to understand temporal DOC dynamics. This thesis shed light on DOC dynamics during precipitation events, but it would be of interest to include much larger precipitation events than the ones for which data could be collected for Study 1. Would extreme precipitation events lead to extreme DOC export numbers or is there a limit for event-based DOC export? Would DOC sources become depleted following extreme precipitation events? How would extreme precipitation events affect the contribution of the steep and flat subcatchments? As Study 3 has revealed that the differences in DOC mobilization between the subcatchments KS and MG are more pronounced than previously thought, it would also be of interest to extend the investigation of event-based DOC mobilization to all three subcatchments. In this context, it would also be interesting to continue the research on DOC quality. Study 2 shows that in-stream DOC quality changes during events. However, it remains unclear how these changes are linked to antecedent wetness conditions and event size. Study 2 has also pointed out the limits of fluorescence and absorbance spectrometry with the goal to investigate DOC origin. Therefore, an analysis of the reliability of DOC quality parameters would certainly be helpful for further studies. This could be connected with the more sophisticated techniques for DOC characterization used in Study 4. Preliminary results of tracer experiments and radon measurements, which are not shown in this thesis, indicated that the lower catchment part is affected by exchange fluxes between the stream and groundwater of the riparian zone. These results suggest that the DOC measured at the catchment outlet is not necessarily the DOC that entered the stream in the upper catchment parts. More tracer experiments could shed light on the extent and importance of exchange fluxes in the catchment. Finally, it would be interesting to expand the data set collected for Study 3 in order to compare different years with varying hydrological conditions. In addition to that, a comparison of the data with neighboring catchments could help to clarify the transferability of results to other catchments or regions.

To conclude, this thesis has shown that topography influences the establishment of hydrological connectivity and, thus, affects DOC quality, DOC mobilization processes and DOC export. Therefore, topography should be taken into account, when investigating DOC and its link to hydrology.

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Study 1: Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment

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Own contribution in %:

Study design	50
Field data collection	90
Data processing and analysis	100
Interpretation of the results	70
Preparation of the manuscript	90

KB, BSG, JHF, SP and LH designed the study. KB planned the field work and collected the DOC data. KB and BB collected the discharge data for the lower subcatchment. BB provided the meteorological data and the deep groundwater data. KB prepared the figures and tables. All co-authors discussed and interpreted the results. KB prepared the manuscript with input from all co-authors. KB is the corresponding author.

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Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment

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Abstract. Understanding the controls on event-driven dissolved organic carbon (DOC) export is crucial as DOC is an important link between the terrestrial and the aquatic carbon cycles. We hypothesized that topography is a key driver of DOC export in headwater catchments because it influences hydrological connectivity, which can inhibit or facilitate DOC mobilization. To test this hypothesis, we studied the mechanisms controlling DOC mobilization and export in the Große Ohe catchment, a forested headwater in a mid-elevation mountainous region in southeastern Germany. Discharge and stream DOC concentrations were measured at an interval of 15 min using in situ UV-Vis (ultraviolet–visible) spectrometry from June 2018 until October 2020 at two topographically contrasting subcatchments of the same stream. At the upper location (888 m above sea level, a.s.l.), the stream drains steep hillslopes, whereas, at the lower location (771 m a.s.l.), it drains a larger area, including a flat and wide riparian zone. We focus on four events with contrasting antecedent wetness conditions and event size. During the events, in-stream DOC concentrations increased up to 19 mg L^{-1} in comparison to 2–3 mg L^{-1} during baseflow. The concentration–discharge relationships exhibited pronounced but almost exclusively counterclockwise hysteresis loops which were generally wider in the lower catchment than in the upper catchment due to a delayed DOC mobilization in the flat riparian zone. The riparian zone released considerable amounts of DOC, which led to a DOC load up to 7.4 kg h^{-1}. The DOC load increased with the total catchment wetness. We found a disproportionally high contribution to the total DOC export of the upper catchment during events following a long dry period. We attribute this to the low hydrological connectivity in the lower catchment during drought, which inhibited DOC mobilization, especially at the beginning of the events. Our data show that not only event size but also antecedent wetness conditions strongly influence the hydrological connectivity during events, leading to a varying contribution to DOC export of subcatchments, depending on topography. As the frequency of prolonged drought periods is predicted to increase, the relative contribution of different subcatchments to DOC export may change in the future when hydrological connectivity will be reduced more often.

1 Introduction

The hydrological and carbon cycles are tightly coupled, as terrestrial systems store and release carbon into aquatic systems, which act as a carrier for carbon through landscapes. Inland waters may influence the global carbon cycle more than previously thought (Battin et al., 2009). Dissolved organic carbon (DOC) export from streams is an important link between the terrestrial and the aquatic carbon cycle and a crucial component of the net ecosystem carbon balance (Kindler

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et al., 2011). The global DOC export reaching inland waters annually from the terrestrial environment is estimated at 5.1 Pg C, whereas a large part (3.9 Pg C) outgasses to the atmosphere in form of the greenhouse gases CO_2 or CH_4 (Drake et al., 2018). As DOC is converted to these greenhouse gases, it plays an important role in the context of climate change.

DOC concentrations in freshwater systems usually vary from 1 to 10 $mg\,L^{-1}$ in streams and lakes but can reach up to 60 $mg\,L^{-1}$ in swamps and bogs (Thurman, 1985). Since the beginning of the 1980s, an increase in DOC concentrations has been observed in a large number of streams, rivers and lakes of the Northern Hemisphere (Evans et al., 2005; Roulet and Moore, 2006; Monteith et al., 2007). Rising DOC concentrations indicate an increased leaching from soils and peatlands and have the potential to deplete the terrestrial carbon pools, which are of global importance for carbon storage (Batjes, 2014; Dixon et al., 1994; Kindler et al., 2011). Moreover, elevated DOC concentrations can cause problems for drinking water treatment via chlorination as DOC acts as a precursor of trihalomethanes, which have potentially carcinogenic and mutagenic properties (Alarcon-Herrera et al., 1994; Ledesma et al., 2012; Sadiq and Rodriguez, 2004). DOC can form complexes with organic pollutants (Hope et al., 1994) and toxic metals such as mercury (Ravichandran, 2004) or lead (Dörr and Münnich, 1991) and, thus, strongly influence drinking water quality. Several hypotheses have been proposed in order to explain the increase in DOC in many surface waters, including a decline in atmospheric sulfur deposition (Evans et al., 2006; Monteith et al., 2007; Ledesma et al., 2016; Hruška et al., 2009), a decline in nitrogen deposition (Musolff et al., 2016), temperature increase (Weyhenmeyer and Karlsson, 2009) and increased precipitation (Hongve et al., 2004). However, Roulet and Moore (2006) stress that it is difficult to isolate a single factor, as there are many different variables influencing DOC production and export, and Clark et al. (2010) highlight the difficulties resulting from the fact that drivers of rising DOC concentrations operate on varying temporal and spatial scales.

DOC export varies strongly between catchments. Annual exports between 1.2 and 56 946 $kg\,C\,km^{-2}$ were found in a meta-analysis of 550 catchments worldwide (Alvarez-Cobelas et al., 2012). Besides external factors influencing runoff (e.g., precipitation) a multitude of internal landscape-based factors may influence DOC export, such as temperature controls on production (Moore et al., 2008; Wen et al., 2020) or chemical parameters, such as pH and ionic strength (Hruška et al., 2009; Monteith et al., 2007), as well as redox processes (Knorr, 2013). Of particular relevance for DOC mobilization may be land cover type and changes in land use (Seybold et al., 2019; Larson et al., 2014; Aitkenhead-Peterson et al., 2007), as mobilization processes depend on the DOC source area. Wetlands and the riparian zone are often particularly important DOC sources to streams and lakes as they are often characterized by large amounts of stored carbon, which can then be mobilized as DOC (Harrison et al., 2005; Creed et al., 2008; Ogawa et al., 2006; Zarnetske et al., 2018; Weiler and McDonnell, 2006; Ledesma et al., 2015; Musolff et al., 2018).

Many studies have shown that DOC concentrations usually increase with discharge (Q; Hobbie and Likens, 1973; McDowell and Fisher, 1976; Meyer and Tate, 1983; Easthouse et al., 1992). However, at the event scale, this concentration–discharge relationship is seldom linear, and hysteretic loops have been observed at many sites. Although it is difficult to merge the C–Q relationships to analyze annual hysteretic loops as their characteristics depend on specific event conditions (Fazekas et al., 2020), the direction and shape of specific hysteretic loops can be a useful indicator for the underlying mobilization mechanisms. Clockwise hysteretic loops are generally explained by (1) a DOC source close and well connected to the stream (Blaen et al., 2017; Hood et al., 2006; Vaughan et al., 2017), (2) flushing of DOC from upper soil horizons during the rising limb (Buffam et al., 2001; Jeong et al., 2012) or (3) a depletion of the DOC source during the course of an event (Bowes et al., 2009; House and Warwick, 1998; Jeong et al., 2012). Counterclockwise hysteretic loops usually indicate a delayed arrival of DOC at the stream, which can be caused by source areas being located further away from the stream (Hood et al., 2006; Vaughan et al., 2017), with the sources being connected via flow paths with slow transport velocities (Musolff et al., 2017) or by changes in the dominant flow paths and associated changes in the hydrological connectivity change of flow pathways (Brown et al., 1999; Hagedorn et al., 2000; Schwarze and Beudert, 2009; Strohmeier et al., 2013; Cerro et al., 2014; Ågren et al., 2008; Pacific et al., 2010).

Hydrological connectivity is generally regarded to be of paramount importance for biogeochemical fluxes through catchments. As it controls runoff response during events, it has a direct impact on solute export (Kiewiet et al., 2020; Detty and McGuire, 2010). Therefore, it influences nutrient dynamics across different temporal and spatial scales (Covino, 2017). Hydrological connectivity and, therefore, runoff and solute response are dependent on the antecedent wetness conditions in a catchment and the event characteristics itself (Penna et al., 2015; Detty and McGuire, 2010; McGuire and McDonnell, 2010) and appear to be controlled by catchment topography and morphology. Weiler and McDonnell (2006) showed that the hillslope shape influences the hysteresis pattern of DOC during storm events as mobilization processes differ with the geometrical properties of hillslopes. Catchment morphology appeared to strongly influence DOC transport and storage in streams, as the temperature sensitivity of respiration depends on geomorphic features (Jankowski and Schindler, 2019).

In this study, we investigated DOC mobilization during different rain events and antecedent wetness conditions at two different topographical positions of a headwater stream within the Bavarian Forest National Park (BFNP) using high-resolution in-stream DOC spectrometers. The setting in the BFNP allowed us to investigate DOC export mechanisms in a region with little anthropogenic influence, which is important against the backdrop of rising DOC concentrations in freshwater systems. There are few studies focusing on the influence of topography on the DOC mobilization mechanisms. Another aspect that is of increasing importance is the possible impact of climate change and, associated therewith, prolonged drought periods on DOC export. In particular, we compared two different subcatchments with regards to DOC–Q relationships and DOC export during four precipitation events in order to understand the influence of event size, antecedent wetness conditions and topography on DOC mobilization and export. We hypothesized that DOC mobilization processes and DOC export are controlled by the underlying hydrological processes, in particular connectivity, and are strongly affected by the antecedent wetness conditions and event size. We further hypothesized that different topographical positions (steep hillslopes vs. flat riparian zones) within the catchment promote different hydrological mobilization and transport processes, and therefore, DOC–Q relationships and DOC export will differ between the two subcatchments.

2 Material and methods

2.1 Study site

The Große Ohe catchment (19.2 km^2) is part of the BFNP, which is located in southeastern Germany and shares a border with the Czech Republic. The BFNP covers an area of 243 km^2. Measurements were conducted in the nested subcatchments of Hinterer Schachtenbach (HS; 3.5 km^2) and Markungsgraben (MG; 1.1 km^2), which are part of the Große Ohe catchment, an experimental forested catchment run by the BFNP (see Table 1).

The Hinterer Schachtenbach catchment includes the subcatchments of Markungsgraben and Kaltenbrunner Seige (Fig. 1). The subcatchment of Kaltenbrunner Seige was not part of the monitoring presented here, but contributes to discharge and DOC export at the outlet of HS. Elevation in the Große Ohe catchment ranges from 770 to 1435 m above sea level (a.s.l.), with a mean slope of 7.7°, whereas MG represents the upper part of the catchment with a steeper mean slope (15.9°) than HS (7.4°). The geology of the Große Ohe catchment is dominated by biotite granite and cordierite–sillimanite gneiss. The soils are mainly Cambisols, podzols and hydromorphic soils, whereby the proportion differs between the subcatchments. The mean annual precipitation (1990–2010) is 1379 mm in the subcatchment HS and 1600 mm in the subcatchment MG. Mean annual temperature is 6.2 °C. The entire catchment is almost exclusively covered by forest. However, large parts of the catchment are in a stage of rejuvenation due to bark beetle outbreaks in the mid-1990s and 2000s (Beudert et al., 2015). Dominant tree species in the forest are Norwegian spruce (*Picea abies*, 70 %) and European beech (*Fagus sylvatica*; Table 1).

2.2 Collection of field data

2.2.1 Location of the two high-frequency sampling points at different topographical positions

In total, two high-frequency sampling points with contrasting topographical positions were established for the period from June 2018 until October 2020 (Fig. 1), and HS is the measurement site located at the outlet of Hinterer Schachtenbach. It drains the Hinterer Schachtenbach subcatchment, which is referred to as the lower catchment and includes a large and flat riparian zone, as well as the upper subcatchments of Kaltenbrunner Seige, which was not monitored, and Markungsgraben. MG is the measurement site located at the outlet of Markungsgraben. This subcatchment drains steep hillslopes and is referred to as the upper catchment.

2.2.2 Climate and deep groundwater data

Precipitation and air temperature data were provided by the BFNP. Precipitation has been measured since 1978 at the station Taferlruck (48°56.182′ N, 13°24.819′ E), close to our sampling site at HS (Fig. 1; red diamond) and at the station Racheldiensthütte (48°57.309′ N, 13°25.544′ E), next to our sampling site at MG (Fig. 1; yellow diamond). In order to assess the general meteorological conditions during the sampling period 2018, 2019 and 2020, long-term mean values for the two stations for the period from 1990 to 2010 were calculated using daily measurements. As temperature data were not available for both stations during the same period, data measured at Waldhäuser (48°55.771′ N, 13°27.890′ E, 953 m a.s.l.; outside of the map section shown in Fig. 1), a station 3.8 km east of the catchment outlet, was used. Groundwater (GW)-level data were provided by the Bavarian State Office for the Environment for GW2 (964 m a.s.l.; 17.5 m depth). For the other two locations, GW1 (969 m a.s.l.; 16.5 m depth) and GW3 (819 m a.s.l.; 10.3 m depth), groundwater-level data were provided by the BFNP (Fig. 1). The groundwater wells are completed into granitic regolith.

2.2.3 Discharge measurements

Starting in June 2018, the water level was measured every 15 min at HS using a pressure transducer (Solinst Canada Ltd., Georgetown, ON, Canada; SEBA Hydrometrie GmbH & Co. KG, Kaufbeuren, Germany). Flow velocities were measured periodically at the same location with an electromagnetic current meter (FlowSens; SEBA Hydrometrie GmbH & Co. KG, Kaufbeuren Germany) and via tracer dilution (TQ-S; Sommer Messtechnik, Koblach, Austria). Corresponding discharge was calculated following Kreps (1975). For MG, the discharge data at a 15 min interval for the com-

Table 1. Characteristics of the entire Hinterer Schachtenbach catchment and the studied subcatchments of Hinterer Schachtenbach (HS) and Markungsgraben (MG). The subcatchment of Kaltenbrunner Seige was not included in the monitoring. The colored squares represent the subcatchments shown in Fig. 1.

Catchment	Entire Hinterer Schachtenbach ▫	Subcatchment Hinterer Schachtenbach (HS) ▨	Subcatchment Markungsgraben (MG) ▫
Area (km^2)	3.5	1.5	1.1
Elevation (m a.s.l.)	771–1355	771–1085	888–1355
Mean slope (°)	12.0	7.4	15.9
Soils (%)			
Cambisols	66	66	55
Podzols	15	0	34
Hydromorphic soils	17	34	5
Lithic Leptosol	2	0	6
Vegetation (%)			
Rejuvenation	34	21	57
Deciduous forest	41	42	29
Coniferous forest	9	17	4
Mixed forest	15	19	8
Other	1	1	2

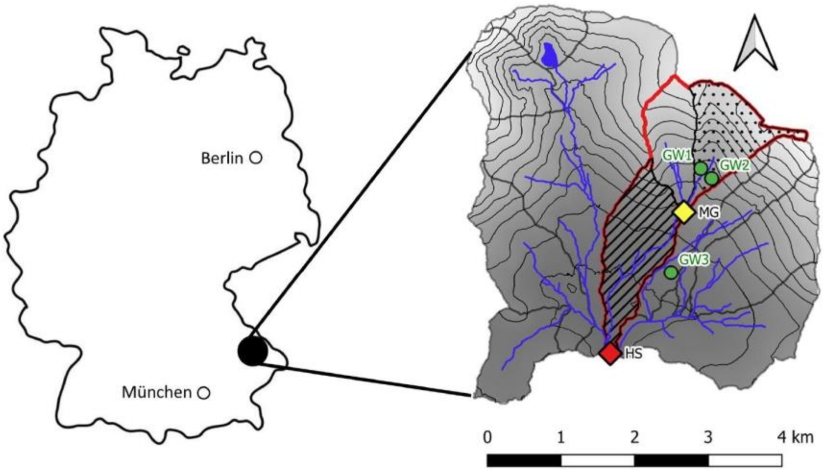

Figure 1. The Große Ohe catchment is located in southeastern Germany (left-hand side). The high-frequency sampling sites were located at the outlet of Hinterer Schachtenbach (red diamond) and Markungsgraben (yellow diamond). The red outline shows the total area contributing to the outlet of Hinterer Schachtenbach, including the subcatchment Markungsgraben (dotted), Hinterer Schachtenbach (hatched) and Kaltenbrunner Seige (no pattern). The deep groundwater wells (green dots) were located in the subcatchment Markungsgraben and in the riparian zone of a neighboring subcatchment. Stream channels were identified using a 5 m resolution digital elevation model (DEM). Both the location of the stream channels and the DEM were provided by the Bavarian State Office for Environment.

plete sampling period were taken from the database of the Bavarian State Office for Environment (2020).

2.2.4 High-frequency measurements of DOC concentration at different topographical positions

DOC concentrations were measured in situ at HS and MG using two UV-Vis (ultraviolet–visible) spectrophotometers (spectro::lyser; s::can GmbH, Vienna, Austria). The spectrometric devices recorded the absorption spectrum of stream water from 200 to 750 nm with a resolution of 2.5 nm every 15 min. DOC concentrations were quantified using the internal calibration based on the absorption values using the software ana::pro. In order to refine the internal calibration, the DOC concentrations measured by the UV-Vis spectrophotometers were calibrated using 52 (HS) and 21 (MG) grab stream samples taken over the course of the sampling period at various discharge conditions. Due to a technical failure, the device at MG had to be exchanged in 2020. Therefore, the data in 2020 were calibrated using 45 grab samples. Samples were filtered in the field using polyethersulfone membrane filters (0.45 µm) or polycarbonate track etched membrane (0.45 µm). All samples were stored until further analysis at 4 °C. DOC concentrations of the grab samples were analyzed in the laboratory by thermo-catalytic oxidation (TOC-L analyzer; Shimadzu, Kyoto, Japan). For further analysis, the calibrated values (R^2 for HS = 0.98 for all events, R^2 for MG = 0.77 for the events in 2018 and 2019 and $R^2 = 0.97$ for the event in 2020) were used. As no drift of the DOC concentration could be identified in the measured signal, we decided against a correction for biofouling as done by Werner et al. (2019). However, the sensor optics were manually cleaned in the field every 2 weeks using cotton swabs. DOC concentrations were measured from June to November 2018, from April to November 2019 and from April to October 2020. In this study, we focus on the analysis of the four largest events for which complete data sets at both locations were available. The events were characterized by contrasting antecedent wetness conditions, as can be seen in Figs. 2 and 4, and took place in June 2018, October 2018, May 2019 and September 2020.

2.3 Analysis of event characteristics

The start of a runoff event was classified as the last time step measuring baseflow. The start of Q increase, and thus the end of baseflow, was defined as the first value higher than the sum of the average Q and the twofold standard deviation of the 3 h prior to the start of precipitation. The end of a runoff event was defined as the moment when Q returned to pre-event values. In October 2018, the observed event was quickly followed by a second event, which led to slightly overlapping hydrographs at HS. As Q was already within 0.003 $m^3\,s^{-1}$ of pre-event baseflow, we did not simulate the end of the first hydrograph but rather used the incomplete hysteretic loop for load calculations. In September 2020, post-event baseflow was higher than pre-event baseflow and was defined as the first value lower than the 3 h average plus the twofold standard deviation prior to the start of the next event several days later.

For each event, DOC concentrations were plotted as a function of Q at a 15 min interval, and the hysteresis index (h), as proposed by Zuecco et al. (2016), was calculated. The index is based on the computation of definite integrals at fixed intervals of normalized Q and represents the difference between the integrals on the rising and falling curves computed for the same interval. A positive hysteresis index indicates a clockwise hysteresis, whereas a negative hysteresis index indicates an counterclockwise hysteresis. The larger the absolute value of h, the wider the hysteretic loop. Additionally, DOC fluxes were calculated by multiplying the 15 min discharge value with the corresponding 15 min DOC concentration. These were cumulated to a total DOC export per event and divided by the duration of the runoff events to obtain DOC load values. When comparing the contribution of different subcatchments to total Q and DOC export, we used the value 0.31, which is the ratio of the areas (Table 1) of the subcatchments (MG / HS), as a benchmark.

In order to compare the specific characteristics of the precipitation events and the response of discharge and DOC concentrations in the stream, we used the following parameters. P_{tot} is the total amount of precipitation during the event. The antecedent precipitation (AP_{14}) is the cumulative precipitation 14 d prior to the start of the event, following van Verseveld et al. (2009). The sum of P_{tot} and AP_{14} represents the total catchment wetness. The P–Q lag is defined as the time (in minutes) between the start of precipitation and the start of the first Q increase as a response to the precipitation. The Q lag time is the time in minutes from the first Q increase to the Q peak (Q_{max}). Runoff ratios were calculated as the ratio of cumulative area normalized discharge during the event to the amount of precipitation. DOC lag time is the time in minutes from Q_{max} to the DOC peak (DOC_{max}). We also introduce a new index called DOC_{90}. It represents the period of time in minutes during which the DOC concentrations exceed 90 % of DOC_{max} during the event. It provides a measure for the formation of a plateau of the hysteretic loop before the decrease in DOC concentrations. The precipitation-specific DOC load is defined as the DOC load per catchment area per precipitation amount (kilograms per square kilometer per millimeter; hereafter kg $km^{-2}\,mm^{-1}$). Due to the low sample size, no statistical analyses were performed.

3 Results

3.1 Hydrological preconditions and discharge response

The sampling periods in all 3 years were characterized overall by warmer temperatures and less precipitation when compared to the long-term mean monthly precipitation sums and monthly average temperatures. The annual precipitation at HS was 1126 mm in 2018, 1125 mm in 2019 and 1072 mm in 2020, which was considerably lower than the long-term average of 1379 mm (1990–2010). The annual precipitation at MG was 1274 mm in 2018, 1380 mm in 2019 and 1293 mm in 2020 compared to the long-term average of 1600 mm (1990–2010). The annual mean temperature was between 1.4 and 1.6 °C higher than the long-term average of

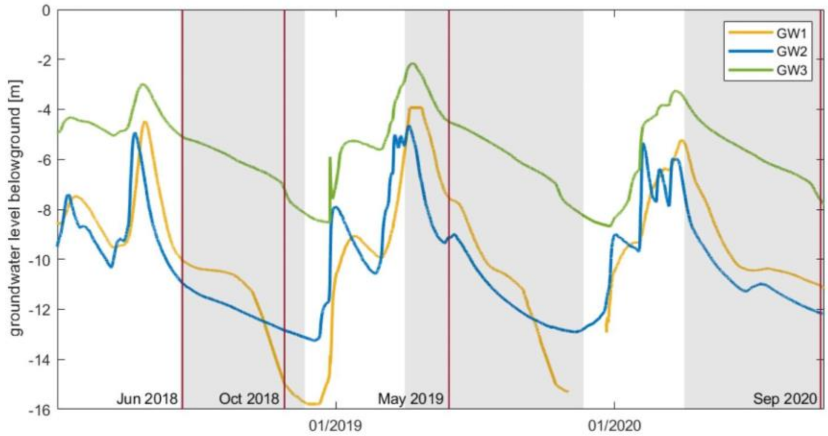

Figure 2. Groundwater (GW) levels at GW1, GW2 and GW3 from 2018 to 2020. The shaded areas represent the three sampling periods and the red lines the selected events.

6.2 °C. In general, the two events in late spring/early summer (June 2018 and May 2019) were preceded by long periods of higher deep groundwater tables following winter precipitation and snowmelt (Fig. 2).

The two early fall events (October 2018 and September 2020) followed dry summers characterized by pronounced decline in the deep groundwater table. The three events analyzed in June 2018, May 2019 and October 2018 were of similar size but differed markedly in their antecedent wetness conditions (Table 2). In June 2018, several larger events occurred prior to the analyzed event, which led to a very high AP_{14} at both sites. The value at HS exceeded the value at MG due to a large local event in the beginning of June. In May 2019, a succession of several events led to an intermediate AP_{14}, compared to the event in June 2018. The amount of precipitation was also slightly lower in May 2019 than during the June event in 2018. The October event followed a prolonged dry period,leading to the lowest AP_{14} value of the four events. The event in September 2020 was much larger than the other three events, with almost twice the amount of precipitation. The AP_{14}, however, was very low and comparable to the October 2018 event. This offered the opportunity to evaluate the effect of event size, representing the total amount of precipitation during an event, using these two early fall events with similar AP_{14}. In contrast, total catchment wetness values ($AP_{14} + P_{tot}$) of the events in May 2019 and September 2020 were very similar, providing an additional opportunity to evaluate the relative importance of event size vs. antecedent wetness conditions. At HS, the highest Q_{max} value of the four events was found in June 2018. At MG, the highest Q_{max} value for the four studied events was measured for the October 2018 event (Fig. 3a), which was still not close to the mean high-flow discharge of MG of $0.869\,m^3\,s^{-1}$. The baseflow of MG during the sampling period varied mostly between the lowest low-flow discharge ($0.006\,m^3\,s^{-1}$) and the mean low-flow discharge ($0.013\,m^3\,s^{-1}$). No comparison is possible for HS as discharge monitoring only started in June 2018. At HS, Q_{max} values varied as a function of total catchment wetness, whereas, at MG, Q_{max} was not significantly affected by total catchment wetness. At both sites, the runoff ratio was highest during the event following snowmelt in May 2019 and lowest during the event in October 2018 following the dry summer. The runoff ratios were higher at MG than at HS, with the exception of June 2018, which is the event with the highest total catchment wetness. MG generally showed a faster Q response than HS, which is represented by the shorter P–Q lag time. During the events in June 2018 and May 2019, the P–Q lag time was very similar at both locations. During the events in October 2018 and September 2020, following a dry summer, the P–Q lag time at HS was much longer than at MG. Q lag time at HS, however, was shorter than at MG during these events and longer during the events in June 2018 and May 2019.

3.2 DOC dynamics and DOC-Q-hysteresis patterns

Our long-term measurements showed that DOC concentrations during baseflow were very similar at the two locations and usually varied between 2 and $3\,mg\,L^{-1}$. In general, we observed rapidly rising DOC concentrations with rising discharge after precipitation events (Fig. 4). Peak DOC concentrations for the four studied events varied, for HS, between 10.2 and $18.6\,mg\,L^{-1}$ and, for MG, between 8.5 and $16.9\,mg\,L^{-1}$, without a clear relation (Table 2) to P_{tot}, AP_{14} or total catchment wetness. The increase in DOC concentration occurred faster at MG than at HS, which led to shorter DOC lag times at MG (Table 2). The longest DOC lag time was found in May 2019. However, the event with the shortest lag time was in September 2020 at MG, whereas, at

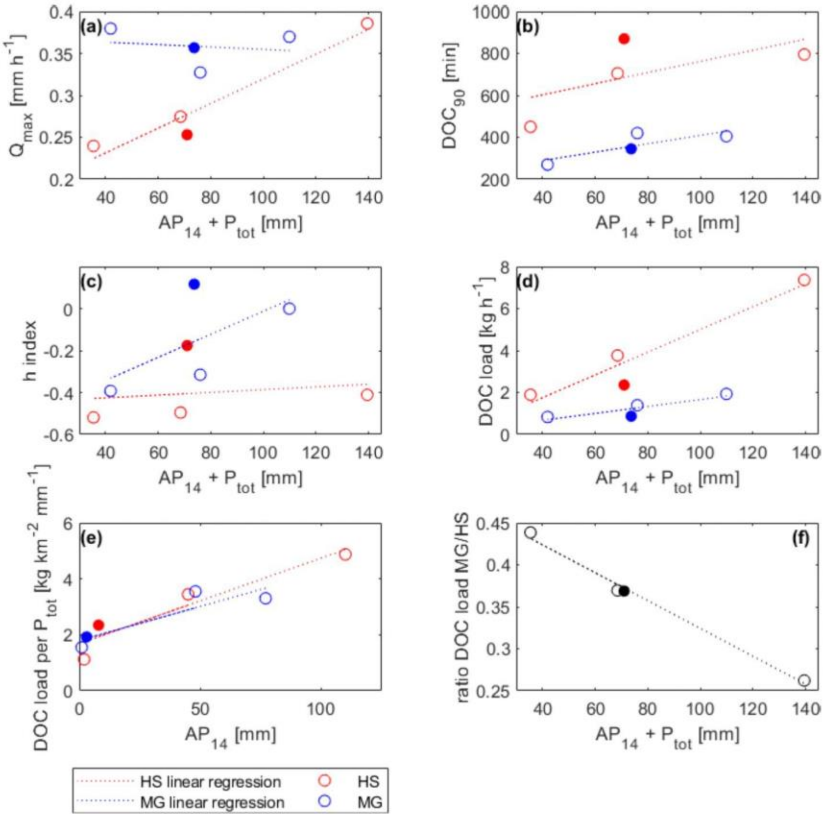

Figure 3. (a–d) Event parameters as a function of the sum of AP_{14} and P_{tot} (total catchment wetness) at the upper site (HS) and the lower site (MG). The closed symbols indicate the September 2020 event with its much larger amount of precipitation. **(e)** Precipitation-specific DOC load (kg km^{-2} mm^{-1}) as a function of AP_{14}. **(f)** The ratio of the DOC load of MG / HS as a function of total catchment wetness.

HS, it was in June 2018. DOC concentrations at HS generally maintained their DOC_{90} concentrations during a longer time than at MG, and values were higher at HS during all events (Fig. 3b). This resulted in wider hysteretic loops at HS than at MG (larger absolute values of h), as the concentrations at MG decreased soon after reaching the DOC peak. The DOC–Q relationships during events showed almost exclusively counterclockwise hysteresis patterns at both sites (Fig. 5), resulting in negative hysteresis indices (h; see Table 2). Exceptions were the events in June 2018 and September 2020 at MG, where the hysteresis exhibited no clear loop form and an h value close to zero. With increasing total catchment wetness, the h value approached zero at MG (Fig. 3c). At both sites, the lowest absolute h value and, thus, the narrowest hysteretic loop was found in September 2020 during the largest event. The largest absolute h value and, thus, the widest hysteretic loop was found in October 2018 following the extreme dry period.

3.3 DOC export from subcatchments during events with different antecedent wetness conditions

The DOC export was higher during all events at HS than at MG due to the larger catchment area. We observed the highest DOC load at both locations during the event in June 2018 with 7.4 kg h^{-1} at HS and 1.9 kg h^{-1} at MG (Table 2). At both locations, we observed the lowest DOC load during the event in October 2018, with 1.9 kg h^{-1} and 0.8 kg h^{-1}, respectively. At both locations, the total DOC load increased with total catchment wetness (Fig. 3d), whereby the relationship at HS is more pronounced. And at both locations, the precipitation-specific DOC load increased clearly with the AP_{14} (Fig. 3e).

Assuming that the difference between the total DOC arriving at HS and the total DOC arriving at MG originated from the subcatchments of Kaltenbrunner Seige and HS, the relative contribution of MG to DOC export can be evaluated. The comparison of the ratio of cumulative water volumes and of cumulative DOC loads measured at MG and HS (Fig. 6) illustrated the varying relative contribution of the upper catch-

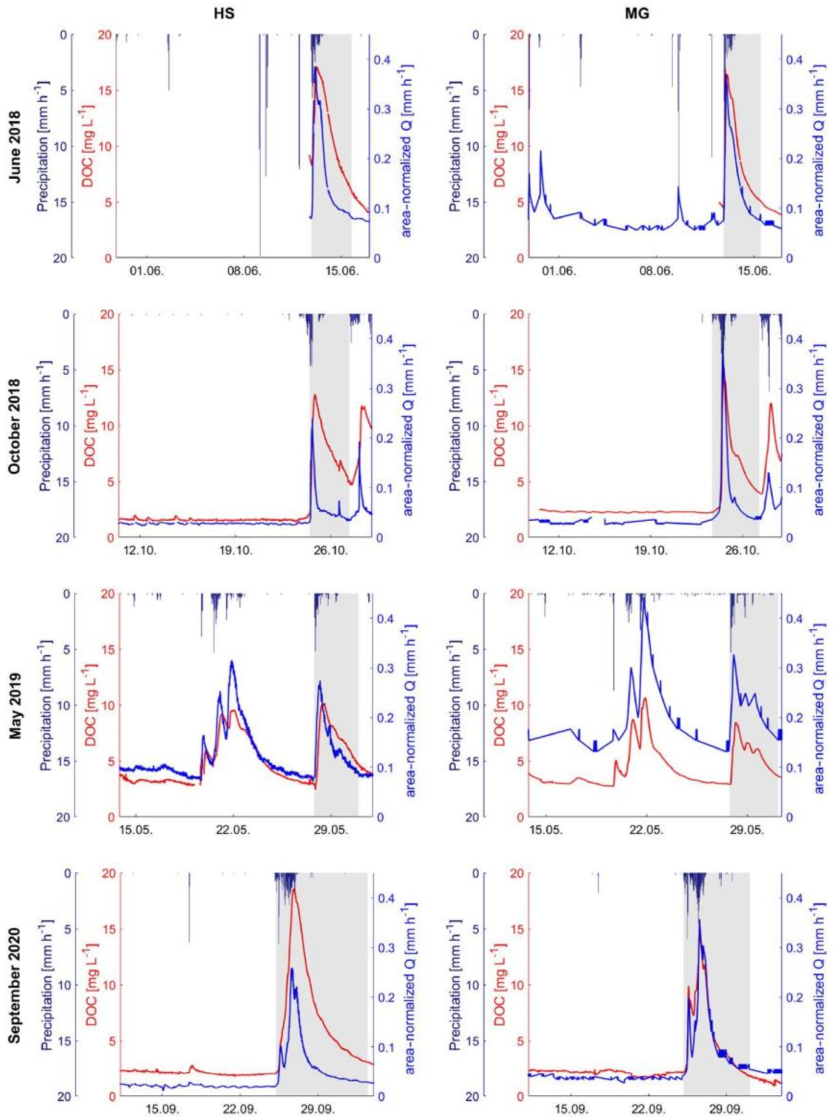

Figure 4. DOC concentrations and area-normalized Q starting 14 d prior to the events in June 2018 (top row), October 2018 (second row), May 2019 (third row) and September 2020 (bottom row) at HS (left) and MG (right). The shaded areas highlight the events described in detail in Table 2.

ment. Although it is unlikely that the entire catchment area served as a DOC source area, we compared the contribution of the upper catchment to the expected ratio based on catchment area alone, which would be 0.31. However, only the events in June and May showed MG / HS ratios close to this value for both cumulative Q and DOC. The events in October and September showed a considerably higher MG contribution for both Q and DOC, especially at the beginning of the events. Over time, the ratios approached the expected value of 0.31 as the contribution of MG decreased. In June and May, the Q and DOC ratios showed similar values, with Q being slightly higher than DOC. In contrast, during October and September, DOC ratios were higher than Q ratios most of the time. The MG contribution to the DOC load at HS was strongly negatively correlated to the total catchment wetness of the catchment (Fig. 3f).

Table 2. Event characteristics of the four selected events at HS and MG, namely P_{tot} (total precipitation in millimeters during the event), AP_{14} (antecedent precipitation; cumulative precipitation in millimeters 14 d prior to event start), total catchment wetness (sum of P_{tot} and AP_{14} in millimeters), P–Q lag time (time in minutes from the start of precipitation to the start of Q increase), Q lag time (time in minutes from the start of Q increased to Q_{max}), Q_{max} (peak discharge in cubic meters per second; hereafter $m^3 s^{-1}$), runoff ratio, h (hysteresis index, following Zuecco et al., 2016; see Sect. 2.2), DOC lag time (time in minutes from Q_{max} to DOC_{max}), maximum DOC concentration (DOC_{max} in milligrams per liter; hereafter $mg L^{-1}$), DOC_{90} (time in minutes during which the DOC concentrations exceed the 90 % of DOC_{max}), DOC load in $kg h^{-1}$ (kilograms per hour; hereafter $kg h^{-1}$) and precipitation-specific DOC load in kilograms per square kilometer per millimeter; hereafter $kg km^{-2} mm^{-1}$.

	Start date	P_{tot} (mm)	AP_{14} (mm)	Total catchment wetness (mm)	P–Q lag time (min)	Q lag time (min)	Q_{max} ($m^3 s^{-1}$)	Runoff ratio
HS	12 Jun 2018	30	110	140	60	345	0.375	0.36
	23 Oct 2018	33	2	35	1110	270	0.233	0.10
	27 May 2019	24	45	69	30	540	0.267	0.49
	25 Sep 2020	63	8	71	225	1755	0.252	0.18
MG	12 Jun 2018	33	77	110	30	225	0.113	0.30
	23 Oct 2018	41	1	42	15	1170	0.116	0.14
	27 May 2019	28	48	76	30	375	0.100	0.62
	25 Sep 2020	71	3	74	15	2040	0.109	0.26

	Start date	h	DOC lag time (min)	DOC_{max} ($mg L^{-1}$)	DOC_{90} (min)	DOC load ($kg h^{-1}$)	Precipitation-specific DOC load ($kg km^{-2} mm^{-1}$)
HS	12 Jun 2018	−0.411	165	17.1	795	7.4	4.9
	23 Oct 2018	−0.519	255	12.8	450	1.9	1.1
	27 May 2019	−0.496	465	10.2	705	3.8	3.4
	25 Sep 2020	−0.176	285	18.6	870	2.4	2.3
MG	12 Jun 2018	0.000	120	16.9	405	1.9	3.3
	23 Oct 2018	−0.393	90	15.2	270	0.8	1.5
	27 May 2019	−0.315	225	8.5	420	1.4	3.6
	25 Sep 2020	0.116	0	14.6	345	0.9	1.9

4 Discussion

4.1 Discharge response depends on topographical positions and antecedent wetness conditions

The sampling period was defined by prolonged dry conditions and few rain events. However, we were able to compare the reaction of the catchment at two contrasting locations to three similarly sized events and to one event that was unusually large for the observation period. The events were characterized by contrasting antecedent wetness conditions. Q_{max} at HS was clearly linked to the total catchment wetness prior to the event (Fig. 3a), which is in contrast to MG. This correlation suggests that precipitation events are not the only driver of Q generation, but that Q generation in the lower catchment depends highly on the antecedent wetness conditions. The Q lag times were longer at HS than at MG during the events with wet antecedent conditions and shorter during the events with dry antecedent conditions. What is even more pronounced is that P–Q lag times at HS exceeded the values at MG, especially after the prolonged dry periods, indicating a slower response to rainfall events at the lower catchment. To some extent, this observation can be attributed to the larger catchment area contributing to water fluxes at HS, resulting in longer flow pathways and a delayed Q response (Laurenson, 1964; Kirkby, 1976). We argue that topographic differences also play a key role in the response of discharge to rainfall events, especially under dry conditions. Steeper slopes in the upper catchment generate a faster delivery of water to the stream than at the lower catchment, which is characterized by a low gradient topography. Processes such as the transmissivity feedback (Bishop et al., 2004), which describes how a rising groundwater table together with increasing hydraulic conductivity in upper soil layers may lead to a delayed increase in discharge in the receiving stream (Frei et al., 2010), could be of importance in the extensive flat riparian zone of the lower catchment. Pictures taken with a time lapse camera (data not shown) indicated that here the shallow groundwater table can quickly rise into the upper soil layers. We suggest that hydrological connectivity between the wide riparian zone and the stream is the major control on delivering water to the stream. The hydrological connectivity is dependent both on topography and on the antecedent wetness conditions (Detty and McGuire, 2010; Penna et al., 2015; McGuire and McDonnell, 2010) as we will explain in the following.

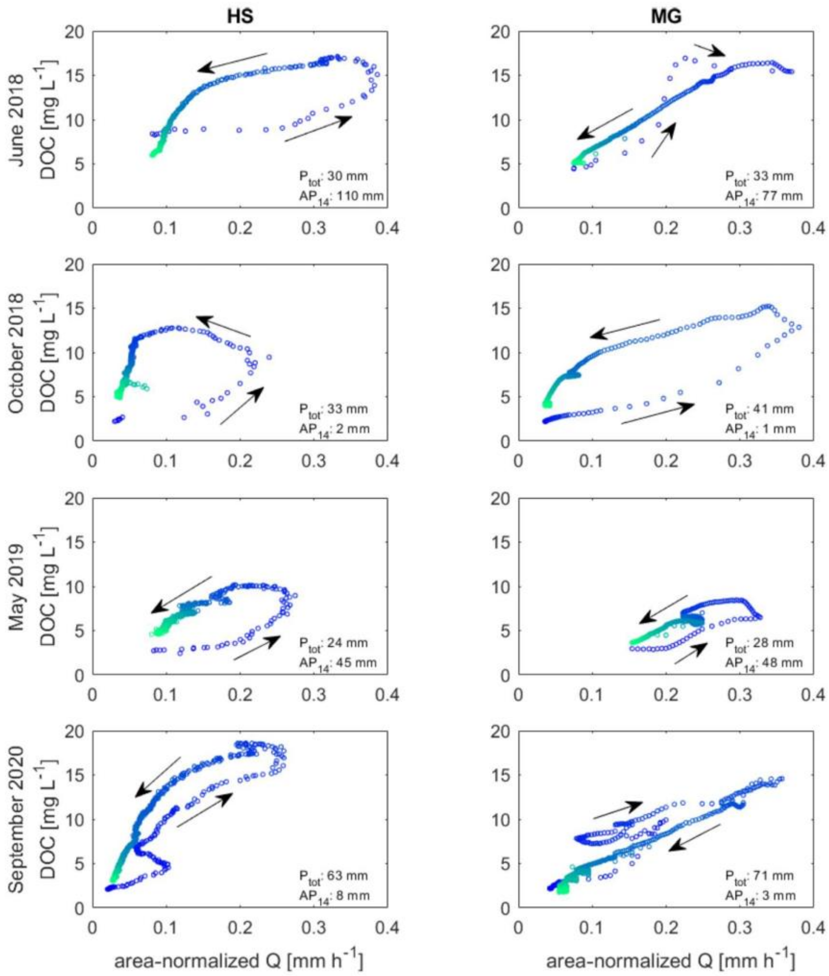

Figure 5. DOC–Q hysteresis during the events in June 2018, October 2018, May 2019 and September 2020 (see gray areas in Fig. 4). The dots represent 15 min time steps, starting from dark blue to green.

As seen in Fig. 6, the upper catchment delivered relatively more water than the lower catchment after long dry periods. This proportion changed over time, with a larger fraction of discharge being contributed by the lower catchment. Zimmer and McGlynn (2018) made similar observations in an ephemeral-to-perennial basin with a humid subtropical climate and drew the conclusion that, in the headwaters, shallow flow paths can be rapidly activated, whereas, in the lowlands, slower moving groundwater is of importance. They also suggest that groundwater could be lost in the transition from upstream to downstream areas. Both of these mechanisms could play a role in the catchment studied here as well. The relationship between Q_{max} and total catchment wetness in our study suggests that the lower catchment is highly dependent on the establishment of hydrological connectivity for discharge generation, which is in contrast to the upper catchment. Rinderer et al. (2016) showed that the groundwater response during an event in a pre-Alpine catchment happens faster in flat areas than in steep areas. However, sites with low soil moisture showed a slower groundwater response time. This result is in line with our observation that the lower catchment is generally more important for runoff generation, with the exception of very dry conditions. The lower catchment with the low topography and large riparian zone has a larger water storage capacity in contrast to the upper catchment due to deeper soils. This effect is also reflected in the lower runoff ratios at HS than at MG, with the exception of the event with the wettest antecedent conditions (Table 2). After dry periods, the soils in the lower catchment need to be rewetted before flow pathways towards the stream become activated, whereas, in the steeper upper catchment, runoff generation is faster and, thus, contributes rela-

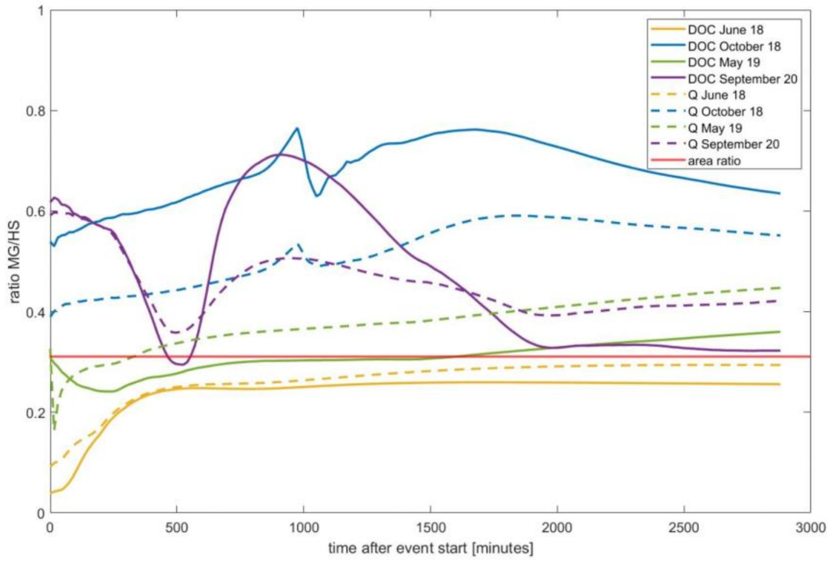

Figure 6. Ratio of cumulative Q (dashed lines) and DOC load (solid lines) at HS and MG during the four selected events. The red line indicates the expected ratio in terms of area (0.31). We included a 3 h lag of the arrival from MG at HS based on flow velocity measurements taken at high discharge.

tively more to the total flux, especially at the beginning of the event. Over time, the water contribution becomes balanced as flow paths in the lower catchment are connected to the stream. The correlation between the total catchment wetness and Q_{max} also shows that the antecedent conditions are pivotal for Q generation in the lower catchment as they strongly influence top and subsoil water stores. Even during the large event in September 2020, Q_{max} of HS was lower than during the events in May 2019 and June 2018, which were characterized by a smaller precipitation amount but much wetter antecedent conditions. Event size alone is, therefore, not a good predictor for peak discharge values.

4.2 The interplay of event size and antecedent wetness conditions as a controlling factor for DOC mobilization and export

As observed in previous studies, DOC concentrations did not vary strongly during baseflow but increased rapidly in response to increasing discharge following precipitation events. Concentrations were similar to values found in other temperate forested catchment in low mountain ranges (Musolff et al., 2018; Schwarze and Beudert, 2009). Larger events often lead to higher DOC concentrations in streams (McDowell and Likens, 1988; Kawasaki et al., 2005; Dawson et al., 2008). In some catchments, successive events can lead to the depletion of DOC sources (Bartsch et al., 2013; Butturini et al., 2006; Jeong et al., 2012; van Verseveld et al., 2009) and, consequently, to lower DOC concentrations. Our results showed that, after successive events, peak DOC concentrations did not decrease (Fig. 4, May 2019). We conclude, therefore, that DOC fluxes in the stream are limited by transport from the riparian zone in the Große Ohe catchment rather than being source limited, at least for the event frequency and magnitude observed during the study period. This is also the case for most of the > 1000 catchments studied by Zarnetske et al. (2018), which varied in area, stream order and ecoregion type. Our data show that transport limitation is clearly linked to the antecedent wetness conditions, which strongly influence the hydrological connectivity of the catchment as it has been shown in other studies as well (Detty and McGuire, 2010; Penna et al., 2015).

In the following, we will focus on processes referring to the entire catchment, which could be observed at HS. AP_{14} and total catchment wetness and DOC load were positively related (Fig. 3d). The event in June 2018 with the highest AP_{14} and highest total catchment wetness led to the highest DOC concentrations and the highest DOC load. This becomes particularly clear in comparison with the slightly larger event in the following October. The strong relation between AP_{14} and the precipitation-specific DOC load confirms the importance of antecedent wetness conditions for DOC mobilization during events (Fig. 3e). The link between wet antecedent conditions, a higher connectivity and, subsequently, a higher DOC export was also observed by Zimmer and McGlynn (2018), as explained above. This observation is similar to Inamdar and Mitchell (2006), who suggested that, with increasing soil moisture, previously disconnected DOC source areas become active, leading to a strong increase in DOC export. We also observed a clear link between total catchment wetness and DOC_{90} (Fig. 3b). As DOC appears to be transport limited rather than source limited, the persistently high concentrations, in combination with a high discharge generation due to the existing connectivity, could then cause the pronounced DOC export during events following wet antecedent conditions.

We propose that the delayed DOC increase observable in the stream upon an increase in discharge, which is represented by the counterclockwise hysteresis loops (Fig. 5), reflects not only the larger catchment size but also the slow saturation of DOC-rich soil layers and the slow establishment of connectivity to the stream, similar to systems where the transmissivity feedback mechanisms are the dominant control on DOC fluxes (Bishop et al., 2004). In addition, connectivity with near-stream small pools could contribute to a delayed increase in DOC concentrations. We observed pools in the riparian zone that only contained water during very wet conditions. These pools then connected to a small tributary of the stream. Analyses of the pool water showed very high DOC concentrations that were between 30 and 50 $mg\,L^{-1}$ (data not shown). The possibility that these pools contribute to DOC export when filled with water later during the event is also supported by the observation that topographic depressions can play a very important role in DOC accumulation and DOC transport to the stream (Ploum et al., 2020). In general, the riparian zone saturates over the course of a precipitation event (Ledesma et al., 2015; Tunaley et al., 2016). This process happens faster after wet antecedent conditions which lead to a larger hydrologically connected area of the riparian zone with longer flow paths in organic-rich layers on the way to the stream. These lateral subsurface flows through the upper soil horizon are an important process for DOC mobilization (Bartsch et al., 2013; Birkel et al., 2017). If the soils are wet prior to an event, connected flow paths can quickly be established, and DOC transport to the stream occurs faster than during dry conditions, which highlights that the DOC export is transport limited in this catchment. This could explain why the highest DOC exports were found during wet conditions, which is in contrast to other studies that have shown that DOC concentrations and export are especially high during events following longer dry periods due to stagnant pools in the stream (Inamdar and Mitchell, 2006; Granados et al., 2020) and an increased DOC production through oxidation of organic matter and accumulation after a dry and warm summer (Tunaley et al., 2016; Wen et al., 2020; Strohmeier et al., 2013). However, DOC export during the events in October 2018 and September 2020, following the dry summer, was relatively low due to the low discharge generation (see Sect. 4.1). This finding supports our hypothesis of transport limited DOC export and indicates that seasonal effects are of lower relevance for DOC mobilization than hydrological controls.

Hydrological connectivity is not solely influenced by the antecedent wetness conditions and storage capacities but also by the event size (Correa et al., 2019; McGuire and McDonnell, 2010), as large events lead to the expansion of saturated areas (Tetzlaff et al., 2014). Several studies have shown that event size also plays an important role in DOC mobilization as the largest DOC export of a catchment occurs during precipitation events. Large single events can contribute significantly to the annual DOC export in small catchments, whereby the event size is often more important than the event frequency (Raymond and Saiers, 2010; Raymond et al., 2016).

Comparing the two early fall events, which were characterized by equally dry antecedent conditions but different amounts of precipitation (October 2018 and September 2020), we see that the Q peak was similar at both events, although the September event had almost twice the amount of precipitation of October 2018. The lack of connectivity appeared to inhibit discharge generation in September 2020. Nevertheless, DOC export per hour was higher in September 2020, leading to a much higher total DOC export if the duration of this event is taken into account (Fig. 4). We, therefore, conclude that the event size does have an important effect on DOC export when the antecedent conditions are similar.

The two events in May 2019 and September 2020 had a similar value of total wetness (AP_{14} and P_{tot}) but differed markedly in P_{tot} and AP_{14}. The setting in different seasons with contrasting antecedent wetness conditions and the difference in event size led to clear differences in some event characteristics. The September event, a large event after dry conditions, was characterized by higher DOC_{90} and higher DOC_{max} values. Higher DOC concentrations, thus, prevailed for a longer time, which could be due to a larger available DOC pool after the warm summer months (Strohmeier et al., 2013; Tunaley et al., 2016; Wen et al., 2020). The hysteretic loop was narrower in September, indicating a faster DOC mobilization due to the precipitation amount. However, as described above, missing connectivity likely inhibited DOC export, especially at the beginning of the event in September 2020, which could explain the lower DOC load than in May 2019.

Following these observations, we suggest a hierarchy of controlling factors with respect to their relevance for discharge and DOC release (Fig. 7). For Q generation, the antecedent wetness conditions are important, whereas the event size plays a minor role. For DOC export, however, the event size was of importance, as a larger event resulted in a markedly higher DOC mobilization, as observed in September 2020. During the event in June 2018, the small amount of precipitation was offset by a very high AP_{14}, leading to a higher total DOC load than in September 2020 with less than half of the precipitation. Analyzing only the similarly sized events (June 2018, October 2018 and May 2019), total catchment wetness clearly controlled DOC export, thereby offsetting possible seasonal effects which would be expected to lead to a high DOC export during the fall events.

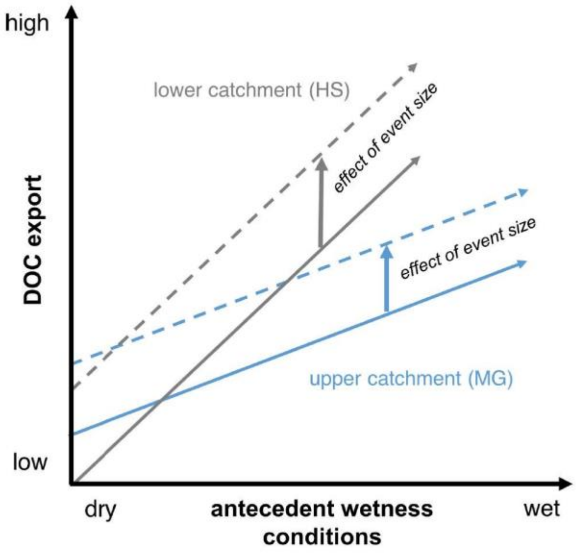

Figure 7. Conceptual figure of the relation between event size, antecedent conditions and DOC export for the upper catchment MG (blue lines) and the lower catchment HS (gray lines). During similarly sized events (June 2018, October 2018 and May 2019), DOC export increased with the antecedent wetness in both subcatchments (solid lines), whereby the relation was more pronounced in the lower catchment. Therefore, the upper catchment contributed proportionally more to the total DOC export during events following dry antecedent conditions due to the low hydrological connectivity in the lower catchment. With increasing antecedent wetness, hydrological connectivity was established in the lower catchment, and its relative contribution to DOC export exceeded the contribution of the upper catchment. Larger events (September 2020) led to a larger DOC export at both subcatchments (dashed lines).

4.3 Clear differences in DOC mobilization and export between topographical positions

Antecedent wetness conditions are also linked to storage capacities and connectivity, which, in turn, are strongly correlated with topography. In contrast to HS, we could not see a correlation between Q_{max} and the total catchment wetness at MG, indicating different hydrological runoff processes which were less dependent on hydrological connectivity (Fig. 3a). At MG, DOC lag times were generally shorter and hysteretic loops narrower, indicating a faster DOC mobilization than at HS. As discussed in Sect. 4.1., we argue that the steeper slopes at MG facilitate a fast connectivity and transport of water and consequently DOC to the stream. In contrast to HS, we do see a relationship between the total catchment wetness and the h index (Fig. 3c). The events in June 2018 and September 2020 led to the only hysteretic loops that were not clearly counterclockwise. The very fast increase and decrease in DOC concentrations led to figure-eight-shaped, almost clockwise, loops at MG. In September 2020, the large event size led to a fast delivery of DOC to the stream. In June 2018, the wet antecedent wetness conditions facilitated a fast connection of close DOC sources to the stream with the start of the event. Correa et al. (2019) made a similar observation in a tropical alpine headwater catchment with counterclockwise hysteresis patterns of several rare Earth elements in the downstream catchment areas and clockwise hysteresis patterns in upstream parts of the catchment, which they attributed to faster-responding end members. Once reaching the maximum, DOC concentrations at MG generally started to decrease quite fast, whereas at HS they remained elevated over several hours, as seen in the DOC_{90} values.

Although Li et al. (2015) suggest that vegetation and the abundance of lakes and wetlands are more important for DOC export than topography alone, other studies have shown that topography can strongly influence DOC mobilization in some catchments. Both Musolff et al. (2018) and Ogawa et al. (2006) observed a correlation between the topographic wetness index, an indicator for potential soil wetness linking slope and upslope contributing area, and DOC concentrations. According to their studies, a flat area would therefore tend to export more DOC than a steep area due to a higher general wetness that favors the buildup of DOC in the soil and hydrological connectivity. Surprisingly, the calculation of DOC load revealed that the lower catchment did not always dominate export. The total DOC export per event was similar to the DOC export observed by van Verseveld et al. (2009). These authors observed export rates varying from below 50 kg km^{-2} per storm for events with slightly more than 40 mm precipitation to 440 kg km^{-2} for an event with 200 mm precipitation. Export rates at MG varied between 63 and 128 kg km^{-2} and at HS between 37 and 148 km^{-2}. Taking into account the upstream catchment area of the sites, one would expect around 31 % of DOC arriving at HS coming from MG, based on the assumption that both sites have the same source strength and no DOC is lost from the stream. We use the value of 31 % for the purpose of comparison and do not intend to imply that the entire catchment area is a DOC source area. Figure 6 shows that the contribution of the upper catchment is much larger than 31 % under certain conditions and even exceeds the contribution of the lower catchment. This relative dominance of DOC originating from the upper catchment was most prominent in October 2018 and September 2020 after the dry summer and decreased with the total catchment wetness (Fig. 3f). During the large event in September 2020, the contribution of each catchment component changed over time. At the beginning of the event, considerably more DOC was mobilized from the upper catchment. Over time, however, the role of the upper catchment for DOC export decreased, and the contribution from the lower catchment increased. One aspect of a large contribution of DOC from the upper catchment might be higher precipitation than at the lower catchment, which could lead to increased DOC mobilization. The proportional amount of Q

arriving from the upper catchment is higher than during the other events; however, the DOC proportion is even higher. Consequently, not all of the mobilized DOC from the upper catchment can be explained by the higher discharge induced by a higher precipitation.

These observations contrast with our expectations that the lower catchment would be more important for DOC export than the upper catchment. Although the upper catchment area has a high deadwood content that might lead to a large DOC pool (Schwarze and Beudert, 2009), the vegetation is currently dominated by mostly regenerating Norwegian spruce forests and by deciduous trees, whereas the lower catchment is partly covered by mature coniferous forest and riparian peatland. Previous studies have shown that soil layers beneath conifers are usually richer in DOC than beneath deciduous trees (Schwarze and Beudert, 2009; Borken et al., 2011), which could contribute to higher in-stream DOC concentrations. In addition, a higher DOC production would be expected in the lower catchment due to the elevation differences and, subsequently, different temperatures (Borken et al., 2011; Tunaley et al., 2016; Wen et al., 2020; Andersson et al., 2000). Another reason for a higher DOC export from the lower catchment would be the importance of large riparian zones for DOC mobilization (Ploum et al., 2020; Mei et al., 2014; Ledesma et al., 2015, 2018; Inamdar and Mitchell, 2007; Strohmeier et al., 2013; Musolff et al., 2018). The importance of the riparian zone for in-stream DOC concentrations is confirmed by DOC measurements performed in a low-elevation subcatchment next to HS with more than 40 % hydromorphic soils (Beudert et al., 2012) and with stream DOC concentrations being higher ($6.3\,\mathrm{mg\,L^{-1}}$) at baseflow than in the lower catchment.

Nevertheless, the upper catchment contributes strongly to DOC export of the catchment, especially after dry antecedent conditions (Fig. 7). We suggest that the main reason for this reversed contribution to DOC export is rather a decreased DOC export from the lower catchment during events after dry conditions than an increased DOC export of the upper catchment during wet conditions. The variation in the DOC load between the events was much higher at HS than at MG, which indicates a high dependency on the hydrological preconditions. As explained above, connectivity seems to be important for the DOC mobilization, especially in the lower catchment where the missing connectivity in October and September seems to inhibit DOC mobilization more than in the upper catchment. A consequence of the reduced connectivity of the lower catchment could be that the riparian pools mentioned above are not connected and, thus, an important DOC source is not active. We suggest that the different topography also plays a role as flow paths in the lower catchment are not as easily connected as in the steep area. Due to the low-gradient terrain, saturated soils are necessary to transport water laterally through the DOC-rich soil layers towards the stream. In contrast, the steeper hills in the upper catchment facilitate a rapid transport to the stream independent of the rather dry soil layers, leading to a relatively high DOC export during the rain events. The change in contribution over the course of the large event in September 2020 confirms our reasoning that connectivity is the limiting factor of DOC mobilization in the lower catchment.

5 Conclusions

In this study, we showed that DOC mobilization and export depend on event size, antecedent wetness conditions and catchment topography. The amount of precipitation has a strong impact on the DOC export. However, if events are similar in size, the antecedent wetness conditions control DOC export. After wet antecedent conditions, we observed a larger DOC export than after dry conditions. Especially in the lower catchment, DOC was not mobilized at the beginning of an event as the soils in the riparian zone first needed to saturate. This led to a disproportionate contribution of the upper catchment to the total DOC export early in the events characterized by dry antecedent wetness conditions. In-stream mineralization processes will most likely not be relevant for a change in DOC concentrations as DOC in headwater catchments is usually transported conservatively during large precipitation events (Ejarque et al., 2017; Bernal et al., 2019). We cannot provide data on lateral exchange fluxes between stream and surrounding riparian area over the course of the stream, i.e., we cannot conclude if the DOC that is released at the upper catchment is still in the stream at the outlet of the lower catchment. Here, DOC quality characterization and the investigation of exchange fluxes would be helpful. DOC export is strongly dependent on antecedent moisture conditions. The dry antecedent conditions during the summer months offset possible seasonal effects linked to a higher biological activity as the drought inhibits the development of soil saturation and, thus, hydrological connectivity to streams. Different topographic positions react differently to precipitation inputs over the course of an event due to the influence of hydrological processes, which define the evolution of connectivity between DOC source zones and the streams, either facilitating or inhibiting DOC transport to the stream. As the frequency and intensity of droughts is likely to increase in the future due to climate change (Pachauri and Mayer, 2014), our study highlights that the relative contribution of different subcatchments to DOC export from mountainous catchments may change if DOC export is transport limited as it was the case in the catchment presented here. Especially the importance of riparian zones for DOC export might decrease as hydrological connectivity would be interrupted more often and, therefore, inhibit DOC mobilization. Longer drought periods could possibly reduce DOC export and slow down the current trend of rising DOC concentrations in freshwater systems.

Data availability. Data supporting the findings of this study are available from the corresponding author upon reasonable request.

Author contributions. The study was conceptualized with contributions from all co-authors. KB collected the field data, with the support of BB, and analyzed the data. KB, LH, BSG, JHF, SP and BB discussed and interpreted the results. KB prepared the paper with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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Study 2: Riparian Microtopography Affects Event-Driven Stream DOC Concentrations and DOM Quality in a Forested Headwater Catchment

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Own contribution in %:

Study design	70
Field data collection	60
Laboratory analyses	50
Data processing and analysis	80
Interpretation of results	70
Preparation of the manuscript	80

KB, PG, BSG, JHF, SP and LH designed the study. KB and PG planned the field work and collected the shallow groundwater data. KB and LH conducted the soil sampling. KB and MPS sampled the precipitation event. KB and PG conducted the analysis of water chemistry parameters and spectroscopic measurements and were responsible for the corresponding data processing and analyses. MPS was responsible for FT-ICR-MS measurements and processing. KB prepared the figures and tables. All co-authors discussed and interpreted the results. KB prepared the manuscript with input from all co-authors. KB is the corresponding author.

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Key Points:
- This study found small-scale differences in dissolved organic carbon (DOC) concentrations and dissolved organic matter (DOM) quality in the riparian zone
- Microtopographical depressions were characterized by high DOC concentrations and aromatic DOC
- In-stream DOC concentrations and DOM quality during a precipitation event resembled shallow groundwater below microtopographical depressions

Supporting Information:
Supporting Information may be found in the online version of this article.

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Riparian Microtopography Affects Event-Driven Stream DOC Concentrations and DOM Quality in a Forested Headwater Catchment

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Abstract The transport of dissolved organic carbon (DOC) from the soils to inland waters plays an important role in the global carbon cycle. Widespread increases in DOC concentrations have been observed in surface waters over the last few decades, affecting carbon balances, ecosystem functioning and drinking water treatment. However, the primary hydrological controls on DOC mobilization are still uncertain. The aim of this study was to investigate the role of microtopography in the riparian zone for DOC export and DOM quality. DOC concentration and DOM quality in the shallow groundwater of a riparian zone and in streamflow in a forested headwater catchment was investigated using fluorescence and absorbance characteristics. We found higher DOC concentrations with a higher aromaticity in the microtopographical depressions, which were influenced by highly dynamic shallow groundwater levels, than in the flat forest soil. As a result of the frequent wet-dry cycles in the upper soil layers, aromatic DOC accumulated in the shallow groundwater within and below the microtopographical depressions. Rising groundwater levels during precipitation events led to the connection of the microtopographical depressions to the stream, resulting in a change toward more aromatic DOC in the stream. Increasing stream DOC concentrations were accompanied by increasing concentrations of iron and aluminum, suggesting the coupled release of these metals with DOC from the riparian zone. Our results highlight the importance of the interplay between microtopography and groundwater level dynamics in the riparian zone for DOC export from headwater catchments.

Plain Language Summary Dissolved organic carbon (DOC) is the result of the continuous breakdown of organic material, such as leaves. It accumulates in the soil and is transported to streams mainly during precipitation events. In this study, we analyzed the shallow groundwater of two differing sites in the Bavarian Forest National Park. Both sites were located close to the stream, but one was characterized by typical forest soil and one by small ponds, which were occasionally filled with water. The site with ponds showed much higher DOC concentrations and the DOC was chemically different from the other site. During a precipitation event, we observed a shift in chemical composition of stream water parameters toward the chemical characteristics found at the site with ponds. Therefore, we conclude that the ponds contribute substantially to DOC mobilization, once they fill with water and get connected to the stream.

1. Introduction

Despite freshwater systems covering less than 3% of the Earth's surface, carbon fluxes from terrestrial into freshwater systems play an important role in the global carbon cycle (Battin et al., 2009; Cole et al., 2007; Raymond et al., 2013). A recent study estimated that 5.1 Pg terrestrial carbon are transported into inland waters every year (Drake et al., 2018). However, there are still many uncertainties regarding the export of carbon from terrestrial systems, which includes particular organic carbon, dissolved inorganic carbon and dissolved organic carbon (DOC). DOC is an important component of dissolved organic matter (DOM), which is a complex mixture of heterogeneous compounds. As carbon is the main element of DOM, DOC is often used as a proxy for DOM

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amount (Jaffé et al., 2008; Leenheer & Croué, 2003). DOC also plays an important role in the context of climate change as the largest part of carbon in inland waters (3.9 Pg yr^{-1}) is lost to the atmosphere as the greenhouse gases CO_2 and CH_4 as a result of respiration processes (Drake et al., 2018).

During the last few decades, increases in DOC concentrations in surface waters in the Northern Hemisphere have been observed (Evans et al., 2005; Monteith et al., 2007; Roulet & Moore, 2006), possibly influencing terrestrial carbon storage as a result of leaching (Batjes, 2014; Dixon et al., 1994; Kindler et al., 2011), greenhouse gas emissions (Battin et al., 2009) and drinking water quality (Alarcon-Herrera et al., 1994; Ledesma et al., 2012; Sadiq & Rodriguez, 2004). Several hypotheses have been proposed to explain these increases in DOC in surface waters. The majority of studies suggest the decline in atmospheric sulfur deposition as the main factor (Evans et al., 2006; Hruška et al., 2009; Ledesma et al., 2016; Monteith et al., 2007), whereas other studies suggest alternative explanations such as a decline in nitrogen deposition (Musolff et al., 2016), temperature increase (Weyhenmeyer & Karlsson, 2009), increased iron reduction (Knorr, 2013) and an increase in precipitation (Hongve et al., 2004).

DOC concentrations in discharge from forested catchments in humid, temperate as well as boreal zones positively correlate with the area of wetland soils within these catchments (Laudon et al., 2011; Musolff et al., 2018). Although not all riparian zones are wetlands, many riparian zones are similar to wetlands especially regarding the biogeochemistry of the saturated soils (Vidon, 2017). Riparian zones might also include so-called cryptic wetlands, which are hidden under forest canopy and can strongly contribute to DOC export from catchments (Creed et al., 2003). Indeed, the riparian zone is generally regarded to be of great importance for DOC export due to the accumulation of soil organic matter and the often high groundwater level (Grabs et al., 2012; Inamdar & Mitchell, 2007; Ledesma et al., 2015; Ledesma, Kothawala, et al., 2018; Mei et al., 2014; Musolff et al., 2018; Ploum et al., 2020; Strohmeier et al., 2013). Therefore, hydrological connectivity between the riparian zone and streams has important implications for DOC export (Birkel et al., 2017; Bishop et al., 2004; Blaurock et al., 2021; Broder et al., 2017; Werner et al., 2021). Hydrological connectivity and, therefore, runoff and solute response to precipitation are dependent on the antecedent hydrological conditions in a catchment as well as individual event characteristics (Blaurock et al., 2021; Detty & McGuire, 2010; McGuire & McDonnell, 2010; Penna et al., 2015). Hydrological connectivity influences which parts of the riparian zone contribute to discharge and DOC export. However, the riparian zone is often very heterogeneous, varying in width (Ledesma, Futter, et al., 2018), vegetation (Kuglerová et al., 2014; Park & Kim, 2020), carbon content (Blazejewski et al., 2009), soil composition (Grabs et al., 2012), permeability (Vidon & Hill, 2004) and hydrological connectivity (Ledesma, Futter, et al., 2018; Ploum et al., 2020). It has been shown that surface microtopography in wetland systems can strongly influence hydrological connectivity, internal biogeochemical cycling and runoff generation (Antoine et al., 2009; Frei et al., 2010) as well as the formation of biogeochemical hot spots (Frei et al., 2012).

Several studies have investigated biogeochemical differences in relation to microtopographical heterogeneity (Courtwright & Findlay, 2011; Cresto Aleina et al., 2015; Diamond et al., 2021; Mazzola et al., 2021). Werner et al. (2021) have recently shown that wet depressions contributed strongly to DOC export in the riparian zone of a forested catchment. In a previous study, we used high-frequency, in-stream DOC data to demonstrate that DOC export from the riparian zone of a headwater catchment in the Bavarian Forest National Park (BFNP) is strongly dependent on hydrological connectivity between the riparian zone and the stream (Blaurock et al., 2021). The present study expands this with the aim to identify the source areas of DOC in the same riparian zone. The focus of the present study was on understanding the role of microtopography for DOC mobilization and DOM quality in the stream and riparian zone. In addition to measuring DOC concentrations, we used absorbance and fluorescence spectrometry as well as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to investigate DOM quality in the riparian zone. We linked our observations of DOC concentrations and DOM quality to the local microtopography and hydrological connectivity between the riparian zone and the stream. We hypothesize that groundwater dynamics, DOM quality, and geochemical characteristics differ between locations with and without a pronounced microtopography in the riparian zone. Moreover, we hypothesize that microtopographical depressions (called "ponds" hereafter) influence the amount of DOC exported to the stream during precipitation events and that the contribution of this DOC can subsequently alter stream DOM quality.

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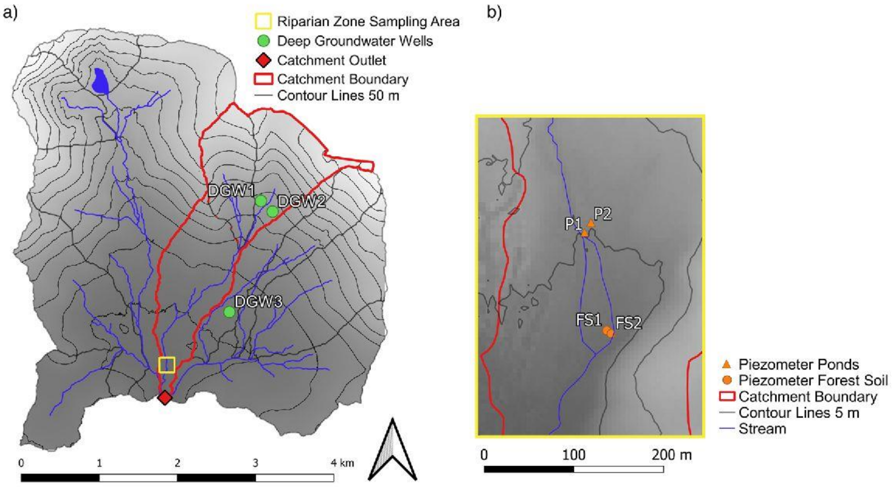

Figure 1. (a) The Hinterer Schachtenbach catchment (outlined in red) as part of the Groβe Ohe catchment. The elevation in this catchment ranges from 771 m a.s.l. (dark gray) to 1,373 m a.s.l. (light gray). Discharge, precipitation, and stream chemistry parameters were measured at the catchment outlet (red diamond). Deep groundwater samples were taken at three wells located at different topographical positions (green dots). Shallow groundwater was sampled in piezometers located in the riparian zone sampling area (yellow square), which is shown in more detail on the right side. (b) The riparian zone sampling area with the locations of the two piezometers located in the forest soil (orange circles) and the two piezometers located in the ponds (orange triangles). The stream splits in two parts, whereas the Western branch is the main stream and the Eastern branch is smaller and of lower discharge. Note that panel "b" does not fully represent the riparian zone sampling area depicted in panel "a". Stream channels were identified using a 5 m resolution digital elevation model (DEM). Both the location of the stream channels and the DEM were provided by the Bavarian State Office for Environment.

2. Materials and Methods

2.1. Study Site

The study was conducted in the Groβe Ohe catchment (19.2 km^2) within the BFNP (243 km^2), located in Southeast Germany. Measurements were conducted in the sub-catchment Hinterer Schachtenbach (3.5 km^2; Figure 1a).

The elevation in this sub-catchment ranges from 771 to 1,355 m a.s.l. with a mean slope of 12°. The geology of the catchment is dominated by biotite granite and cordierite-sillimanite gneiss. The soils are mainly cambisols (66%) together with hydromorphic soils (17%) and podzols (15%). Mean annual precipitation is 1,323 mm and mean annual temperature is 6.5°C (1990–2019). The entire catchment is covered by forest, with Norway spruce (*Picea abies*, 70%) and European beech (*Fagus sylvatica*) as dominant tree species. Large parts of the catchment are in a stage of rejuvenation after bark beetle outbreaks in the mid-1990s (Beudert et al., 2015).

2.2. Collection of Field Data

In order to characterize possible DOC source areas in the riparian zone and gain further insights into their role for DOC export during a precipitation event, we collected field data over the sampling period from May until October 2020. With the goal to identify differences in DOM quality and water chemistry of shallow groundwater, which can be linked to microtopography, we sampled shallow groundwater at two representative locations in the riparian zone: below the typical forest soil and below small ponds (ca. 2–3 m^2, see Figure 4 for an example), which are a common feature of the large flat riparian zone of the catchment. The origin of these ponds is unclear. Those two locations are representative for two typical types of shallow groundwater in the riparian zone, which we assume is important for DOC export in this catchment. To investigate if potential differences between the shallow groundwaters can be traced back to differences in the solid phase, soil samples were taken at the same locations. Although it can be assumed that shallow groundwater is the most important DOC source during events, we took additional samples of deep groundwater to account for its possible influence on event-based DOC export. With the goal to elucidate the influence of the possible DOC source areas on in-stream DOC concentrations and

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quality, we investigated chemical in-stream changes during one precipitation event, which was unusually large for the sampling period. In the following, we explain the sampling methods and measurements in detail.

2.2.1. Precipitation and Discharge Data

Precipitation was measured with a resolution of 10 min at a meteorological station at the catchment outlet (770 m a.s.l.) and was provided by the BFNP. Starting in June 2018, the water level was measured every 15 min at the catchment outlet using a pressure transducer (Solinst Canada Ltd., Georgetown, Canada and SEBA Hydrometrie GmbH, Kaufbeuren, Germany). Discharge was measured periodically at the same location with an electromagnetic current meter (FlowSens, SEBA Hydrometrie GmbH, Kaufbeuren, Germany) and via tracer-dilution (TQ-S, Sommer Messtechnik, Koblach, Austria) to establish a rating curve and generate continuous flow data.

2.2.2. Deep Groundwater Sampling

Each of three deep groundwater wells (Figure 1) were sampled in March 2021: DGW1 (969 m a.s.l., 16. 5 m depth), DGW2 (964 m a.s.l., 17.5 m depth) and DGW3 (819 m a.s.l., 10.3 m depth). Monthly long-term DOC concentrations were provided by the BFNP (unpublished data) for the sites DGW1 (2002–2020) and DGW3 (2001–2020) and showed few long-term temporal variations (0–1.26 mg L^{-1} with a mean of 0.34 mg L^{-1} for DGW1 and 0.06–2.15 mg L^{-1} with a mean of 0.57 mg L^{-1} for DGW3). As the DOC concentrations in the samples from March 2021 (0.74 mg L^{-1} for DGW1, 0.67 mg L^{-1} for DGW2 and 0.78 mg L^{-1} for DGW3) were in the range of long-term DOC concentrations (Figure S1 in Supporting Information S1), we assumed that measured absorbance characteristics and water chemistry parameters were representative for the deep groundwater.

2.2.3. Shallow Groundwater Monitoring and Sampling

Two piezometers ($P1$ and $P2$) were installed in two different vegetation-free ponds at a depth of 40 and 84 cm BGL (below ground level), respectively. They were located close to the main stream (ca. 600 m upstream of the catchment outlet) and to a branch-off of the stream (5 m for $P1$ and 17 m for $P2$; Figure 1b) with the pond bottom being higher than the stream level but lower than the surrounding topography. Two piezometers (FS1 and FS2) were installed in the grass-covered, flat forest soil at a depth of 87 and 50 cm BGL, respectively. They were located close (19 m for FS1 and 5 m for FS2) to the small branch of the stream but further away from the main stream (33 and 49 m; Figure 1b). Depth varied due to local differences in soil penetrability. All piezometers were screened over 9 cm starting 8 cm from the tip. The shallow groundwater level (called "water level" hereafter) was measured in FS1, FS2, and $P1$ (but not in $P2$) at a 15 min interval starting in June 2020 using pressure transducers (Solinst Canada Ltd., Georgetown, Canada). The pressure transducers were barometrically corrected and water depth was adjusted to manual measurements of the water level. From 25th of July until 21st of September 2020 and from 8th of October until 30th of October 2020, a time lapse camera took pictures of the pond $P1$ at an interval of 30 min. To test for temporal concentration changes, shallow groundwater was sampled from all four piezometers manually using a bailer approximately every three weeks from May until October 2020 resulting in a total of 11 samples per piezometer. Additionally, the pond water itself was sampled at $P1$ and $P2$ on five dates. Before the shallow groundwater sampling, all water was removed completely from the piezometers and samples were taken from the refilled water. The samples used for molecular analysis (using FT-ICR-MS, see Text S1 in Supporting Information S1) were collected separately: A sample of FS1 and a sample of FS2 were manually collected using clean glass bottles (rinsed with ultrapure water and heated for 4 hr at 400°C) in September 2020, but no samples from $P1$ and $P2$ were collected.

2.2.4. Soil and Pore Water Sampling

The soil profile at FS1 was sampled once by taking six samples using a soil corer over the depth of 5–65 cm in October 2020. Furthermore, one grab sample of the topmost 5 cm at $P1$ was taken in June 2020. Pore water was sampled at $P1$ and $P2$ with a resolution of 2 cm to a depth of 20 cm using peepers filled with deionized water which were left to equilibrate with soil water between 16 and 22 days. As for most parameters and sampling dates, no variation with depth was observed and DOC concentrations as well as DOM quality of the pore water samples were similar to the shallow groundwater sampled with the piezometers (Figure S2 in Supporting Information S1), only shallow groundwater data are shown in this study.

2.2.5. Sampling of a Precipitation Event

During an event from 25th to 27th of September (63 mm), stream water was sampled hourly using a portable water sampler (ISCO Sampler, Teledyne, Thousand Oaks, United States) close to the catchment outlet (red diamond,

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Figure 1a) resulting in 47 samples. One sample was taken during baseflow shortly before discharge started to increase in order to compare changes to pre-event conditions. For the molecular analysis, which requires a higher volume of sample, five to six stream samples from the portable water sampler were pooled before filtration (Table S1 in Supporting Information S1). Therefore, the first sample point in the FT-ICR-MS data also includes the very early event flow in addition to pre-event baseflow.

2.3. Laboratory Analysis

2.3.1. Analysis of Water Chemistry Parameters

All water samples were filtered using polycarbonate track etched membrane filters (LABSOLUTE, 0.4 µm) for the samples taken during the precipitation event and polyethersulfone membrane filters (0.45 µm) for all other samples. All samples were stored until further analyses at 4°C in the laboratory (up to 11 days with the exception of the first sampling date where 41 days elapsed before measurement). DOC concentrations of 23 event samples (out of 47), 44 shallow groundwater samples and three deep groundwater samples were analyzed by thermo-catalytic oxidation (TOC-L-Analyzer, Shimadzu, Kyoto, Japan). Samples for cation analysis (47 event samples, 44 shallow groundwater samples, and three deep groundwater samples) were stabilized with 1 vol% 1M HNO_3. Cation concentrations of Al, Ca, Fe, Mg, and Mn were determined using inductively coupled plasma optical emission spectrometry (ICP-OES XL 3200, PerkinElmer, Waltham, United States).

Concentrations of Fe(II) of six shallow groundwater samples were determined photometrically at 512 nm (DR 3800, Hach Lange, Düsseldorf, Germany) after adding phenanthroline (0.5%) to the samples (Tamura et al., 1974). Subsequently, Fe_{tot} was measured by reducing Fe(III) to Fe(II) with ascorbic acid (10%). Fe(III) concentrations were calculated by subtracting Fe(II) from Fe_{tot}. In addition to the laboratory analyses, pH of all water samples was measured in the field on two sampling dates.

2.3.2. Spectroscopic Measurements for the Characterization of DOM Quality

All spectroscopic measurements were conducted at 20°C. Samples were not acidified to avoid the flocculation of DOC and other spectroscopic artifacts. Absorbance measurements of samples (23 out of 47 event samples, 44 shallow groundwater samples and three deep groundwater samples) were performed using UV-Vis spectrophotometry (Cary 100, Varian, Palo Alto, United States), which recorded the absorption spectrum of water samples from 200 to 800 nm with a resolution of 0.5 nm. Blanks were subtracted from the absorbance spectra. Two commonly used absorbance metrics were determined: The ratio between the absorbance at 254 and at 365 nm (A_{254}/A_{365}), which is negatively correlated to the molecular weight of DOC (Dahlén et al., 1996), and the specific UV absorbance defined as the DOC concentration normalized absorbance at 254 nm ($SUVA_{254}$), which is positively correlated to DOC aromaticity (Weishaar et al., 2003). As iron was present mainly as Fe(II), we refrained from correcting the SUVA values for samples with high iron concentrations (Poulin et al., 2014). The spectral slope ratio (S_R) was calculated 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. S_R has been shown to be inversely related to molecular weight (Helms et al., 2008).

Fluorescence parameters in shallow groundwater were measured for eight out of eleven sampling dates, for a total of 32 samples. Prior to analysis, samples were diluted to absorption at 254 nm < 0.3 cm^{-1} to reduce inner-filter effects if necessary. A fluorescence spectrometer (LS-55, PerkinElmer, Waltham, United States) recorded fluorescence Excitation-Emission Matrices in 5 nm steps over an excitation range of 240–450 nm and in 0.5 nm steps over an emission range of 300–600 nm. Blanks were subtracted from the fluorescence spectra. No Raman normalization was conducted, as ratios were used for further analysis instead of the absolute values. The Fluorescence Index was calculated as the ratio between emission at wavelengths of 470 and 520 nm at an excitation wavelength of 370 nm. Higher values are related to a lower aromatic content and greater fraction of microbially derived material and lower values are related to a higher aromatic content, which is typical for DOC of terrestrial origin (Cory & McKnight, 2005; McKnight et al., 2001). The Freshness Index was calculated as the ratio between emission at 380 nm and the emission maxima between 420 and 435 nm at an excitation of 310 nm. The Freshness Index is positively correlated with the contribution of recently produced versus more decomposed DOC (Parlanti et al., 2000). The Humification Index (HIX) was calculated by dividing the emission intensity in the 435–480 nm region by the sum of emission intensities in the 300–345 and 435–480 nm at an excitation of 255 nm (Ohno, 2002). HIX has been shown to range from 0 to 1 with an increasing degree of humification,

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aromatic content, and molecular complexity. Fluorescence results of the deep groundwater samples were not included in the analysis as the very low DOC and very low fluorescence values in general may bias the ratios. Absorbance and fluorescence indices have been used in a large number of studies with the goal to gain insights into DOM origin and composition. They were developed partly for very different environments (e.g., the Fluorescence Index on lake samples from Antarctica or the Freshness Index for marine ecosystems). Generally, it remains unclear if these indices can be interpreted in terrestrial ecosystems in the same way as for their original purpose. In this study, we use the indices primarily to highlight qualitative differences between DOC sources and not to characterize DOC itself. In the following, we refer to the calculated absorbance and fluorescence metrics as "DOM quality parameters".

2.3.3. FT-ICR-MS Measurements and Processing

To calculate the probability of the existence of aromatic structures, the modified aromaticity index (AI mod) was used (Koch & Dittmar, 2006, 2016). DOM composition was analyzed based on aggregated DOM molecular descriptors (H/C_{wa}, O/C_{wa}, and AI mod_{wa}) calculated from the intensity-weighted average (wa) of AI mod and elemental ratios (H/C and O/C) of all molecular formulas present in the samples. The detailed description of FT-ICR-MS measurments and processing can be found in Text S1 in Supporting Information S1.

2.3.4. Soil Sample Analysis

Reactive iron was extracted by shaking 200 mg of soil mixed with 20 mL 1M HCl for 24 hr. Subsequently, Fe(II) and Fe_{tot} were measured photometrically as described in 2.3.1. Pedogenic iron oxides were extracted by heating 1 g of soil with 20 ml of 0.3 M sodium citrate ($C_6H_5Na_3O_7$ x 2 H_2O), 5 ml of 1M sodium hydrogen carbonate ($NaHCO_3$) and 0.5 g solid sodium dithionite ($Na_2S_2O_4$) following Mehra and Jackson (1958). The extracts were filtered (0.45 µm) and diluted to 1:10. Fe and Al concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES XL 3200, PerkinElmer, Waltham, United States). C and N content were determined using an elemental analyzer (FlashEA1112, Thermo Fisher Scientific, Waltham, USA).

2.4. Data Analysis

2.4.1. Analysis of Differences in Groundwater Dynamics

As a measure of event flow, the 0.9 quantile ($Q_{0.9}$) of all discharge values during the sampling period was calculated. For all data points with discharge values above $Q_{0.9}$, the mean shallow groundwater level for each location was calculated, representing the mean groundwater level during event flow. Additionally, we used the metric t_R, which was defined as the time (in minutes) needed for the water level to recede by 2 cm from the water level maximum during an event. t_R was calculated for 15 events, for which water level data was available and which resulted in a visible water level peak at all three locations (FS1, FS2, *P*1). The presented t_R values refer to the mean of the 15 analyzed events ± standard deviation.

2.4.2. Statistical Analysis of Potential DOC Source Areas

The sampled locations FS1, FS2, *P*1, *P*2, and DGW were interpreted as representing different source areas of DOC. We call these source areas also "end-members" hereafter, following the terminology used in hydrograph separation studies. However, our intention was not to perform a full hydrograph separation, but to focus on the role of different source areas in the riparian zone for stream chemistry during events. Moreover, our sampled end-members exhibited slightly varying concentrations over time for some of the parameters and were thus not strictly consistent with the assumptions made in an end-member mixing analysis (Christophersen et al., 1990). Therefore, instead of using the end-members to quantify their contribution to streamflow, we investigated the qualitative differences between the end-members and their qualitative influence on the composition of the stream water. The sampled locations were grouped according to their physiographic characteristics: (a) FS1 and FS2 as representatives for sites with a typical forest soil (called FS, hereafter), (b) *P*1 and *P*2 as representatives for sites with ponds (called *P*, hereafter) and (c) DGW1, DGW2, and DGW3 as representatives for the deep groundwater (called DGW, hereafter). A cluster analysis was performed to verify the similarity of the grouped end-members. $SUVA_{254}$ and concentrations of DOC, Fe, Al, Mn, Mg, and Ca were included in the cluster analysis. The other parameters were excluded due to the low concentrations in the groundwater samples. All samples, for which all selected parameters were available, were included ($n_{FS1} = 10$, $n_{FS2} = 11$, $n_{P1} = 10$, $n_{P2} = 11$, $n_{DGW1} = 1$, $n_{DGW2} = 1$, $n_{DGW3} = 1$). All data were normalized prior to analysis by centering and scaling the data to a mean of 0 and a

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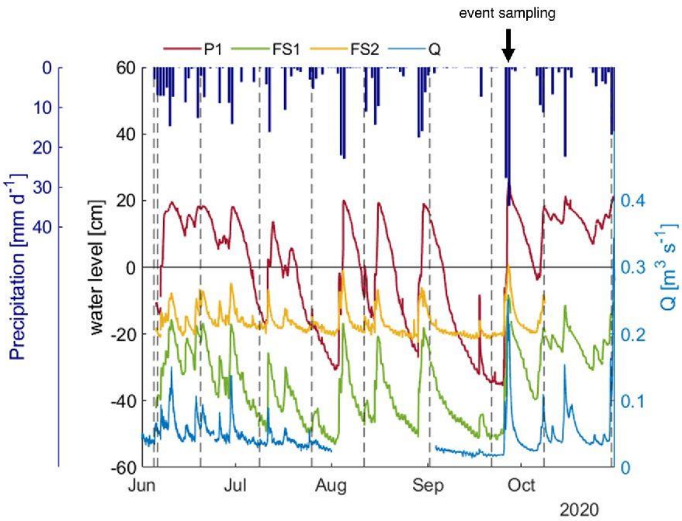

Figure 2. Water levels below ground [cm] during the sampling period from June to October 2020 at the locations FS1, FS2, *P*1, precipitation [mm d^{-1}] and discharge (Q [m^3 s^{-1}]) at the catchment outlet. Positive water level values of *P*1 indicate that the pond *P*1 was filled with water, that is, 0 cm refers to the pond bottom (black horizontal line). The highest water level of *P*1 corresponds to the point of spillover. Due to a technical failure, the water level values for FS2 are only available until the beginning of October and there is a data gap for discharge during August. Dashed lines indicate the dates when shallow groundwater was sampled from the piezometers. As the first sampling date was in May, it is not visible in this figure. The sampled event took place from 25th to 27th of September (black arrow).

standard deviation of 1. Following the cluster analysis, a Wilcoxon ranksum test for all analyzed parameters (DOC, $SUVA_{254}$, A_{254}/A_{365}, Freshness Index, Fluorescence Index, HIX, S_R, Fe, Al, Mn, Mg, Ca) was performed in order to test the similarity between the sampled end-members *P* and FS (but not DGW). To investigate chemical in-stream changes, a linear regression between the parameters and stream discharge during the precipitation event was performed. All statistical analyses were performed using MATLAB (MATLAB R2019b).

3. Results

3.1. Meteorological Conditions and Hydrological Dynamics in the Riparian Zone

The year of our investigation showed some deviations from the long-term hydro-meteorological conditions in the catchment (reference period 1990–2019). The total annual precipitation in 2020 was 1,134 mm, which was lower than the long-term average of 1,323 mm. The sampling period (June–October) was slightly drier in 2020 (523 mm) than the long-term mean precipitation of the reference period (541 mm). The annual mean temperature for 2020 was 1.1°C higher than the long-term average while the sampling period was 0.7°C warmer than the long-term mean temperature of the same months. The sampled event at the end of September was an unusually large event (63 mm of total precipitation) for the sampling period.

The water levels in the riparian zone were highly dynamic during the entire sampling period and responded strongly and quickly to precipitation (Figure 2).

The largest changes in water level were observed at *P*1, varying between 36 cm BGL and 26 cm above ground level (AGL), resulting in a difference of 62 cm. The water level did not increase to levels higher than 26 cm AGL, even with further increasing discharge. The changes in water level at the locations in the forest soil were smaller. At FS1, the water level was lowest and fluctuated between 53 and 8 cm BGL, resulting in a difference of 45 cm. At FS2, the water level varied between 23 cm BGL and 1 cm AGL, resulting in a difference of 24 cm. The water levels started to decrease faster at FS1 and FS2 (t_R of 587 ± 230 and 520 ± 250 min, respectively) after reaching the maximum in contrast to *P*1, where water levels stayed high during a longer period (t_R of 1,504 ± 1,130 min).

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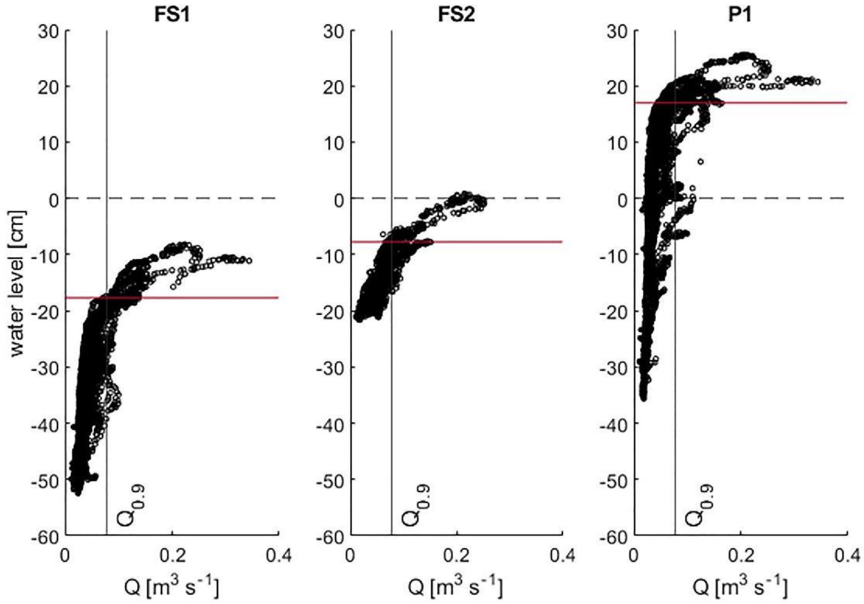

Figure 3. The relationship between the water level [cm] in the piezometers at the locations FS1, FS2, and *P*1 and stream discharge *Q* [$m^3\ s^{-1}$] during the complete sampling period. The dots represent 15 min time steps. The horizontal black dashed line indicates the soil surface, where the piezometer emerge from the soil. The vertical black line indicates the 0.9 quantile ($Q_{0.9}$) for all discharge values. The horizontal red line indicates the mean water level for all data points with discharge values above the $Q_{0.9}$.

At all three sites, a nonlinear relationship between water level and discharge was visible, showing a stronger water level increase at lower discharge values and a lower water level increase at higher discharge values (Figure 3). The mean water level for discharge values above $Q_{0.9}$, varied between the locations: For FS1, it was located at 17.7 cm BGL, for FS2, it was located at 7.8 cm BGL and for *P*1, it was located at 16.9 cm AGL.

The filling and emptying of the ponds could also be monitored using the time lapse camera. No images were available for the event in September, which we will discuss in detail in Section 3.3. As an example of the water level reaction in the ponds (Figure 4) we, therefore, show here the water levels in *P*1, FS1, and FS2 and images of the temporal changes at *P*1 during an event at the beginning of August.

The water level at *P*1 typically started to rise one to 2 hr after the beginning of a precipitation event. Large events led to a filling of the pond. During most events, the water in the pond continued to rise after the end of the precipitation event, reaching the maximum several hours later. When the water level in the ponds reached the level of the surrounding ground surface, the ponds would spill and connect in a cascading manner with each other and eventually to the stream, thereby creating short periods of overland flow toward the stream. If no precipitation event followed, the water level decreased slowly over the course of days (Figure 4).

3.2. Characterization of DOC Source Areas

The cluster analysis confirmed the selection of the end-members FS, *P*, and DGW (Figure S3 in Supporting Information S1). Most parameters determined in the aqueous phase showed clear differences between the end-members FS, *P*, and DGW. DOC, SUVA, Freshness Index, Fluorescence Index, HIX, Al, Mn, Ca, and Mg showed significant differences between the shallow groundwater end-members FS and *P* ($p < 0.05$; Figure 5). In contrast, the parameters A_{254}/A_{365}, S_R, and Fe did not show significant differences between FS and *P* ($p > 0.05$; Figure 5). DGW showed the lowest concentrations of DOC, SUVA, Al, Fe, Mg, and Mn and an intermediate concentration of Ca. Site FS was characterized by lower DOC and Al concentrations than *P* and higher Ca, Mg,

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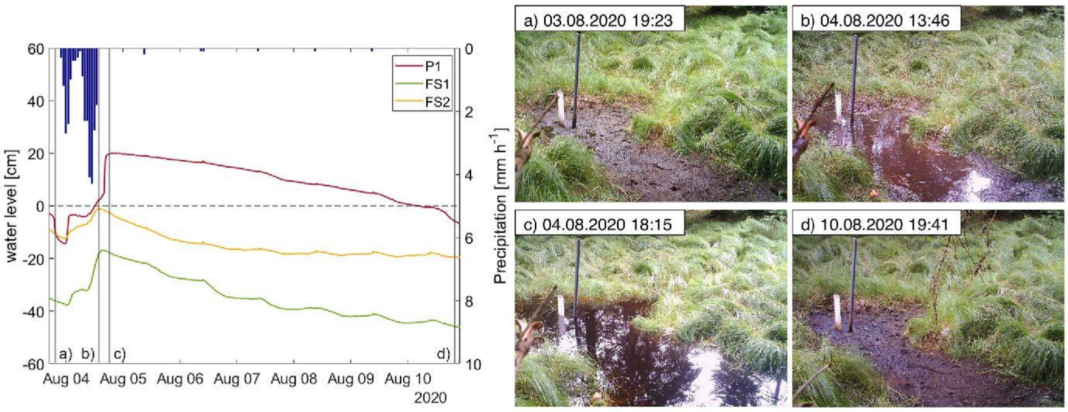

Figure 4. Left side: Hourly precipitation and water levels in the piezometers at the locations FS1, FS2, and *P*1 during the event of 4 August 2020. Values above the horizontal dashed line indicate that the groundwater is rising above the surface and filling the pond. Right side: Pictures taken at *P*1 with a time lapse camera (a) before the event, (b) during the rising limb of the hydrograph, (c) at the maximum water level, and (d) at the lowest water level before the start of the next event. The times correspond to the vertical gray lines in the left side figure.

and Mn concentrations. On average, 88.3% ± 9.7% of the dissolved Fe at site FS was present as Fe(II). The Freshness Index and Fluorescence Index were higher at site FS than at site *P*, whereas HIX and SUVA were lower at site FS than at site *P*. On average, 91.6% ± 5.4% of the dissolved Fe at site *P* was present as Fe(II). Site FS had a higher pH (mean value of 6.2) than site *P* (mean value of 4.8). In the solid phase, site FS had higher contents of reactive iron and of pedogenic iron, but a lower content of pedogenic aluminum and of total carbon than site *P* (Tables S2 and S3 in Supporting Information S1).

Analyses of DOC concentrations, absorbance parameters and fluorescence parameters in the pond water itself (data not shown) revealed no significant difference to the shallow groundwater at site *P* for DOC concentrations, A_{254}/A_{365}, Freshness Index and HIX (Wilcoxon ranksum, $p > 0.05$) but a significant difference for the Fluorescence Index and S_R (Wilcoxon ranksum, $p < 0.05$).

3.3. Hydrochemical Response of the Stream Water During the Analyzed Event

There were clear changes in various parameters in the stream water over the course of the investigated event. DOC, SUVA, Al, Fe, and Mn showed a significant positive relationship with discharge (Figure 6; $p < 0.05$; $R^2_{DOC} = 0.75$, $R^2_{SUVA} = 0.52$, $R^2_{Al} = 0.75$, $R^2_{Fe} = 0.81$, $R^2_{Mn} = 0.91$). Mg showed a significant negative relationship with discharge ($p < 0.05$; $R^2_{Mg} = 0.16$). Ca, Fluorescence Index, Freshness Index, A_{254}/A_{365}, HIX and S_R showed no relationship with discharge ($p > 0.05$; $R^2_{Ca} = 0.02$, $R^2_{Fluorescence} = 0.05$, $R^2_{Freshness} = 0.04$, $R^2_{A254/A365} = 0.12$, $R^2_{HIX} = 0.17$, $R^2_{SR} = 0.01$). For DOC, SUVA, HIX, Al, Fe, Mn, and Mg, there was a significant difference ($p < 0.05$) between the in-stream values during the first half of the event, when the ponds were empty, and the second half of the event, when they were full (Figure 7). For DOC, SUVA, HIX, Al, and Mg the values clearly changed into the direction of the values found at *P* (red line in Figure 6). Mn and Fe are generally higher at both FS and *P* than in the stream. For the molecular data, no comparison with *P* was possible. However, a clear change in H/C_{wa}, O/C_{wa}, and AI mod_{wa} was visible over the course of the event. When the ponds were full, all molecular parameters deviated from the values found at FS as H/C_{wa} decreased, whereas O/C_{wa} and AI mod_{wa} increased.

4. Discussion

4.1. Hydrological Dynamics in the Riparian Zone

The sampling period was characterized by declining discharge values with only a few large precipitation events. However, we saw a highly dynamic shallow water level. Generally, a high level of saturation in the riparian zone needs to be reached to establish a significant degree of hydrological connectivity along shallow subsurface and

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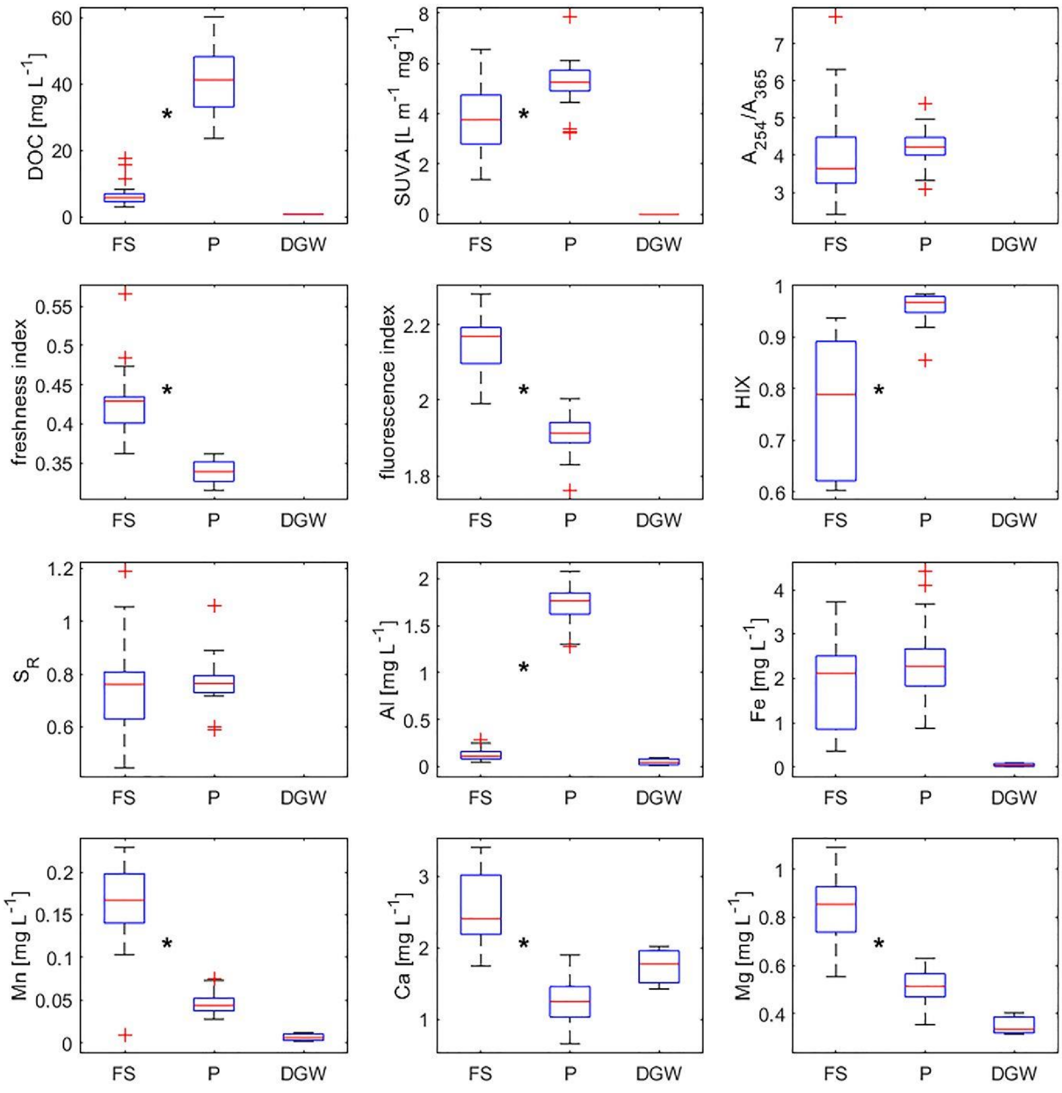

Figure 5. Water chemistry and dissolved organic matter (DOM) quality parameters of the piezometers located in the forest soil (FS), the ponds (*P*), and deep groundwater (DGW). Some parameters do not include DGW data because measured values were too low to be reliable (A_{254}/A_{365}, Freshness Index, Fluorescence Index, HIX, S_R). The bottom and top of each box indicate the 25th and 75th percentiles, respectively. The red line in the middle of each box is the sample median. The red crosses represent outliers and the whiskers extend to the most extreme data points not considered outliers. Asterisks indicate a significant difference ($p < 0.05$, Wilcoxon ranksum test) between FS and *P*.

surficial flow paths to the stream (Blaurock et al., 2021; Ledesma, Futter, et al., 2018; Ploum et al., 2020). At all sites, we observed the characteristic nonlinear relationship between discharge and groundwater level often found in riparian zones (Frei et al., 2010; Ledesma, Futter, et al., 2018; Seibert et al., 2009), which is commonly attributed to a nonlinear increase of the soil transmissivity toward the soil surface. At site FS, the rising water level would lead to the saturation of upper soil layers and a subsequent lateral movement of water through the soil, whereas at site *P* the water level would often rise above the surface. Following a water level rise, the ponds were

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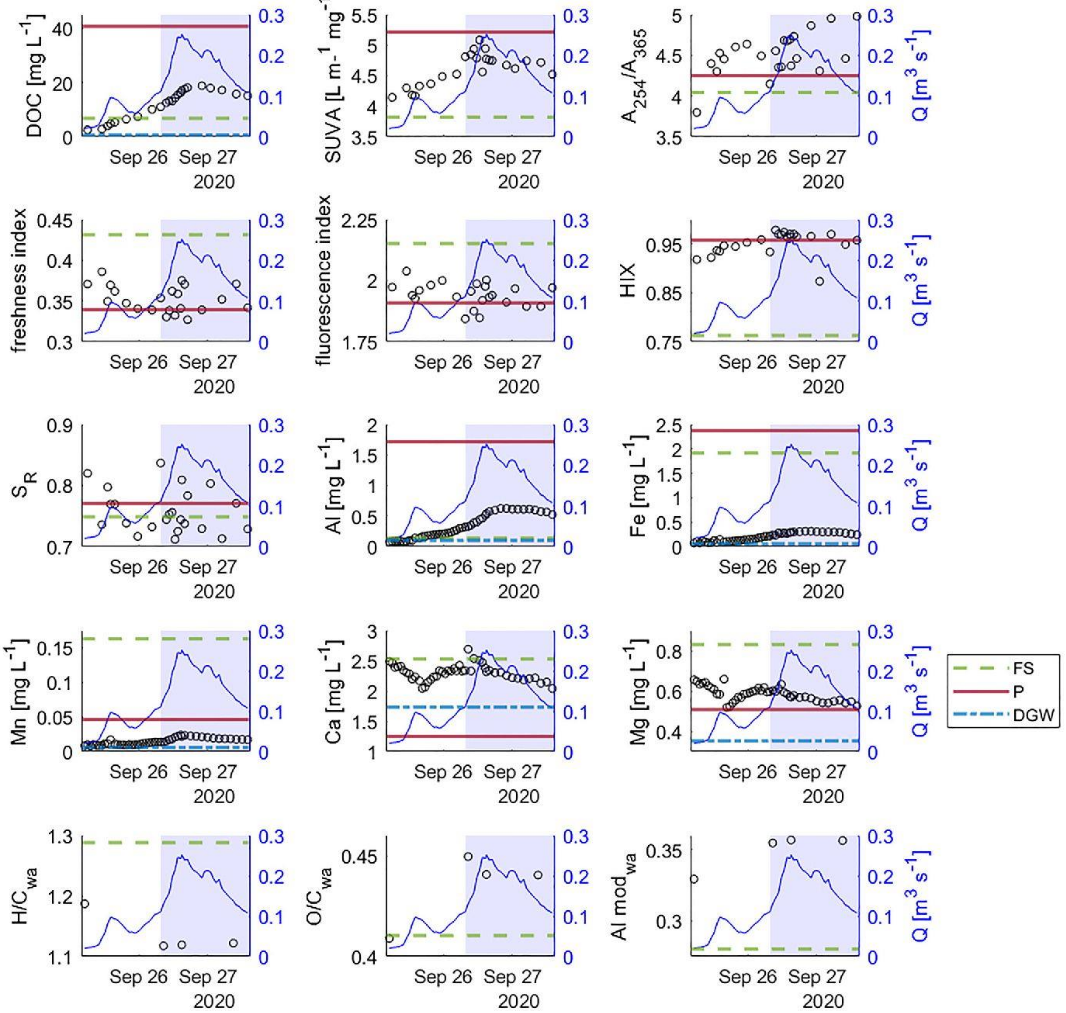

Figure 6. Discharge (blue line) and changes of the hydrochemical and dissolved organic matter (DOM) quality parameters (black circles) of the stream during the event in September 2020 in comparison to the mean concentration of the values found in the piezometers located in the forest soil (green dashed line) and the ponds (red line) as well as the values of the deep groundwater (blue dashed line). The blue shaded area corresponds to the time, during which the ponds were filled with water. The first dot in all panels except for the molecular data represents pre-event conditions. For the molecular data (last row), the dots represent the collection time of the first of the pooled samples (Table S1 in Supporting Information S1).

connected to the stream via overland flow as has been observed in other catchments (Fitzgerald et al., 2003; Frei et al., 2010; Werner et al., 2021). The continuous increase of the water level at site *P* even several hours after the end of precipitation events indicates a time-delayed contribution of water components originating further away from the ponds. Moreover, t_R values showed that the water at site *P* recedes more slowly than at site FS, keeping the upper soil layers wet for a longer time. In summary, the differences in water level dynamics between the locations with and without ponds highlight the structural heterogeneity of the riparian zone, which can strongly influence flow pathways and source waters (Lessels et al., 2016).

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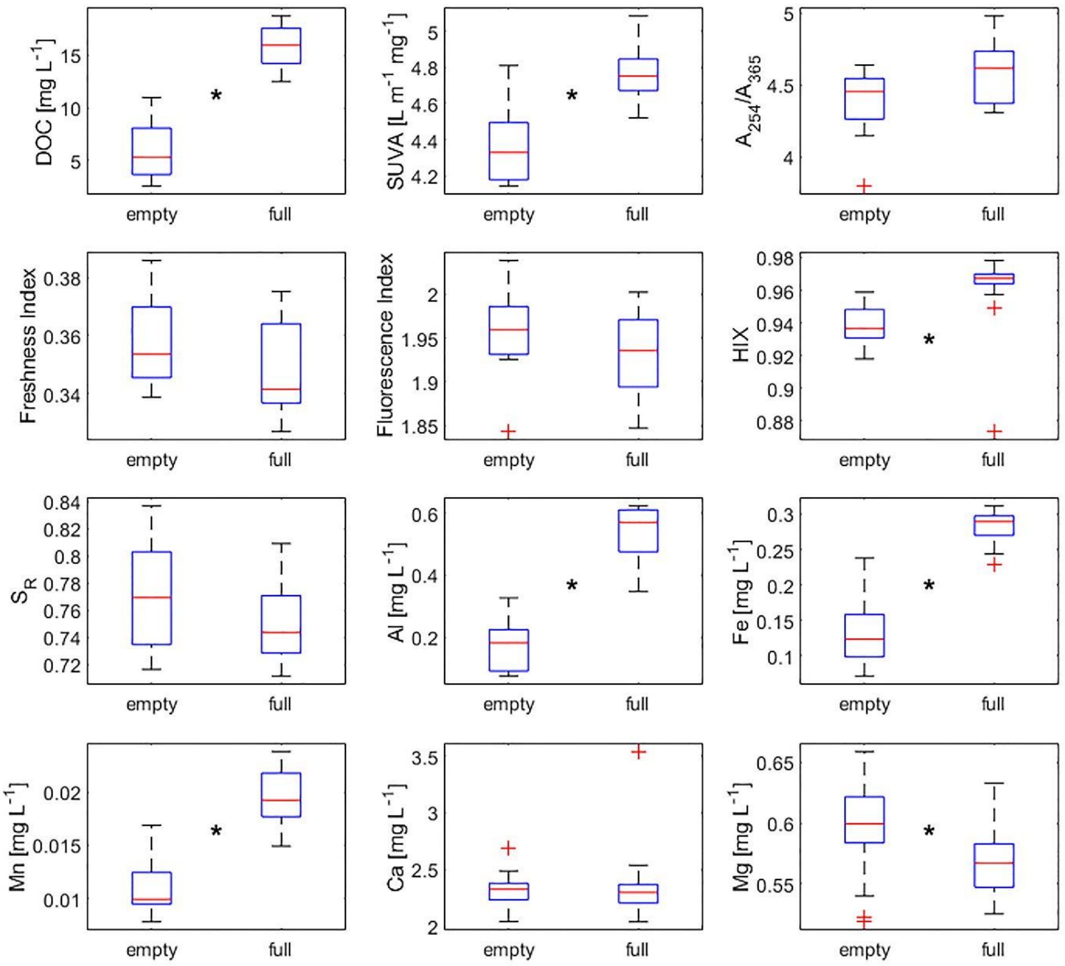

Figure 7. Stream water chemistry and dissolved organic matter (DOM) quality parameters during the event sampled in September 2020 while the ponds were not yet filled with water (empty; unshaded area in Figure 6) and while the ponds were filled with water (full; shaded area in Figure 6). The bottom and top of each box are the 25th and 75th percentiles, respectively. The red line in the middle of each box is the sample median. The red crosses represent outliers and the whiskers extend to the most extreme data points not considered outliers. Asterisks indicate a significant difference ($p < 0.05$, Wilcoxon ranksum test) between empty and full conditions. Molecular data was not included due to the low sampling size.

4.2. Spatial Differences in DOM Quality of Shallow Groundwaters in the Riparian Zone

Pronounced spatial differences in DOC concentrations, DOM quality, and geochemistry were observed between the shallow groundwaters of sites FS and *P* despite the sampling locations being in close proximity to each other relative to catchment size. DOC concentrations in the shallow groundwater exceeded the concentrations found in the stream during baseflow and precipitation events investigated in previous studies (Blaurock et al., 2021; Da Silva et al., 2021). The convergence of DOC-rich subsurface flow pathways (Ploum et al., 2021) or the accumulation of DOC-rich surface water (Scheliga et al., 2019) could have led to the higher DOC concentrations in the topographic depressions at site *P*. Moreover, the large oscillations of the water table at site *P* could indicate a larger dominant carbon source layer and a more frequent activation of it (Ledesma et al., 2015; Ledesma, Futter, et al., 2018). A larger dominant source layer would indicate a larger potential DOC pool. Another reason for the

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higher DOC concentrations at site *P* could be a reduced DOC mobility at site FS that exhibited a lower carbon content in the solid phase than site *P*. In subsoil horizons with low carbon content DOC may bind strongly to mineral surfaces, thereby decreasing the mobility of DOC (Kalbitz et al., 2000).

All DOM quality parameters except A_{254}/A_{365} and S_R revealed differences between site FS and site *P*. These differences in DOM quality parameters indicate that the DOM at site *P* is derived from a source that has a different DOM composition than at site FS. Higher SUVA, higher HIX, and lower Fluorescence Index values all indicate a higher DOC aromaticity at site *P* than at site FS (Huguet et al., 2009; McKnight et al., 2001; Weishaar et al., 2003). DOC derived from wetlands or the riparian zone has been described in the literature to be generally more aromatic than DOC derived from other sources (Ågren et al., 2008; Kothawala et al., 2015; Ledesma, Kothawala, et al., 2018; Pisani et al., 2020). As site *P* is more wetland-like than FS due to the regular rewetting, slow drying and the high soil carbon content, a higher aromaticity at site *P* is in line with studies that have found a high aromaticity of DOC in wetlands. Werner et al. (2021) also found that wet areas were characterized by higher DOC concentrations and higher aromaticity than less wet areas. Creed et al. (2003) demonstrated that topographic depressions in forested ecosystems are often hidden wetlands, which contribute strongly to DOC export. Studies have shown that the DOC in upper soil layers is characterized by a higher aromatic content and higher molecular weight than in deeper soil layers (Bausenwein et al., 2008; Corvasce et al., 2006). Upper soil layers also exhibit higher decomposition rates due to the availability of oxygen, nutrients, and higher microbial activity (Fontaine et al., 2007), which leads to the accumulation of aromatic organic matter (Marschner & Kalbitz, 2003). The wet-dry cycles in the ponds are likely to result in a site with high microbiological activity, facilitating DOC production via decomposition of the organic substrate (Borken & Matzner, 2009; Marschner & Kalbitz, 2003). This would explain the occurrence of higher DOC concentrations and more aromatic DOC at site *P* than at site FS.

A second explanation for the distinct DOC characteristics could be the convergence of different flow paths. The delayed increase of the water level following precipitation during some events at site *P* could indicate the connection of flow paths and potentially also DOC sources that are located further away, for example, in the marginal zones of the riparian zone. However, the establishment of hydrological connectivity in the riparian zone and adjacent areas would probably only be linked to large precipitation events or extended wet periods, for example, during snowmelt. One could also argue that differences in DOM quality parameters are a consequence of the source material rather than differences in flow paths or wet-dry cycles. Such differences could be a result of differences in vegetation (Mastný et al., 2018; Spencer et al., 2008). In this study, however, an effect of vegetation on DOM quality is unlikely, as vegetation did not differ among the sampled study sites.

The results highlight that spatial differences in DOM composition can be found not only between forested and wetland catchments (Ågren et al., 2008; Broder et al., 2017; Kothawala et al., 2015) or between riparian zones and upslope soils (Ledesma, Kothawala, et al., 2018), but also at a much smaller scale in the riparian zone itself (Werner et al., 2021). Although there was essentially no significant difference between shallow groundwater and pore water (Figure S2 in Supporting Information S1), vertical heterogeneity in the soils could also play a role in influencing DOM quality at the two sampling sites. However, based on our results we argue that the hydrological differences due to the microtopography are one likely explanation for the observed differences in DOC concentrations and DOM quality. Our findings confirm that local hydrological conditions affect DOC chemistry in the riparian zone (Findlay et al., 2001; Grabs et al., 2012; Ledesma, Kothawala, et al., 2018).

4.3. The Importance of the Ponds for DOC Mobilization During a Precipitation Event

4.3.1. Changes of In-Stream DOM Quality Parameters During a Precipitation Event

Several studies have shown that events contribute substantially to the annual DOC export from catchments (Raymond & Saiers, 2010; Raymond et al., 2016). Large events are known to lead to a larger DOC export as a result of increasing discharge and increasing DOC concentrations (Dawson et al., 2008; Kawasaki et al., 2005; McDowell & Likens, 1988). However, the DOC sources that contribute to DOC export during events depend on catchment and event characteristics. The riparian zone is often a major source for DOC export as the soils are typically DOC rich and hydrological connectivity facilitates DOC export to the stream.

The study design did not allow us to quantify the contribution of the ponds to stream discharge or carbon fluxes as detailed measurements of surface and subsurface fluxes would have been necessary. The contribution of the ponds is also likely to vary with changing antecedent wetness and precipitation. However, our data suggest that

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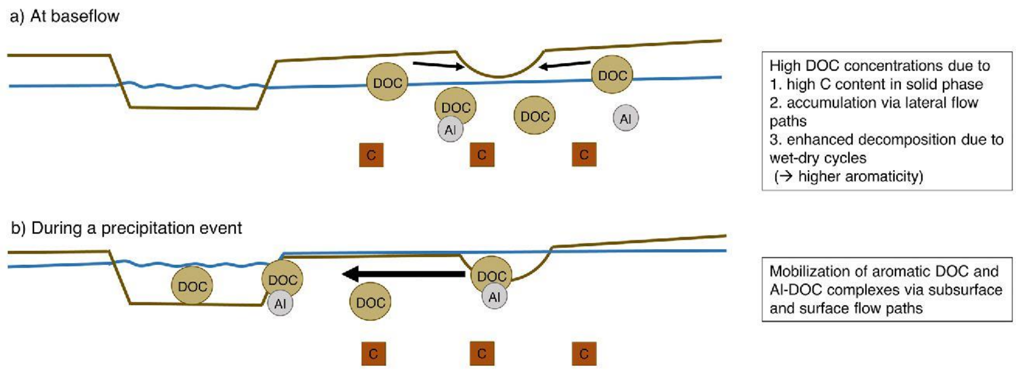

Figure 8. Mechanisms of dissolved organic carbon (DOC) supply in the ponds and its mobilization toward the stream during (a) baseflow and (b) a precipitation event.

the ponds we observed in the riparian zone during wet conditions and the shallow groundwater below could be an important DOC source during precipitation events. During the precipitation event in September 2020, in-stream DOC concentrations increased to over 18 mg L^{-1}, thereby significantly exceeding the shallow groundwater concentrations below the forest soil. This indicated that another source contributed to the in-stream DOC increase during the event. We argue that the shallow groundwater below the ponds, characterized by considerably higher DOC concentrations, probably contributed to event-driven DOC export. As the water level increased at the pond site during the event, DOC-rich water was transported through upper soil layers, which are typically characterized by a higher hydraulic conductivity (Jacks & Norrström, 2004). The water could therefore rapidly transport DOC via subsurface flow toward the stream, possibly exporting even more DOC by passing through the DOC-rich upper soil layer. The formation of cascading sequences of ponds could lead to an even faster transport of the DOC rich water to the stream via overland flow (Figure 8), which could enhance the contribution of the shallow groundwater at site *P* to stream discharge. This is supported by the fact that several stream DOM quality parameters showed a clear trend toward the values found below the ponds. Whereas $A_{254}/A_{365,}$ the Freshness Index, the Fluorescence Index, and S_R did not show a clear trend, possibly due to a low sensitivity to compositional changes during storm runoff (Nguyen et al., 2010, 2013), SUVA increased with discharge as shown in other studies (Fellman et al., 2009; Hood et al., 2006; Vidon et al., 2008) and, at peak discharge, reached almost the same values as found at site *P*. HIX values also significantly increased toward the values found at site *P* during the time, when the ponds were full. Earlier studies have also observed an increase of HIX during precipitation events, which the authors attributed to the increased soil leaching and input of allochthonous organic matter (Nguyen et al., 2010, 2013; Xu et al., 2016).

The additional information on molecular DOC composition provided by FT-ICR-MS data showed that H/C_{wa}, O/C_{wa}, and AI mod_{wa} during the precipitation event deviated from the values found in the shallow groundwater below the forest soil. All pre-event molecular signatures (H/C_{wa}= 1.19, O/C_{wa}= 0.41, AI mod_{wa} = 0.33) were similar to values found in water of a spring close to the stream in an earlier study (H/C_{wa}= 1.18, O/C_{wa}= 0.43, AI mod_{wa} = 0.31; Da Silva et al., 2021). This DOC pool was characterized by aliphatic-like, saturated compounds. The changes in the molecular signatures found during the course of the event indicate that another source contributed to DOC export into the stream. The decrease in H/C_{wa} values pointed to an increase in the unsaturation of compounds. Wagner et al. (2019) also observed decreasing in-stream H/C_{wa} during a precipitation event in a forested catchment and attributed this finding to the export of lignin degradation products and tannins. The proxies for aromaticity calculated from absorption (SUVA) and mass spectrometry data (AI mod_{wa}) are in agreement and indicate an increase in aromaticity over the course of the event. Werner et al. (2021) concluded in their study that the aromatic, H-poor, O-rich DOC that they identified in the stream during an event originated from wet areas. These wet areas were responsible for a large part of DOC export during the event mainly via overland flow. Their findings are in line with our observations that the ponds are contributing to streamflow during precipitation events and that they are exporting aromatic DOC. As similar ponds are located downstream of the investigated area, it is likely that DOC with similar characteristics gets transported into the stream at several input points over the entire reach to the outlet. Possible in-stream processes (Bernal et al., 2019; Lupon et al., 2019) probably play

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a minor role for DOC export and quality at the catchment outlet due to (a) the short in-stream residence time between site *P* and the catchment outlet, and (b) input from several ponds along the reach.

4.3.2. Changes of the Stream Water Chemistry During a Precipitation Event

The unclear pattern in Ca and Mg concentrations during the event cannot be used to explain the contribution of potential DOC sources. The increase of Mn concentrations during the precipitation event can be linked to the high Mn concentrations in the upper soil layers below spruce forest as observed in a neighboring catchment (Schwarze & Beudert, 2009). As DOC concentrations were increasing concomitantly with Fe and Al concentrations during the precipitation event, it is likely that DOC, Fe, and Al export were coupled. This observation is consistent with previous studies that observed coupled DOC and Fe concentrations (Bol et al., 2015; Curtinrich et al., 2021; Karlsson & Persson, 2012; Knorr, 2013; Peiffer et al., 1999). The rising water table during events could result in reducing conditions, inducing the release of Fe(II) and DOC via reductive dissolution (Curtinrich et al., 2021; Knorr, 2013; Nieminen et al., 2015; Selle et al., 2019). Subsequently, Fe(II) and DOC could be transported as complexes to the stream. This process could also explain the export of aromatic DOC, which preferentially adsorbs to Fe (Adhikari & Yang, 2015; Grybos et al., 2009; Pan et al., 2016; Riedel et al., 2012). In-stream Fe concentrations clearly increase with discharge and there is a significant difference between the earlier event concentrations, when the ponds were empty, and the later event concentrations, when the ponds were full. However, FS and *P* are both characterized by high Fe concentrations. Therefore, the increase in in-stream concentrations during the event cannot be seen as a sign of an increased contribution of site *P*. Nevertheless, the processes discussed are likely to play a role in DOC mobilization.

In contrast to Fe, Al concentrations are much higher at site *P* than at site FS. Al has also been shown to build complexes with organic matter and therefore it is exported concomitantly without the need for a redox transition (Cory et al., 2007; Palmer et al., 2005; Pellerin et al., 2002; Vogt & Muniz, 1997). The high concentrations likely are a result of the higher Al concentrations in the solid phase at site *P* as well as a result of the increased solubility of Al at low pH (Pellerin et al., 2002). As in-stream Al concentrations during the precipitation event clearly exceeded the concentrations found at site FS and were approaching the concentrations found at site *P*, it is likely that site *P* contributed to the Al increase during the event, as shown in Figure 7. We argue that the concomitant increase of Al and DOC concentrations in the stream indicates the mobilization of Al complexed by DOC from site *P* and, thus, supports the importance of the ponds as source areas for in-stream DOC.

4.4. The Relevance of Riparian Microtopography for Catchment-Scale DOC Export

At our study site, the origin of the microtopographic depressions is unknown. However, microtopographic depressions are a common feature in many catchments worldwide and can often be found in wetlands (Diamond et al., 2021; Nungesser, 2003). Moreover, they can occur after windthrow of trees, resulting in a pit and mound microrelief (Bormann et al., 1995; Ulanova, 2000) or be caused by anthropogenic disturbances, for example, mining activities (Gilland & McCarthy, 2014), the use of heavy machinery in forests during timber harvest (Laudon et al., 2016), exploration activities (Stevenson et al., 2019) or peat extraction from wetlands (Zajac et al., 2018). Also wildfires (Benscoter et al., 2015) or flooding (Stoeckel & Miller-Goodman, 2001) may cause microtopography.

Many studies have shown that microtopography does influence soil properties, soil moisture, and soil biochemical processes (Bormann et al., 1995; Clinton & Baker, 2000; Kooch et al., 2014; Stoeckel & Miller-Goodman, 2001). Moreover, microtopography can have an impact on nutrient availability and dynamics (Minick et al., 2019; Moser et al., 2009; Rogers et al., 2021) and influence the formation of biogeochemical hot spots as a result of complex water flow patterns (Frei et al., 2012).

In this study, we were able to demonstrate that microtopographic depressions could act as hot spots for DOC export as a result of the favorable conditions for DOC accumulation and subsequent transport to the stream. Our finding underpins recent observations demonstrating DOC export is often linked to specific source areas in the riparian zone, which contribute disproportionally to DOC export. Such areas can be narrow soil layers (Ledesma, Futter, et al., 2018) or topographical depressions that determine where water accumulates in the catchment (Ploum et al., 2021; Werner et al., 2021). Ploum et al. (2021) presented the concept of discrete riparian inflow points consisting of topographic depressions that are consistently wetter than the surrounding areas. As a consequence, hydrological pathways are developing that are subsequently enhancing DOC export. Werner et al. (2021) recently

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found that microtopographic depressions, which made up 15% of the studied riparian area, were responsible for 1.5 times the DOC export of the remaining 85% of the area. These results point to a disproportional contribution of microtopographic depressions of the riparian zone to DOC export in comparison to their limited area extent.

Hence, microtopographical depressions in riparian zones appear to act as potential hot spots for catchment-scale DOC export. Since they are a very common feature in the riparian zone of many catchments, they may have a much larger influence on in-stream water quality than previously assumed.

5. Conclusions

Our observations show that there are substantial small-scale differences of DOM quality in the riparian zone of our study site. Following precipitation events, hydrological connectivity leads to the export of aromatic DOC and Fe- and Al-DOC complexes into the stream. The in-stream changes of DOC concentrations, DOM quality parameters as well as water chemistry parameters suggest that microtopographic depressions are important sources of DOC that could be rapidly delivered to the stream via overland flow once a threshold water level is reached. These results show that microtopographical structures can be an important DOC source. Moreover, they can alter in-stream DOM quality during events. As a result of climate change, prolonged drought periods and more extreme rain events are to be expected in temperate ecoregions. Longer drought periods would probably reduce the importance of the ponds in terms of exported DOC quantity. However, stronger contrasts in hydrological connectivity and water level dynamics could have an impact on the DOC processing in the upper soil layers, which would lead to more pronounced small-scale spatial differences in DOM quality of the shallow groundwater. These differences could then possibly be seen in the stream during events and influence the further processing of DOC. In summary, we show that the strong interplay between biogeochemical and hydrological processes influences DOC mobilization and processing at small scales in the riparian zone of a headwater catchment. As headwater catchments make up an important part of the global stream length (Downing, 2012), they have the potential to influence large downstream areas (Gomi et al., 2002; Wohl, 2017). Therefore, changes in DOC concentrations or DOM quality in the riparian zone of headwater catchments could also affect DOC export, drinking water quality, or greenhouse gas emissions of downstream river reaches.

Data Availability Statement

The data set used in this study is available at Figshare via https://doi.org/10.6084/m9.figshare.19086455. The original FT-ICR-MS data can be found at https://doi.org/10.48758/ufz.12908.

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Supporting Information for

Riparian microtopography affects event-driven stream DOC concentrations and DOM quality in a forested headwater catchment

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Text S1. FT-ICR-MS measurements and processing

Samples were filtered with polycarbonate track etched membrane filters (LABSOLUTE, 0.4 µm pore size), acidified with hydrochloric acid (HCl) to pH 2 and stored in a refrigerator until analysis in cleaned glass bottles (rinsed with ultrapure water and heated for 4 h at 400 °C). All samples were measured using high temperature catalytic oxidation (multi N/C 3100, Analytik Jena, Jena, Germany). Samples were extracted with an automated sample preparation system as described elsewhere (Da Silva et al., 2021) and according to Dittmar et al. (2008) and Raeke et al. (2016) in order to load 200 µg carbon on the cartridges, with volume ranging from 10 to 100 mL. The carbon-based extraction recovery was 57 ± 17% and is within the range of typical extraction efficiencies obtained for freshwater samples (Dittmar et al., 2008). Immediately prior to FT-ICR-MS measurement, samples were diluted 1:1 (v/v) with ultrapure water (Milli-Q Integral 5, Merck, Darmstadt, Germany) to 20 mg L^{-1}. Samples were measured using a solariX XR 12 Tesla FT-ICR-MS (Bruker Daltonik GmbH, Bremen, Germany) with dynamically harmonized analyzer cell equipped with an autosampler (infusion rate: 10 µL min^{-1}) and electrospray ionization (ESI) source in negative mode. Samples were measured in random order with ESI mode (capillary voltage 4.2 kV), 4 megaword time-domain, and 256 co-added scans in the mass range of 147-1000 mass-to-charge ratio (m/z). FT-ICR-MS data were recorded in absorption mode due to its proven higher resolution of mass spectra compared to magnitude mode (Da Silva et al., 2020). All spectra were internally calibrated with a reference mass list of known NOM masses ($n = 188$; $250 < m/z < 640$) and the mass accuracy after linear calibration was better than 0.2 ppm ($n = 101$). The signal-to-noise ratio (S/N) threshold was set to three. Molecular formulas were assigned using element ranges $C_{1-180}H_{1-198}N_{0-3}O_{0-40}S_{0-1}$ and according to published rules (Herzsprung et al., 2014; Kind & Fiehn, 2007; Koch et al., 2014).

2

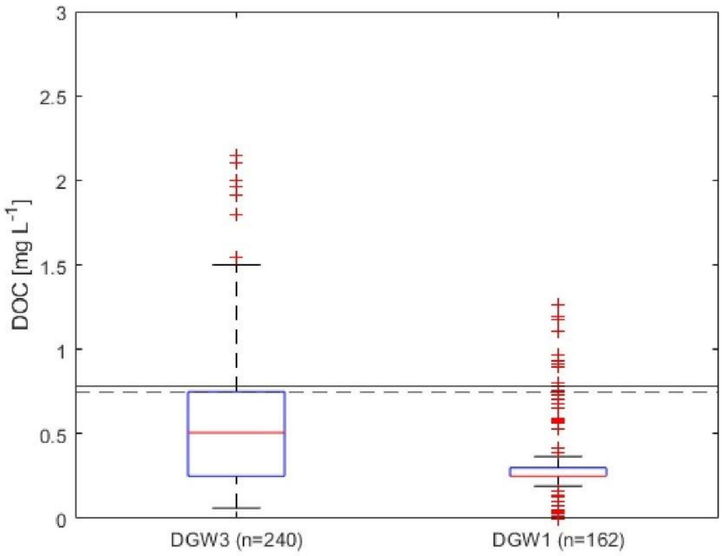

Figure S1. Monthly long-term DOC concentrations for DGW1 (2001 – 2020) and DGW3 (2002 – 2020). The horizontal lines represent the DOC concentrations of the samples collected in March 2021 for DGW1 (dashed line) and DGW3 (continuous line).

3

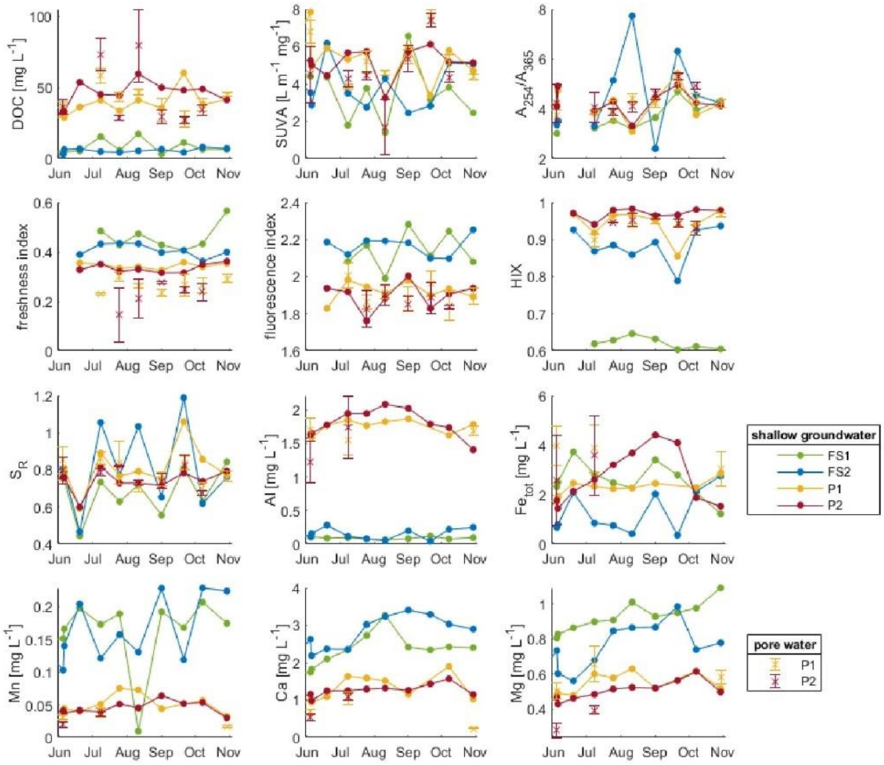

Figure S2. Water chemistry and DOC quality parameters of the shallow groundwater at sites FS1, FS2, P1 and P2 as well as the pore water at sites P1 and P2. Error bars show the variation of the pore water data over depth per sampling date. A Wilcoxon ranksum test revealed that pore water data and shallow groundwater data at location P1 and P2 were similar ($p > 0.05$) for DOC, SUVA, A_{254}/A_{365}, Fluorescence Index, S_R and Al. HIX and Mg data were also similar ($p > 0.05$) at location P1, but were different at location P2 ($p<0.05$). Freshness Index, Mn and Ca were different ($p<0.05$) at both locations.

4

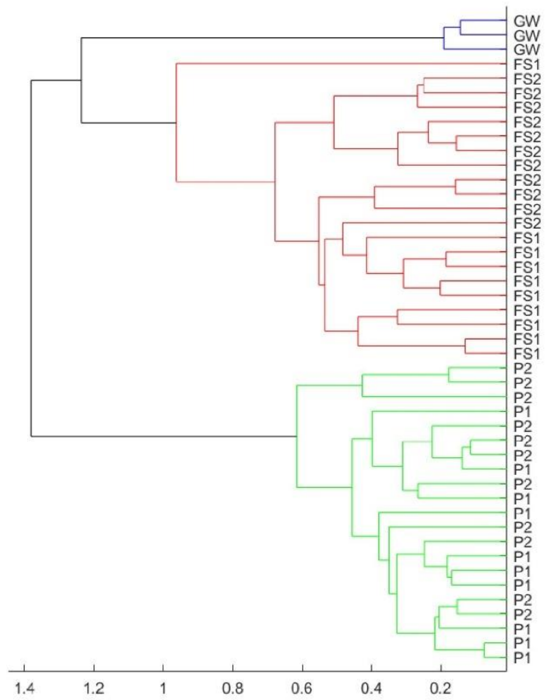

Figure S3. The cluster analysis revealed three clusters: Cluster 1 consists of the samples taken at P1 and P2 (green), cluster 2 consists of the samples taken at FS1 and FS2 (red) and cluster 3 consists of the deep groundwater samples (blue).

5

Table S1. Details about the samples collected for FT-ICR-MS measurements.

Location	Date	Number of samples pooled	Method of sampling	DOC concentration [mg L^{-1}]
HS	25/09/2020	5	autosampler	3.3
HS	26/09/2020	6	autosampler	15.8
HS	26/09/2020	6	autosampler	15.7
HS	27/09/2020	5	autosampler	21.3
FS2	24/09/2020	-	Manual	2.2
FS1	24/09/2020	-	Manual	4.8

Table S2. Reactive Fe concentrations [µmol g^{-1}], pedogenic Fe and Al content [mg g^{-1}], total C and N content [%] at FS1 over depth.

depth [cm]	Fe(II) [µmol g^{-1}]	Fe_{tot} [µmol g^{-1}]	Fe [mg g^{-1}]	Al [mg g^{-1}]	C (%)	N (%)
5 - 10	n.a.	n.a.	n.a.	n.a.	19.6	1.3
10 - 27	13.5	151.5	4.8	3.1	8.1	0.5
27 - 34	18.7	139.2	4.6	3.4	4.3	0.3
34 - 47	19.3	152.3	4.6	3.4	8.3	0.5
47 - 52	6.9	79.2	4.7	3.6	12.0	0.7
52 - 60	17.5	165.1	6.5	4.0	3.9	0.2
60 - 65	10.6	72.5	2.7	3.8	7.7	0.4

Table S3. Reactive Fe concentrations [µmol g^{-1}], pedogenic Fe and Al content [mg g^{-1}], total C and N content [%] at P1 over depth.

depth [cm]	Fe(II) [µmol g^{-1}]	Fe_{tot} [µmol g^{-1}]	Fe [mg g^{-1}]	Al [mg g^{-1}]	C (%)	N (%)
1 - 10	14.34	35.65	1.38	6.87	32.2	1.41

6

Study 3: High-resolution DOC measurements indicate seasonal differences in the contribution of three nested forested subcatchments to DOC export

Status: In preparation

Authors: Katharina Blaurock, Burkhard Beudert, Luisa Hopp

Own contribution in %:

Study design	90
Field data collection	90
Data processing and analysis	100
Interpretation of the results	80
Preparation of the manuscript	90

KB and LH designed the study. KB planned the field work and collected the DOC data at all subcatchments. BB provided the meteorological data and the discharge data of the subcatchment Hinterer Schachtenbach. KB and BB collected the discharge data of the subcatchment Kaltenbrunner Seige. KB performed all data analyses and prepared the figures and tables. All co-authors discussed and interpreted the results. KB prepared the manuscript with input from all co-authors. KB is the corresponding author.

High-resolution DOC measurements indicate seasonal differences in the contribution of three nested forested subcatchments to DOC export

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Abstract

Assessing DOC export from inland waters reliably is of paramount importance to understand and assess all processes of the global carbon cycle. Using high-frequency measurements of DOC concentrations via UV-Vis spectrometry, we quantified the DOC export of three nested forested subcatchments in the Bavarian Forest National Park, Germany, during a 12 months investigation period. We observed a high DOC export from the entire catchment (3.5 km^2) during snowmelt and spring as well as during autumn with 48.8 – 56.4 kg d^{-1}. In contrast, in summer and winter, DOC export was low with 16.7 kg d^{-1} and 9.5 kg d^{-1}, respectively. The low export during summer and winter was a result of a limited hydrological connectivity as well as a limited DOC production. However, DOC export did not only vary between seasons but also between the three topographically contrasting subcatchments. The subcatchment with the highest elevation (876 – 1373 m a.s.l.) and the steepest slopes (15.8° mean slope) contributed most to total DOC export over the entire sampling period, which we attribute to its topographic characteristics. Another upstream subcatchment (877 – 1279 m a.s.l.) with steep slopes (14.5° mean slope) contributed strongly to total DOC export during autumn and winter, probably as a result of the additional leaf litter input due to the high proportion of deciduous trees in this subcatchment. The flat downstream subcatchment (771 – 1085 m a.s.l., 7.4 °) with a wide riparian zone contributed less than expected to total DOC export. Due to the flat topography, hydrological connectivity in the downstream subcatchment is primarily established during periods with a high degree of wetness, e.g. during snowmelt. However,

during and after drought periods, hydrological connectivity and, therefore, DOC export is limited. Our data show that seasonal DOC export is influenced by both DOC production and hydrological connectivity. As the dependence on hydrological connectivity varies with topography, the contribution of topographically different subcatchments varies seasonally. Spatial and temporal DOC export patterns are likely to change depending on topography since climate change is predicted to influence not only temperature but also precipitation patterns.

1. Introduction

Dissolved organic carbon (DOC) is an important link between the terrestrial and the aquatic carbon cycle. Recent studies found that DOC in inland waters strongly influences the global carbon cycle due to the role they play for sequestration, transport and mineralization of organic carbon (Battin et al., 2009; Cole et al., 2007). The global DOC export to inland waters from terrestrial systems amounts to 5.1 Pg C (Drake et al., 2018) and therefore influences the net ecosystem balance (Kindler et al., 2011). But DOC also affects drinking water quality (Alarcon-Herrera et al., 1994; Ledesma et al., 2012; Sadiq & Rodriguez, 2004) and the transport of pollutants (Dörr & Münnich, 1991; Hope et al., 1994; Ravichandran, 2004). Moreover, it plays an important role in the context of climate change as the largest part of DOC in inland waters (3.9 Pg yr^{-1}) outgasses to the atmosphere as the greenhouse gases CO_2 and CH_4 as a result of respiration processes (Drake et al., 2018; Raymond et al., 2013). Therefore, it is important to quantify the amounts of exported DOC as accurately as possible.

A meta-analysis of DOC export data found that DOC export from catchments worldwide ranged from 1.2 to over 50 000 kg C km^{-2} yr^{-1} depending on catchment characteristics as well as precipitation and discharge (Alvarez-Cobelas et al., 2012). The main source of DOC in forested catchments is soil organic matter (Batjes, 2014; Borken et al., 2011; Kaiser & Kalbitz, 2012; Kalbitz et al., 2000), whereas it has been shown that a high proportion of wetlands in a catchment leads to a high DOC export (Laudon et al., 2011; Zarnetske et al., 2018). Riparian zones are especially regarded to be of importance for DOC export due to the accumulation of soil organic matter and the often high groundwater level that facilitate transport into the streams (Ledesma et al., 2018; Mei et al., 2014; Musolff et al., 2018; Ploum et al., 2020; Strohmeier et al., 2013). It has been shown that the largest amounts of DOC are exported during precipitation events (Raymond et al., 2016; Raymond & Saiers, 2010) and that DOC

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concentrations increase with rising discharge (Hobbie & Likens, 1973; Meyer & Tate, 1983). In order to capture the DOC export dynamics precisely, it is necessary to measure DOC concentrations at a high temporal resolution, especially during events. Earlier DOC export estimates have mostly been based on weekly or bi-weekly grab samples leading to a large uncertainty in export numbers, especially in small catchments (Schleppi, Waldner, & Fritschi, 2006; Schleppi, Waldner, & Stähli, 2006). By using novel techniques, high-frequency measurements over long periods are rendering DOC export estimates much more precise.

DOC export does not only vary with event characteristics but also during seasons as a result of varying temperature and wetness conditions (Blaurock et al., 2021; Wen et al., 2020; Werner et al., 2019). Wetness conditions largely influence hydrological connectivity (Detty & McGuire, 2010; McGuire & McDonnell, 2010; Penna et al., 2015), which is of paramount importance for solute export (Covino, 2017; Kiewiet et al., 2020). However, patterns and dynamics of hydrological connectivity do not only depend on antecedent wetness conditions and event characteristics but are also controlled by catchment topography, e. g. shape and slope angle of hillslopes and riparian zones (Detty & McGuire, 2010; Tetzlaff et al., 2014). For example, virtual experiments have shown that the hillslope shape influences DOC mobilization processes (Weiler & McDonnell, 2006). Therefore, topography is a factor that should not be neglected when investigating DOC export.

In an earlier study, we showed that the contribution of topographically different subcatchments to event-based DOC export depends on the establishment of hydrological connectivity (Blaurock et al., 2021). The goal of this study was to investigate the contribution of different subcatchments on a longer timescale in order to better understand the temporal and spatial patterns of DOC export in forested headwater catchments. By using high-frequency measurements of DOC concentrations, we were able to quantify the DOC export of three nested subcatchments over the course of one year. Our main objectives were 1) quantifying the total annual DOC export of the catchment, 2) investigating seasonal differences in DOC export and 3) exploring seasonal differences in DOC export between topographically different subcatchments.

2. Material & Methods

2.1. Study site

The study was conducted in the Hinterer Schachtenbach catchment (HS_{tot}, 3.5 km²), which is part of the Große Ohe catchment (19.2 km²) in the Bavarian Forest National Park (BFNP, 243 km²), Germany (Figure 1).

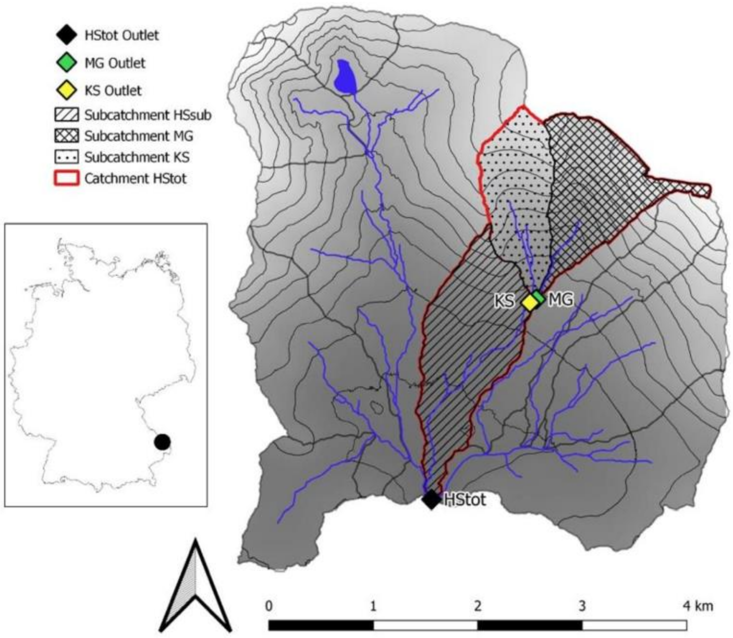

Figure 1: The studied catchment Hinterer Schachtenbach (HS_{tot}) is part of the Große Ohe catchment and located in southeast Germany (black dot). It includes the subcatchments Kaltenbrunner Seige (KS), Markungsgraben (MG) and Hinterer Schachtenbach (HS_{sub}). The high-frequency sampling sites were located at the outlets of the two subcatchments KS (yellow diamond) and MG (green diamond) and at the outlet of the entire catchment HS_{tot} (black diamond). Both the location of the stream network and the digital elevation model were provided by the Bavarian State Office for Environment. The map of Germany was derived from Vemaps (2022).

Mean annual precipitation is 1323 mm and mean annual temperature is 6.5 °C (1990 – 2019). Measurements were conducted in three nested subcatchments of HS_{tot} (Table 1): The streams of the upper subcatchments Markungsgraben (MG, 1.1 km²) and Kaltenbrunner Seige (KS, 0.9 km²) join to form the stream of the lower subcatchment Hinterer Schachtenbach (HS_{sub}, 1.5 km²). Elevation in the entire catchment ranges from 771 m to 1373 m with a mean slope of 12.0°, whereas MG and KS represent the upper part of the catchment with a mean slope of

15.8° and 14.5°, respectively, and HS_{sub} represents the lower part of the catchment with a mean slope of 7.4°. The geology of the Hinterer Schachtenbach catchment (HS_{tot}) is dominated by biotite granite (81 %) and cordierite–sillimanite gneiss (14 %). KS and MG are dominated by Cambisols and Podzols with a larger proportion of Cambisols at KS. HS_{sub} is dominated by Cambisols and hydromorphic soils. Almost 40 % of the area of MG are also characterized by rocks, which are interspersed in the soils. Pleistocene solifluction processes created deeper soil layers in the lower catchment parts than in the upper catchment part. The entire catchment is almost entirely covered by forest. Dominant tree species are Norway spruce (*Picea abies* (L.) Karsten) and European beech (*Fagus sylvatica* L.). However, large parts of the catchment are in a stage of rejuvenation due to bark beetle outbreaks in the mid-1990s and 2000s especially in the subcatchment MG (Beudert et al., 2015).

Table 1: Catchment characteristics of the entire catchment HS_{tot} and the subcatchments KS, MG and HS_{sub}.

		HS_{tot}	**KS**	**MG**	**HS_{sub}**
	Area (km²)	3.5	0.9	1.1	1.5
	Area ratio of HS_{tot} (%)	100	26	31	43
	Elevation (m a.s.l.)	771 - 1373	877 - 1279	876 - 1373	771 – 1085
	Mean slope (°)	12.0	14.5	15.8	7.4
Soil (%)	Cambisol	66	79	55	65
	Podzol	15	16	34	0
	Hydromorphic soil	18	5	5	35
	Other	1	0	6	0
Vegetation (%)	Rejuvenation	34	28	57	21
	Deciduous Forest	41	53	29	42
	Coniferous Forest	9	1	4	17
	Mixed Forest	15	17	8	19
	Other	1	0	3	1

2.2. Field measurements

2.2.1. Discharge and precipitation measurements

During the sampling period from May 30th 2020 to May 29th 2021, the water level was measured at HS_{tot} (Figure 1) every 15 minutes using a pressure transducer (SEBA Hydrometrie GmbH & Co. KG, Kaufbeuren, Germany). Discharge was determined via tracer dilution (NaCl, TQ-S; Sommer Messtechnik, Koblach, Austria) at 36 occasions to establish a rating curve and generate continuous flow data. Due to a technical failure, no discharge data for HS_{tot} was available from August 1st to September 3rd, 2020. This data gap was filled using the discharge data of a neighboring catchment within the Große Ohe Catchment of similar size (Vorderer Schachtenbach, 5.9 km^2). Using the discharge values of one year prior to the data gap, a relationship between the discharge of the two catchments was established (R^2=0.94) and calculated values were used to fill the data gap. For MG, the discharge data for the complete sampling period were taken from the database of the Bavarian State Office for Environment (2021) at a 15 minute interval. The discharge at KS was measured via tracer dilution (TQ-S; Sommer Messtechnik, Koblach, Austria) at eight occasions and continuous discharge was derived using a relationship between the highly resolved discharge data of MG and the measured discharge at KS (R^2=0.93). Precipitation was measured using a weighing precipitation gauge (Pluvio² S, OTT Hydromet, Kempten Germany) both close to the outlet of MG and KS and the outlet of HS_{tot} and was provided by the BFNP. A ring heater keeps the orifice rim free from snow and ice. Measuring resolution was one second and storage interval was 10 minutes.

2.2.2. High-frequency measurements of DOC concentration

DOC concentrations were measured in situ at the outlets of the three subcatchments using three UV-Vis (ultraviolet-visible) spectrophotometers (spectro::lyser, s::can GmbH, Vienna, Austria). Device 1 (D1) was installed at the outlet of HS_{tot} over the whole sampling period, Device 2 (D2) started at the outlet of MG but had to be replaced by Device 3 (D3) at the beginning of July 2020 due to a technical failure and was installed again in October 2020 at the outlet of KS. D3 was initially installed at KS and was moved to MG following the technical failure of D2. This means that for MG, there is a gap in DOC concentration data for the period from June 23rd to July 8th, 2020, and for KS, there is a gap in DOC concentration data from July 9th to October 9th, 2020. The spectrometric devices recorded the absorption spectrum of stream water from 200 to 750 nm with a resolution of 2.5 nm every 15 min. DOC concentrations were quantified using the internal calibration based on the absorption values using the software ana::pro. In order to refine the internal calibration, the DOC concentrations measured by the three UV-Vis spectrophotometers were calibrated using grab stream samples taken over the course of the sampling period at various discharge conditions (n_{D1} = 52, n_{D2}= 22, n_{D3} = 45). Samples were filtered in the field using polyethersulfone membrane filters (0.45 μm) or polycarbonate track etched membrane filters (0.45 μm). All samples were stored until further analysis at 4 °C. DOC concentrations of the grab samples were analyzed by thermo-catalytic oxidation (TOCL analyzer; Shimadzu, Kyoto, Japan). For further analysis, the calibrated values (R^2 for D1 = 0.98, R^2 for D2 = 0.87 and R^2 for D3 = 0.97) were used. As no drift of the DOC concentration could be identified in the measured signal, we decided against a correction for biofouling as done by Werner et al. (2019). However, the sensor optics were manually cleaned in the field every 2 weeks using cotton swabs. Here, we use data collected between May 30th 2020 and May 29th 2021, the period for which most DOC data were available for all three subcatchments.

2.2.3. Data analysis

We delineated the seasons by refining calendrical seasons according to changes in precipitation patterns (Table 2). Spring started with the end of snowmelt and ended with the beginning of a dry period in July 2020, which was defined as summer. Summer ended with the end of a long dry period prior to the beginning of a rainy period, which was defined as autumn. Winter started after the last precipitation event that did not fall as snow and when the temperature fell below zero. Snowmelt was defined as the period when temperatures rose above zero, a snow cover was present and snowmelt was clearly visible in discharge data at HS. The length of seasons is presented in days. However, these are rounded values as the start or end of a season was not automatically falling on the start or end of a day. All seasons were delineated using discharge and precipitation data of HS_{tot}. Runoff ratios were calculated as the ratio of cumulative area normalized discharge to the amount of precipitation during each season. For KS and MG, the precipitation measured close to their outlet was used. For HS_{tot} and HS_{sub}, the precipitation measured close to the outlet of HS_{tot} was used. Cumulative discharge for HS_{sub} was calculated as the difference of the discharge of HS_{tot} and the discharge of KS and MG.

Table 2: Delineation of seasons and number of days with measured DOC data for HS_{tot} and for all subcatchments. Due to the technical failure of device D2, there is no period with data for all three subcatchments available during summer.

	Dates	**Total number of days**	**Number of days with DOC data for HS_{tot}**	**Number of days with DOC data for all subcatchments**
Spring	30.05.2020 – 30.06.2020 02.05.2021 – 29.05.2021	60	60	52
Summer	01.07.2020 – 24.09.2020	87	83	0
Autumn	25.09.2020 – 21.11.2020	57	57	34
Winter	22.11.2020 – 21.12.2020 30.12.2020 – 28.01.2021	60	60	58
Snowmelt	22.12.2020 – 29.12.2020 29.01.2021 – 01.05.2021	101	91	87

Seasonal and total DOC export from HS_{tot} and subcatchments was calculated as follows:

$$DOC\ export = \sum_{i=1}^{n} c_i \times Q_i \times 15$$

where c_i is the DOC concentration [mg L^{-1}] and Q_i is the discharge [L min^{-1}] for n 15 minute intervals. Small data gaps of several hours were interpolated linearly. For the investigated year, DOC data for HS_{tot} was available for 351 days out of 365 days. Daily DOC export averages were calculated using the measured data for each season. Total annual DOC export from HS_{tot} for one season was calculated as the sum of the measured DOC export and the calculated daily average (for the corresponding season) for each day without data. For all subcatchments, data was available for 231 days, which are the only days included into the analysis of all subcatchments. When comparing the contribution of different subcatchments to total DOC export, we used the ratio of the subcatchment area to the total catchment area as a benchmark (KS/HS_{tot} = 0.26, MG/HS_{tot} = 0.31, HS_{sub}/HS_{tot} = 0.43). All data that refer to HS_{sub} have not been directly measured but were derived from the difference of HS_{tot} and the upper subcatchments (MG and KS). For these calculations, we assume that DOC, which was exported from the upper subcatchments, was still present at the outlet of HS_{tot} and was not lost to groundwater or in-stream processes on its way.

3. Results

3.1. DOC concentrations, discharge and precipitation during the investigation period

With 1077 mm of precipitation at HS_{tot} and 1280 mm of precipitation at MG, the investigated period was drier than the long-term annual average (1323 mm for HS_{tot}, 1535 mm for MG, 1990 – 2019). The mean temperature during the sampling period was higher (6.8°C) than the long-term annual average (6.5°C, 1990 – 2019).

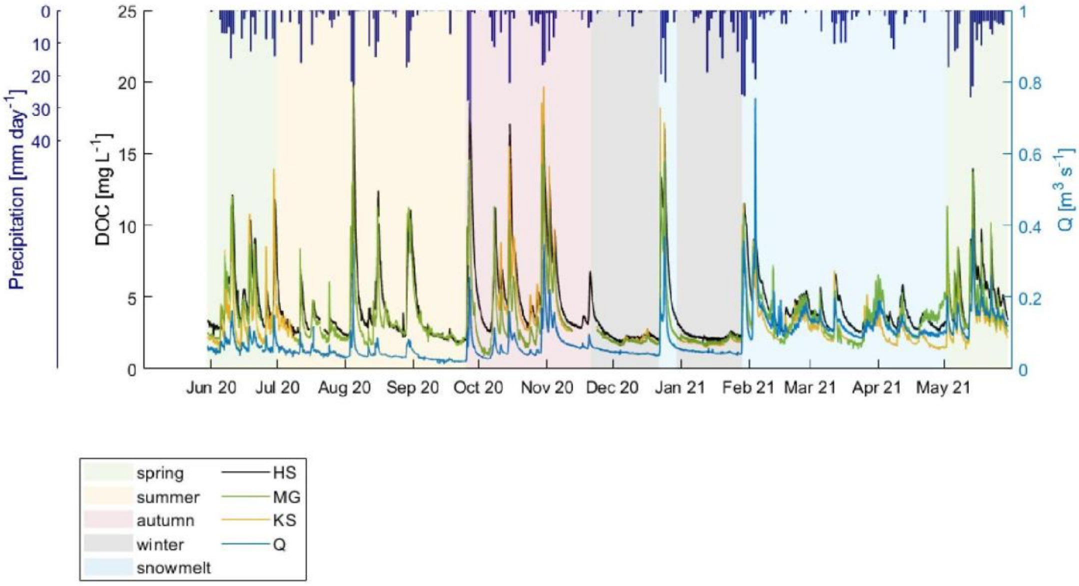

Figure 2: DOC concentrations at the outlets of the three subcatchments KS (yellow), MG (green) and HS (black) and discharge (Q) at HS_{tot} (blue). The shaded areas correspond to the delineated seasons.

Spring was characterized by frequent precipitation events (up to 27 mm d^{-1}). During summer, long dry periods were interrupted by some precipitation events (up to 22 mm d^{-1}). Autumn was characterized by several large precipitation events (up to 35 mm d^{-1}). During winter, precipitation fell as snow, which led to low discharge and low DOC concentrations. Winter was interrupted by one large snowmelt event induced by rising temperatures and rainfall. During spring snowmelt, diurnal fluctuations of discharge and DOC concentrations were visible following the temperature amplitudes. Additionally, some rain events enhanced snowmelt. DOC concentrations clearly increased with discharge during precipitation events (Figure 2), regardless of the season, leading to maximum concentrations of 17.0 mg L^{-1} at MG, 19.7 mg L^{-1} at KS and 17.2 mg L^{-1} at HS_{tot} during the periods for which data was available for all locations. During baseflow, DOC concentrations usually vary between 2 and 3 mg L^{-1} at MG and HS_{tot} (Da Silva et al., 2021).

3.2. Annual DOC export of the entire catchment HS_{tot}

The annual DOC export of HS_{tot} was 13760 kg or 3931 kg km^{-2}, if including both the measured data (13136 kg, **Fehler! Verweisquelle konnte nicht gefunden werden.**) and the days for which DOC export was estimated using the mean daily DOC export.

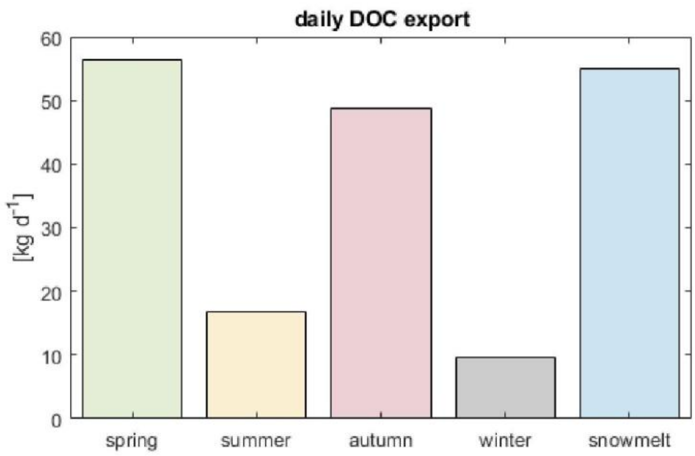

Figure 3: Mean daily DOC export from HS_{tot} during the different seasons (see Table 3 for exact values).

The largest amounts of DOC were exported during snowmelt (40.5 %), spring (24.6 %) and autumn (20.3 %), whereas the export in summer (10.4 %) and winter (4.2 %) was much lower. These seasonal differences were also discernible when calculating a mean daily DOC export by normalizing seasonal total DOC export by length of the respective season (Table 2). Plotting discharge and DOC concentration time series as cumulative curves illustrates the DOC export behavior more clearly (Figure 4).

Table 3: Total DOC export [kg], number of days per season, total precipitation P_{tot} [mm] and mean daily DOC export [kg d^{-1}] at HS_{tot} during the periods for which measured data was available (see Table 2). Note that the days are presented as rounded values as seasons were separated based on discharge and precipitation patterns. For the calculation of mean daily DOC export, non-rounded values were used.

	P_{tot} [mm] at HS_{tot}	**P_{tot} [mm] at MG**	**Total DOC export [kg]**	**Days [d]**	**Mean daily DOC export [kg d^{-1}]**
Spring	284	327	3381	60	56.4
Summer	189	214	1378	83	16.7
Autumn	207	262	2794	57	48.8
Winter	118	129	576	60	9.5
Snowmelt	263	332	5007	91	55.1
All seasons	1061	1264	13136	351	37.4

Cumulative discharge increased almost linearly during the sampling periods with more pronounced step-like increases during an event in autumn and at the beginning of snowmelt. During snowmelt, the slope of the cumulative discharge curve increased, indicating an increased runoff generation during this season. Pronounced step-like increases were also visible in the cumulative DOC export curve, emphasizing the relevance of runoff events for DOC export. During winter, DOC export was very low, whereas cumulative discharge continued to increase.

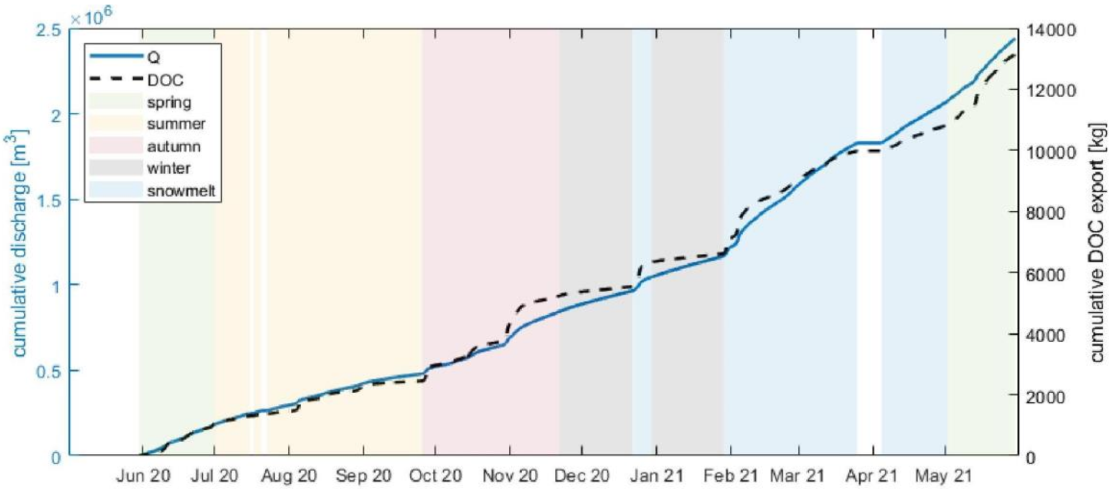

Figure 4: Cumulative discharge (blue line) and cumulative DOC export (black dashed line) from HS_{tot}. A white background indicates that data was missing and that the period was therefore not included in the calculation of cumulative DOC export.

3.3. Cumulative DOC export of the subcatchments

The cumulative export of HS_{sub} and MG showed a similar pattern running parallel until the start of snowmelt, when HS_{sub} began to export more DOC than MG (Figure 5). The cumulative export of KS remained smaller than the export of MG and HS_{sub} throughout the complete sampling period. During autumn, phases of large export (due to precipitation events) followed phases of almost no export. In winter, DOC export was very low. During snowmelt, DOC export was constantly high with the steepest slopes at the beginning of the two snowmelt periods. Strong increases of DOC export could also be seen in spring following precipitation events.

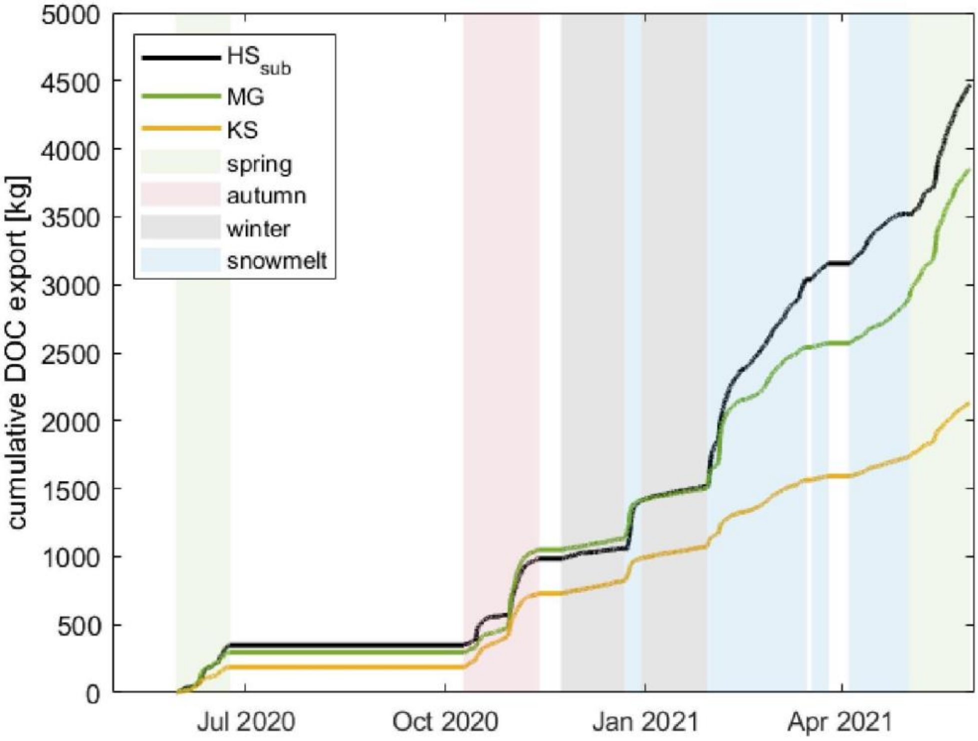

Figure 5: Cumulative DOC export from the subcatchments MG, KS and HS_{sub}. Only dates with data for all subcatchments were included (shaded areas). A white background indicates that data was missing and that the period was therefore not included in the calculation of cumulative DOC export.

3.4. Seasonal DOC export-Q relationships for the subcatchments

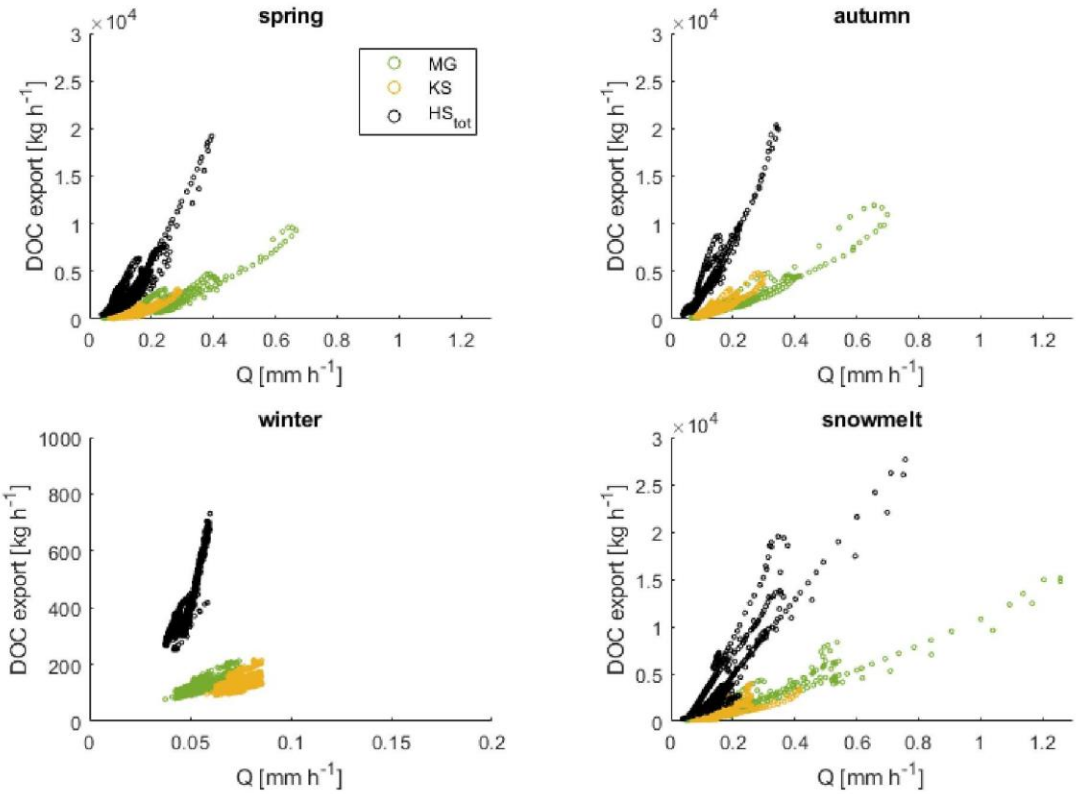

Figure 6: DOC export rates [kg h^{-1}] as a function of area normalized discharge Q [mm h^{-1}] of the entire catchment HS_{tot} and the two subcatchments MG and KS during the four seasons for which measured data for all subcatchments were available. The dots represent 15 min time steps. Please note the different scaling of the axes for the winter plot.

During all seasons and at all discharge conditions, DOC export rates at HS_{tot} were higher than at MG and KS leading to a steeper slope of the export-discharge-relation (Figure 6). Note, however, that the summer period was not included in these analyses since DOC data were not available for all three subcatchments. DOC export rates were similar at all three sampling sites during low flow but diverged during high flow. During high discharge following precipitation and snowmelt events, the relation between export rates and discharge was not linear but showed a hysteresis pattern. The clearest hysteresis pattern was visible for MG during the largest precipitation event of the autumn season leading to a clockwise hysteresis. During the largest snowmelt event, the hysteresis patterns for both HS_{tot} and MG were counterclockwise. In spring, the largest events led to a counterclockwise hysteresis for HS_{tot} and a clockwise hysteresis for MG. During spring, autumn and snowmelt, the maximum of area normalized discharge was found at MG and the minimum at KS. The highest DOC export rates and the highest area normalized discharge could be observed during snowmelt at all sampling sites, followed by spring and autumn, which showed similar values. Both DOC export rates and area normalized discharge were lowest in winter.

3.5. Comparison of subcatchments in terms of DOC export

DOC export from all subcatchments was highest during snowmelt, followed by spring and autumn and was lowest during winter (Figure 7a). Area normalized daily DOC export was also high during snowmelt, spring and autumn and low during winter (Figure 7b). However, the contribution of the subcatchments to total DOC export varied between the seasons (Figure 7c).

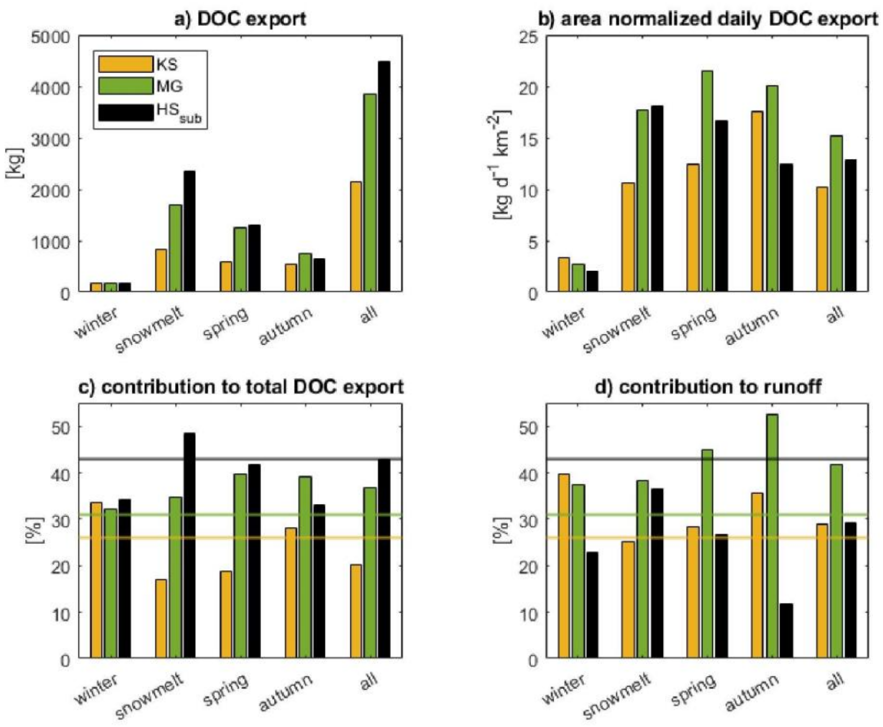

Figure 7: Comparison of seasonal DOC export runoff contribution of the subcatchments KS, MG and HS_{sub} for the seasons winter, snowmelt, spring and autumn and for the sum of those seasons together (all): a) DOC export in kg, b) area normalized daily mean DOC export in kg d^{-1} km^{-2}, c) contribution to total DOC export in %, d) contribution to runoff in %. For c) and d) the horizontal lines correspond to the value expected according to the area ratio (see Table 1).

During snowmelt and spring, the order of contribution to total DOC export was as expected in terms of catchment area as HS_{sub} contributed most, followed by MG and KS. In winter, all subcatchments contributed equally to total DOC export due to a larger contribution than expected of KS and a smaller contribution than expected of HS_{sub}. In autumn, MG contributed most to total DOC export, whereas HS_{sub} contributed less than during the other seasons. The contribution of MG was larger than expected during the complete year and even exceeding the contribution of the larger subcatchment HS_{sub} in autumn. MG also contributed more to runoff than expected during all seasons, whereas HS_{sub} contributed less than expected to runoff. KS contributed more to runoff in autumn and winter, but less during snowmelt and spring. The runoff ratios were highest for MG during all seasons except for winter, when KS showed the highest runoff ratio (Table 4). The runoff ratios were lowest for HS_{sub} during all seasons except for snowmelt, when KS showed the lowest runoff ratio. The highest runoff ratios could be found during snowmelt for all subcatchments. The lowest runoff ratio could be found in spring for KS, in summer for MG and in autumn for HS_{sub}.

Table 4: Runoff ratios for the entire catchment HS_{tot} and the subcatchments KS, MG and HS_{sub} during all seasons.

	HS_{tot}	KS	MG	HS_{sub}
Spring	0.56	0.54	0.68	0.34
Summer	0.43	0.62	0.47	0.20
Autumn	0.51	0.56	0.63	0.17
Winter	0.59	0.82	0.64	0.32
Snowmelt	1.18	0.92	1.15	1.01

When comparing the contribution to DOC export and the contribution to runoff of the subcatchments, differences could be observed. The contribution to DOC export from KS and MG during the entire period is lower than their contribution to runoff. On the contrary, the contribution to DOC export from HS_{sub} is larger than the contribution to runoff.

4. Discussion

4.1. Seasonal variations of annual DOC export of the entire catchment

The annual DOC export of the catchment of 3931 kg km^{-2} is in the range of other European forested catchments (Ågren et al., 2007; Tittel et al., 2013) with values being higher than in a Mediterranean catchment (Bernal & Sabater, 2012), but lower than in a wetland-dominated catchment (Strohmeier et al., 2013). DOC export of the entire Große Ohe catchment was found to be very similar as well with 4200 kg km^{-2} (Beudert et al., 2012). In general, it has been found that precipitation is a primary control for DOC export (Wei et al., 2021) and that wetter years result in a higher export of DOC than drier years (Jager et al., 2009). However, DOC export also strongly varies with seasons. We observed that less DOC was exported during summer and winter than during spring, autumn and the snowmelt period. The beginning of the sampling period in spring was characterized by several precipitation events and the soils were saturated following the snowmelt period. Therefore, hydrological connectivity between the DOC sources and the stream was established facilitating a high DOC export. Furthermore, the increasing temperatures during spring had enhanced DOC production, thereby increasing the potential DOC pool. During summer, precipitation events became less frequent leading to less occasions with the potential to export large amounts of DOC. Less precipitation input and an increased water demand by vegetation probably led to much drier soils. We argue that hydrological connectivity was established less often and at a lesser spatial extent leading to the inhibition of DOC export as explained by Blaurock et al. (2021) . Following a long dry period, the first autumn event at the end of September led to the second highest DOC concentrations of the observation period and was followed by two other large events leading to equally high DOC concentrations. The large precipitation events explain the large DOC export during autumn. Moreover, it is possible that DOC had accumulated in the soils during summer due to 1) the warm temperatures, which enhance biological activity, and 2) the lack of precipitation events, therefore limiting DOC flushing (Dawson et al., 2008; Kawasaki et al., 2005; Seybold et al., 2019; Wei et al., 2021). In autumn, leaf litter from deciduous trees constitutes an additional important DOC source potentially increasing DOC export during this period (Hongve, 1999; Meyer et al., 1998). Long-term observations of phenology and litter fall in the Bavarian Forest National Park show that over 80 % of litter fall is likely to occur during the here defined autumn period at all elevations (Beudert & Breit, 2022). It has also been shown that leaf litter leads to an annual carbon input of 150 000 kg C/km^2 in a neighboring catchment (Forellenbach) and can therefore substantially contribute to DOC export (Nationalparkverwaltung Bayerischer Wald, 2022).

However, DOC export is generally low during winter due to a lower DOC production than during the rest of the year because of cold temperatures (Kalbitz et al., 2000) and snowfall. As precipitation falls as snow, the transport of DOC via flow pathways towards the stream is limited. Therefore, the majority of DOC accumulates in the soils. Shortly before the end of 2020, a snowmelt event interrupted the winter season following rising temperatures and a precipitation event. This led to a sudden and strong increase of discharge and DOC export. However, the actual snowmelt period started at the end of January. Following rising temperatures, snowmelt led to a sudden availability of water, which was transported to the stream and facilitated the reconnection of flow pathways. Additionally, precipitation events occurring as rainfall led to a pronounced increase of DOC export. Several studies have shown that DOC export during snowmelt can be substantial (Jager et al., 2009; Seybold et al., 2019; Wilson et al., 2013). The diurnal fluctuations of discharge and DOC indicated that DOC export was strongly controlled by hydrological processes, which responded to the daily freeze-thaw cycle of the snowpack. The largest DOC export could be observed at the beginning of the snowmelt periods probably due to the flushing of topsoil DOC that had accumulated during winter (Ågren et al., 2010; Boyer et al., 1997) as a result of the leaching of DOC from the autumnal litter input or DOC production in snow-covered soil (Brooks et al., 1999). Once the snow cover was depleted, DOC was exported mainly as a reaction to precipitation events.

To conclude, DOC export in the catchment is strongly related to water fluxes, which drive DOC export during snowmelt and during precipitation events. Nevertheless, temperature is probably also influencing seasonal DOC export variations due to the influence on biological processes (Wei et al., 2021). Therefore, DOC export in the investigated catchment can be seen as a result of the seasonal interplay of DOC production and hydrological connectivity with the latter having a larger influence on DOC export.

4.2. Seasonal differences in the contribution of subcatchments to total DOC export

Besides seasonal differences in DOC export from the entire catchment, clear differences in the contribution of different subcatchments to total DOC export could be observed. Snowfall and low temperatures led to a very low DOC export in winter. The relatively high contribution of KS during autumn and winter could be due to the influence of litterfall on DOC export as KS is the subcatchment with the highest fraction of deciduous trees. The breakdown of this additional input of organic matter could lead to a constant DOC production even during the winter months (Hongve, 1999). Another reason for the high contribution of KS could be the lower elevation in comparison to MG, which led to a larger portion of precipitation falling as rain, therefore maintaining mobilization processes and water flow paths indicated by the high runoff ratio at KS during winter.

During snowmelt, the contribution of the subcatchments to the total DOC export was close to the expected values when taking into account the subcatchment area with HS_{sub} exporting most followed by MG and KS. Moreover, the contribution of HS_{sub} to runoff was higher during this period than during the rest of the year. The melting snow led to constantly wet soils enabling the establishment of hydrological connectivity between DOC source areas and stream and facilitating the export of DOC to the stream. Due to the lower elevation of HS_{sub}, more precipitation was falling as rain and snowmelt began earlier than at the upper catchments, leading to a higher runoff contribution and an early increase in DOC mobilization. Additionally, as DOC export was limited during winter, DOC which had accumulated following litter fall and during the winter months could now be flushed by meltwater and precipitation events (Ågren et al., 2010; Boyer et al., 1997). After the snowmelt period, the relative importance of HS_{sub} decreased, whereas the relative importance of MG increased. The high contribution of MG could be a consequence of a delayed snowmelt in the upper catchment areas. The highest elevation of MG is almost 100 m higher than at KS, which is leading to colder temperatures and a longer existing snowpack (Forschungsverbund Große Ohe, 2022). Therefore, a delayed snowmelt at MG could contribute to the higher DOC export in spring. Similar observations were made by Boyer et al. (1997) who found a delayed contribution of upslope catchment parts to the total DOC export due to an asynchronous melting of the snow in an alpine catchment.

Following the dry summer, the contribution of MG and KS to DOC export increased and the contribution of HS_{sub} to DOC export decreased. We attribute the low contribution of HS_{sub} to DOC export during autumn to a low connectivity in this subcatchment as explained in our earlier study (Blaurock et al., 2021). The flat riparian zone of HS_{sub} is dependent on a high level of hydrological connectivity in the upper soil layers to export DOC, whereas the steeper upper catchments are able to maintain flow towards the stream even during dry conditions. During a large precipitation event at the end of October 2020, the clockwise hysteresis of MG also indicates the fast delivery of DOC to the stream. When analyzing C-Q-hysteresis patterns at MG and HS_{tot} in an earlier study (Blaurock et al., 2021), (near-)clockwise hysteresis patterns could only be observed at MG either following large precipitation events or wet antecedent wetness conditions. We could now confirm that larger precipitation events than previously observed lead to even clearer clockwise hysteresis patterns at MG, at least for DOC export. At HS_{tot}, the only clockwise hysteresis – although not very pronounced – was visible during a large spring event, which confirms that additional hydrological connectivity is needed to facilitate a fast DOC export to the stream at the lower part of the catchment. The under-proportional runoff contribution of HS_{sub} in autumn also confirms that DOC export is limited due to the dry antecedent conditions. Another reason for the low importance of DOC export from HS_{sub} during autumn could be the higher ratio of coniferous trees in this subcatchment. In contrast to MG and KS, a pulsed input of organic matter following litter fall is missing at HS_{sub} (Hongve, 1999).

In general, it is striking that MG contributed more to DOC export than expected in terms of area during the entire year. A higher amount of precipitation in the upper catchments led to an overall higher runoff contribution at KS and MG. Moreover, runoff ratios at KS and MG were higher than at HS_{sub} during all seasons. Runoff contribution of MG was disproportionately high during all seasons. We attribute the high runoff contribution of MG to topographic differences. MG is characterized by steep slopes with over 22 % (in comparison to 2 % at KS) of the area having slopes with 21 – 25°. Whereas precipitation in the steep upper catchment contributes mainly to streamflow, in the flat riparian zone of the lower catchment, a higher portion of water is probably lost to the groundwater. Another reason for the high runoff contribution of MG are the differences in soil properties. MG is characterized by permeable soils interspersed with large rocks, facilitating the occurrence of preferential flow paths and the fast movement of water. In contrast, at KS, interspersed rocks are much less prominent leading to slower flow processes. At HS_{sub}, the soils are much deeper than in the upper catchments. Therefore, runoff processes and the establishment of hydrological connectivity in this catchment are dependent on the saturation of the soils leading to low runoff ratios especially during summer and autumn. In contrast, at MG, the runoff ratio increased again to pre-summer values during autumn indicating that hydrological connectivity was established much faster than at HS_{sub}. As a consequence, DOC export of HS_{sub} is higher during wet periods, but limited by a low hydrological connectivity during dry periods. However, the contribution of HS_{sub} to total DOC export is much higher than the contribution to total runoff. This indicates that the high amounts of DOC being exported during the wet periods offset the limited DOC export during dry periods. It also shows that DOC at HS_{sub} is abundant, but that mobilization is clearly transport limited as it has been shown for many other catchments (Zarnetske et al., 2018). In contrast, it could be possible that the upper subcatchments MG and KS could become source limited more easily as the runoff contribution was usually higher than the contribution to DOC export. This could indicate a limited DOC availability rather than a limited hydrological connectivity.

In summary, the contribution of the three subcatchments to DOC export as well as to runoff varied strongly throughout the year because of differences in topography, vegetation and the establishment of hydrological connectivity. Runoff contribution and, therefore, DOC export at HS_{sub} was often limited by a low hydrological connectivity. DOC export from KS was especially important during autumn and winter, when the contribution to runoff was high and leaf litter led to an additional DOC input. MG, in contrast, delivered water and DOC to the stream throughout the year, probably because of its steep topography and the soil properties.

5. Conclusions

Our high-resolution data show that DOC export varies seasonally as a result both of varying DOC production and of varying hydrological connectivity, which is controlled by topographical position. In next decades, temperate ecoregions are likely to be influenced strongly by climate change as a result of rising temperatures and changing precipitation patterns (Intergovernmental Panel on Climate Change [IPCC], 2021) with potentially large consequences for DOC export. Rising temperatures could increase DOC production and, therefore, the potential DOC pool. Higher temperatures in winter would reduce the amount of precipitation that falls as snow. Consequently, more DOC could be exported during winter and the flushing effect during snowmelt would be reduced. DOC export could be distributed more evenly during the winter and spring months. However, more extreme precipitation events and prolonged drought periods could lead to a stronger contrast in DOC export patterns during summer and autumn. Drought periods would also limit DOC production and a low DOC export in summer and autumn could then lead to a higher DOC export during the following winter and snowmelt (Ågren et al., 2010). Additionally, topography and vegetation seem to influence the contribution of the different catchment parts to DOC export throughout the year. Drought periods could limit DOC export from the lower catchment parts, which are dependent on hydrological connectivity, leading to an increasing importance of the upper catchment parts for DOC export. This effect could be enhanced by longer warm periods at higher altitudes.

In order to gain further insights into DOC export patterns over time and space in the context of climate change, high-resolution data is essential to capture the highly dynamic DOC export behavior and to include fast mobilization processes in DOC export calculations. Therefore, high-resolution data contributes substantially to a better understanding of the seasonally varying contribution of landscape parts to streamflow generation and associated DOC mobilization and export.

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Study 4: Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments

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Own contribution in %:

Study design	5
Field data collection	10
Laboratory analysis	0
Data processing and analyses	10
Interpretation of the results	10
Preparation of the manuscript	5

MPS, TR and OJL designed the study. MPS collected all grab samples for FT-ICR-MS analysis. KB collected the DOC data and was responsible for all corresponding data processing. BB and KB collected the discharge data. MPS conducted all laboratory analyses as well as statistical analyses. MPS prepared all figures and tables. All co-authors interpreted and discussed the results. MPS prepared the manuscript with inputs from all co-authors. OJL is the corresponding author.

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RESEARCH ARTICLE
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Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments

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Key Points:

- High-frequency monitoring of UV absorbance and high-resolution chemical analysis are highly complementary in the study of dissolved organic matter (DOM) dynamics in headwater streams
- Ultrahigh-resolution mass spectrometry revealed a linkage between DOM molecular composition in-stream and in soil
- At comparatively higher dissolved organic carbon (DOC) concentration at baseflow, DOM composition reflects the contribution of more superficial layers of the soil

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Dissolved organic matter (DOM) composition in streams reflects the dynamic interplay between DOM sources, mobilization mechanisms, and biogeochemical transformations within soils and receiving water bodies. The information regarding DOM sources being mobilized during baseflow can improve our ability to predict hydrological and biogeochemical responses to environmental changes, with implications for catchment management strategies. The objective of this study was to characterize the spatial changes in DOM composition along a headwater stream in a small mountainous catchment during baseflow and to link the findings in-stream with possible DOM sources in the catchment. DOM was monitored over 1.5 years at three sites in the Große Ohe catchment (Bavarian Forest National Park, Southeast Germany) which strongly varied in slope between upper and lower part of the catchment, using UV-Vis absorption indicators of aromaticity (SUVA) and molecular weight (E_2:E_3) from high-frequency probe measurements. Additionally, discrete samples were collected and analyzed by ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). At baseflow conditions, dissolved organic carbon (DOC) concentrations, a proxy of DOM amount, ranged from 1.5 to 4.7 mg L^{-1}, but were similar along the stream. However, DOM quality exhibited clear spatial patterns, with overall high aromatic and low molecular weight DOM in the lower part of the catchment, which has a higher proportion of hydromorphic soils. Moreover, molecular data revealed that oxygen-rich, aromatic compounds increased in their abundance at high DOC concentrations in both the steep upper and the flatter lower part of the catchment, with also additional input of oxygen-depleted aromatic compounds identified in the lower part. In contrast, nitrogen-rich aliphatic compounds were negatively correlated with DOC concentration, indicating a higher contribution of deep groundwater at low DOC concentrations.

Plain Language Summary Dissolved organic matter (DOM) is a complex and heterogeneous mixture of substances present in water. Due to its complexity, the concentration of DOM is estimated based on the concentration of dissolved organic carbon. Monitoring DOM composition and concentration is important because of its impact on the aquatic ecosystem and in the treatment of drinking water from surface water reservoirs. In this study, we examined spatial changes in DOM chemical composition and dissolved organic carbon concentration along a headwater stream in the Bavarian Forest National Park (Southeast Germany), focusing on baseflow conditions. For this purpose, in-stream sensors were used to record changes in dissolved organic carbon concentration and discrete water samples were collected along the stream for molecular analysis of DOM. The analyses revealed that at comparatively high dissolved organic carbon concentrations, the composition of DOM in-stream reflects the composition of DOM stored in the superficial soil layers. Whereas at low concentrations, the DOM composition points to greater contribution from deep groundwater flows.

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1. Introduction

Dissolved organic matter (DOM) is a complex mixture composed of different classes of naturally occurring organic compounds (Jaffé et al., 2008). It plays a fundamental role in surface water chemistry, controlling metal bioavailability and mobility, as well as nutrient cycling (Stedmon et al., 2007; Tipping et al., 2002). Due to its heterogeneity and dynamic nature, estimation of DOM amount is based on dissolved organic carbon (DOC) measurements. DOC concentration and DOM quality are strongly connected in headwater streams (Peter et al., 2020). The amount of DOC is limited by the availability and mobilization of diverse sources, which in turn also impacts DOM quality in-stream. Subsequent turnover of terrestrial DOM in aquatic ecosystems can result in the release of CO_2 through mineralization and impacts primary productivity through light attenuation or nutrient release (Coble, 2007; Seekell et al., 2015). Spatial changes in in-stream DOM quality along the river network are hence a superposition of availability of sources and biogeochemical processes (Mosher et al., 2015; Peter et al., 2020). The river continuum concept, although not specifically addressing DOM, describes a decrease in diversity of solutes from headwaters to high-order rivers (Creed et al., 2015; Vannote et al., 1980). Furthermore, changes in baseflow DOC concentration and DOM composition in headwater streams can impact the macroinvertebrate and microbial communities in the aquatic systems (Baker et al., 2021; Parr et al., 2015), and the treatment of drinking water from downstream surface water reservoirs (Raeke et al., 2017).

The organic matter retained in soils represents an important source of allochthonous DOM for inland aquatic systems (Ågren et al., 2007; Kaiser & Kalbitz, 2012). The activation of DOM sources in the soil is governed by the catchment wetness state, which controls the water flow, groundwater levels, and the connection of different flow paths (Lambert et al., 2014). Furthermore, the quality of the mobilized DOM is a result of both soil properties (e.g., sorption-desorption processes) and microbial processing at different depths (Seifert et al., 2016; Steinbeiss et al., 2008). DOM stored in upper organic-rich layers of the soil is young, with a dominance of lignin-derived phenols and plant-derived carbohydrates, while most DOM in the deep layers of the soils is older and of microbial origin, being rich in nutrients such as nitrogen (N) and phosphorus (P) (Kaiser & Kalbitz, 2012). The relationship between hydrological conditions and DOM mobilization from different soil layers has been demonstrated during storm events as it represents a fast change in DOM sources (Fellman et al., 2009; Hood et al., 2006; Wagner et al., 2019). Yet, the main sources and mobilization dynamics of DOM during baseflow conditions over longer periods of time remain poorly characterized. The hydrological and biogeochemical knowledge of headwater stream characteristics during baseflow conditions provides valuable insights into changes in water sources, being especially important for the development of catchment management strategies, especially in light of future drought scenarios (Peralta-Tapia et al., 2015; Smakhtin, 2001). Moreover, low-order streams represent a particularly sensitive system to changes in DOM sources and dynamics due to their immediate interface with adjoining hillslopes and the high riparian soil-to-water area ratio (Aitkenhead et al., 1999; Gomi et al., 2002; Mosher et al., 2015).

DOC concentration and DOM quality are often monitored with spectroscopic techniques integrated in field deployed sensors (Hood et al., 2006; Jaffé et al., 2008). In headwater streams, spectroscopic sensors have been used to reveal temporal variability of DOC concentration and DOM quality during periods of drought, storm events (Broder et al., 2017; Strohmeier et al., 2013), and across seasons (Schwab et al., 2018; Werner et al., 2019). Absorption indices have emerged as an efficient way of characterizing the structure and reactivity of DOM (Ågren et al., 2008; Hansen et al., 2016; Jaffé et al., 2008). Among those indices, specific ultraviolet absorbance (SUVA) (see Weishaar et al., 2003) and absorption ratios (e.g., at 250–365 nm, (De Haan & De Boer, 1987)) can provide information of DOM aromaticity and molecular weight (MW), respectively. However, ultraviolet-visible absorbance (UV-Vis) and fluorescence measurements are limited to the bulk of the chromophore fraction of DOM, which provides only little information on changes in DOM composition. The state-of-art technique to study DOM chemical composition is Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) (Nebbioso & Piccolo, 2013). The ultrahigh-resolution of FT-ICR-MS allows the distinction of characteristic fingerprints in DOM composition on the molecular level that reflect different sources (Lechtenfeld et al., 2014; Raeke et al., 2017; Wagner et al., 2015) and transformation processes (Herzsprung et al., 2020). Moreover, the high resolution of FT-ICR-MS allows the identification of individual molecular formulas for molecules, which may also contain low-abundance heteroatoms like nitrogen and sulfur (Herzsprung et al., 2016). Nonetheless, the high costs and analytical effort

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of FT-ICR-MS analyses have limited the number of samples in previous studies, limiting further advances on the biogeochemical understanding of DOM dynamics (Fellman et al., 2009; Wagner et al., 2019). Therefore, the information provided by high temporal resolution spectroscopic UV-Vis and high mass resolution FT-ICR-MS analyses proves powerful for investigating changes in DOM quality.

The objective of this study is to characterize the spatial changes in DOC concentration and DOM composition along a low-order stream in a temperate, mountainous forested catchment in southern Germany with a focus on baseflow conditions. Previous work has shown that DOC export during rain events reflects varying contribution of different parts of the catchment (upper and lower) triggered by antecedent hydrological conditions and hydrological connectivity (Blaurock et al., 2021). Due to the strong gradient in catchment properties between upper and lower part (mean slope, proportion of hydromorphic soils, see below), we hypothesize that also during baseflow, the DOM composition in the steep (upper) part of the catchment is mainly driven by groundwater input, while in the flat (lower) part, also varying contribution from riparian topsoil shape the DOM composition in the stream. Thus, we also expect that DOM composition will be more variable over the year at the lower part of the catchment compared to upstream. Finally, we expect that due to the high dimensionality of FT-ICR-MS derived DOM composition data, even subtle changes in source contributions can be identified in a small headwater stream Section 2.5.3. To this end, continuous absorption data recorded by spectrophotometers and over 100 discrete samples analyzed by FT-ICR-MS, collected over 1.5 years in the Große Ohe catchment, were used to investigate the spatial and temporal DOM dynamics in unprecedented detail. Specific marker compounds of DOM sources within the catchment were used to support the delineation of source contributions to the mixed-signal observed in the stream.

2. Materials and Methods

2.1. Study Area and Sampling

Samples and data were obtained from the Bavarian Forest National Park (BFNP), which is located in Southeast Germany (Figure 1). The BFNP is the first designated national park in Germany and represents near-natural forests in central-European low mountain ranges. The study was carried out in two sub-catchments of the Große Ohe catchment (with 19.2 km^2 and mean terrain slope of 7.7°), named Markungsgraben (MG, with 1.1 km^2 and mean slope of 15.9°) and Hinterer Schachtenbach (HS, with 1.5 km^2 and mean slope of 7.4°), named as after their respective main streams. The whole hydrological system comprising MG, Kaltenbrunner Seige (KS, another small subcatchment), and HS includes an area of 3.5 km^2. Elevation in the Große Ohe catchment ranges from 770 to 1447 m above sea level. The Große Ohe catchment has been monitored by the BFNP since 1977 (Beudert & Gietl, 2015) and two of the main monitoring sites are located within the studied area. The Große Ohe catchment is almost exclusively (98%) covered by forest, with Norway spruce (Picea abies, 70%), and European beech (Fagus sylvatica) being the dominant species (Beudert et al., 2015). The geology of the area is dominated by biotite granite and cordierite-sillimanite gneiss (Beudert et al., 2015). Overall, soils are mainly cambisols and podzols, but the proportions of hydromorphic soils vary considerably between 5% and 35% at MG and HS, respectively (Beudert et al., 2015). At MG and HS, the mean annual precipitation (1990–2010) is 1600 and 1379 mm, respectively. Mean annual temperature is 6.2°C at a station 3.8 km east of the catchment outlet.

We further divided the study area into three distinct zones along the course of the streams: (a) MGL, lower Markungsgraben, located at the upper part of the Große Ohe catchment, (b) HSU, upper Hinterer Schachtenbach, and (c) HSL, lower Hinterer Schachtenbach, located at the lower part of the Große Ohe catchment and characterized as a floodplain area. In each zone, one continuous monitoring site for discharge (at MGL and HSL) and UV-Vis (at MGL, HSU, and HSL) and three sampling points for FT-ICR-MS analysis were established. Stream water samples were taken monthly between August and November 2018 and April and November 2019 (i.e., 11 sampling dates), summing up to 98 samples across different seasons. The seasonality in this study was defined according to the calendar. Samples were consistently collected at baseflow in the three defined zones, except for April 2019, where baseflow conditions were not met at HSL (Figure S1, see below). However, during the sampling campaign in April 2019, baseflow conditions were identified at MGL and the DOC concentration of this sample (of HSL) was in the range of all samples, therefore this sample was also included in the further analysis. Next to the stream samples, three possible sources of DOM, outside the stream, contributing to the stream DOM were sampled over the period of study: shallow

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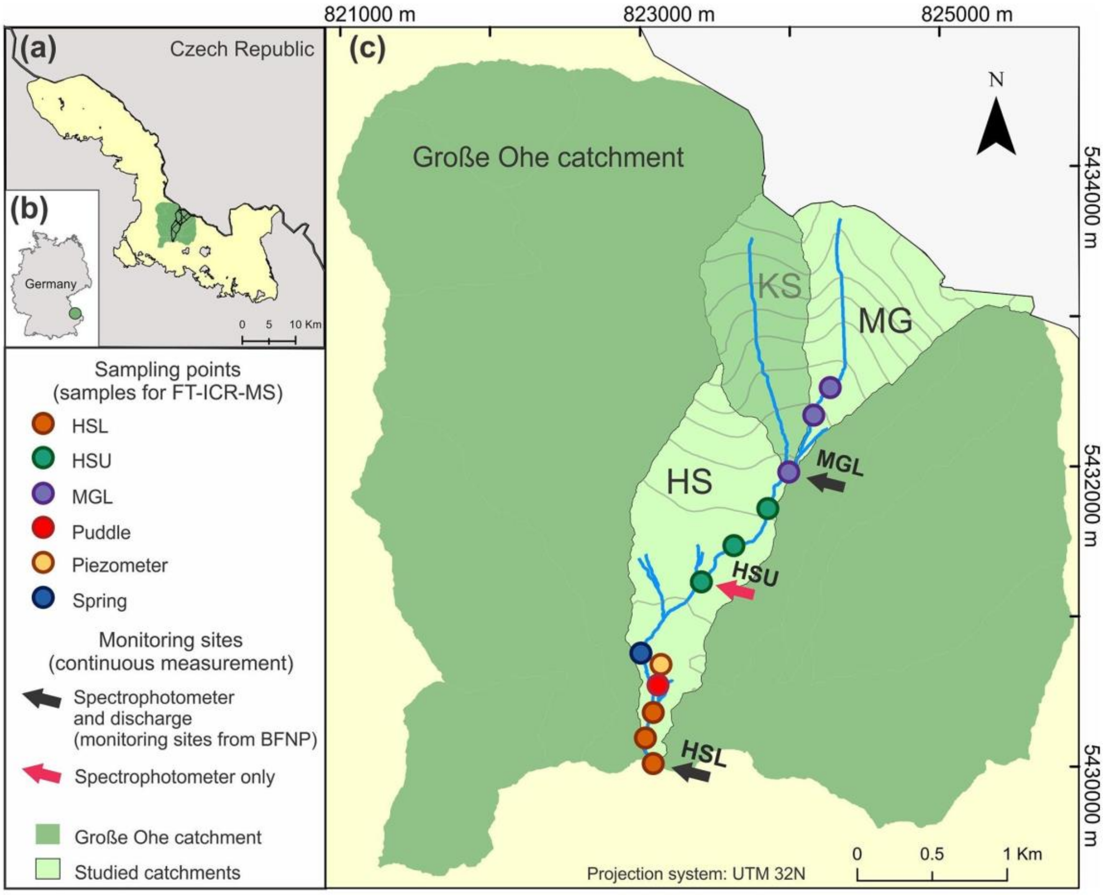

Figure 1. (a) Location of Große Ohe catchment within the Bavarian Forest National Park, (b) located in Southeast Germany at the border with the Czech Republic (c) and details of the two studied sub-catchments of the Große Ohe: Markungsgraben (MG) and Hinterer Schachtenbach (HS), plus the Kaltenbrunner Seige (KS) catchment. In (c), blue lines indicate streams, grey lines elevation contour lines, arrows point to the continuous monitoring sites, where the spectrophotometers were installed and discharge was measured, and dots the sampling points in the three defined zones: lower Markungsgraben (MGL), upper Hinterer Schachtenbach (HSU), and lower Hinterer Schachtenbach (HSL).

groundwater from a spring close to HS main stream (September 2018), riparian soil groundwater from a piezometer (October 2019), and riparian zone surface water (September 2019) from a puddle. The latter two both were located in the riparian zone of the floodplain area along the HS main stream. The piezometer was installed ~65 cm deep in the soil with slots along the full depth and the puddle sample was collected in a small shallow pond resulted from the irregularities of the terrain that are filled with water during wet conditions (see Figure 1, for locations). The spring, piezometer, and puddle samples were representative of DOM sources and refer in the study as shallow groundwater, riparian soil groundwater, and riparian zone surface water, respectively.

The stream and source samples were collected in cleaned glass bottles (burned for 4 h at 400°C), filtered with polycarbonate track etched membrane filters (LABSOLUTE, 0.4 μm pore size), acidified with hydrochloric acid (HCl, ultrapure, Merk, Germany) to pH 2 and, stored in a refrigerator until analysis. The filtered samples were split for dissolved organic carbon (DOC) concentration and FT-ICR-MS analysis.

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2.2. Discharge

Discharge was monitored at the outlet of the HS catchment (Figure 1) during 2018 using pressure transducers (Solinst Canada Ltd., Georgetown, Canada), which measured the water level every 15 min, and regular measurements of flow velocity with an electromagnetic current meter (FlowSens, SEBA Hydrometrie GmbH, Kaufbeuren, Germany). With both data, a stage-discharge rating curve was calculated and used to derive the discharge values, following Kreps (1975). From 2019 on, discharge was monitored by the BFNP. Discharge data at the outlet of the MG catchment (Figure 1) was retrieved from the Bavarian State Office for Environment database for the entire period (2018–2019) (https://www.gkd.bayern.de/en).

Discharge was monitored during the study period between June and November 2018 and between April and November 2019. The minimum of discharge over consecutive 5-day periods was calculated as described in Gustard and Demuth (2009) to separate baseflow and nonbaseflow conditions. Baseflow conditions were defined when the calculated baseflow was in the interval of the actual flow +5% (Figure S1). The calculations were performed in R using the package "lfstat" (Koffler et al., 2016). For HSU zone, discharge was not recorded and, therefore, baseflow conditions at HSU were assumed when discharge at MGL and HSL were defined as base flow. Because of the limitation in the calculation of baseflow conditions at HSU, only the data recorded at identified simultaneous baseflow conditions at MGL and HSL were further analyzed. Rainfall and snowmelt events also occurred during the study period. Their effect on DOC mobilization is discussed in a separate paper by Blaurock et al. (2021).

2.3. DOC Concentration

DOC concentration of the grab samples was determined by high temperature catalytic oxidation (multi N/C 3100, Analytik Jena, Jena, Germany). Performance of the instrument was recorded by daily analysis of in-lab standard solutions.

Stream DOC concentration at the three defined zones (Figure 1) was estimated from UV-Vis spectrophotometers (spectro::lyser, s::can Messtechnik GmbH, Vienna, Austria) using the software ana::pro. The spectrophotometers measured the absorbance between 200 and 750 nm with increments of 2.5 nm, every 15 min. The spectrophotometers recorded data between June and November 2018 and between April and November 2019. However, during the monitoring period, there are data gaps due to instrument failure (Figure S2, Table S1).

The window of the sensors was cleaned every two weeks and no drifts in the absorption caused by obstruction of the windows were detected. The estimated DOC concentration from the spectrophotometers was monthly checked and calibrated with DOC concentration in grab samples measured in the laboratory, with good fit of the calibration curve (Hoffmeister et al., 2020) ($r^2 = 0.91$, 0.98, and 0.95 at MGL [$n = 31$], HSU [$n = 18$], and HSL [$n = 43$], respectively; cf. Text SI for details). Samples used in the calibration of the sensors were collected over periods of base and event flow.

2.4. Absorption Indices

The average absorption coefficient between 700 and 750 nm was used to correct the absorption spectra due to baseline drift, temperature, scattering, and refractive effects (Coble, 2007) before the absorption indices were calculated. Specific UV absorbance (SUVA, L m^{-1} mg-C^{-1}) was calculated as the ratio of DOM absorbance at 254 nm and the DOC concentration, and used as an estimator of DOM aromaticity (Weishaar et al., 2003). The ratio of DOM absorbance measured at 250 and 365 nm (E_2:E_3) is inversely correlated with molecular weight of DOM and it was also used to characterize DOM apparent molecular weight (De Haan & De Boer, 1987). The spectral slope between 275 and 295 nm ($S_{275\text{-}295}$) was also calculated according to Helms et al. (2008) using the Rpackage "cdom" (Massicotte & Markager, 2016) and setting the reference wavelength to 285 nm. Although the data derived from the spectrophotometers (DOC concentration, SUVA, E_2:E_3, and $S_{275\text{-}295}$) have some gaps (Figure S2, Table S1), the overall trend in DOC concentration and DOM quality could still be evaluated.

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2.5. FT-ICR-MS

2.5.1. Solid-Phase Extraction

Solid-phase extraction (SPE) of filtered and acidified samples was performed according to Dittmar et al. (2008) and Raeke et al. (2017). A volume of 5–200 mL was extracted on 50 mg styrene-divinyl-polymer type sorbents (Bond Elut PPL, Agilent Technologies, Santa Clara, CA, United States) using an automated sample preparation system (FreeStyle, LC Tech, Obertaufkirchen, Germany). The sample volume was adjusted to load 200 μg carbon on the cartridges. The SPE-DOM was eluted with 1 mL methanol (Biosolve, Valkenswaard, Netherlands) and stored at −20°C until measurement. Aliquots of the methanol extracts (10 μL) from the SPE samples were evaporated under N_2 gas flow to complete dryness and subsequently redissolved in 10 mL ultrapure water (Milli-Q Integral 5, Merck, Darmstadt, Germany), and DOC concentration measured. The carbon-based extraction recovery was subsequently calculated to be 52 ± 10% (number of samples, $n = 101$) and is within the range of typical extraction efficiencies obtained for freshwater samples (Dittmar et al., 2008; Raeke et al., 2017).

2.5.2. Measurement

Immediately prior FT-ICR-MS analysis SPE-DOM samples were diluted to 20 ppm and mixed 1:1 (v/v) with ultrapure water (Milli-Q Integral 5, Merck, Darmstadt, Germany). Samples were measured using a solariX XR 12 Tesla FT-ICR-MS (Bruker Daltonik GmbH, Bremen, Germany) with dynamically harmonized analyzer cell equipped with an autosampler (infusion rate: 10 μL min^{-1}) and electrospray ionization (ESI) source (Apollo II) in negative mode. Samples were measured in random order with negative ESI mode (capillary voltage 4.2 kV), 4 megaword time domain, and 256 coadded scans in the mass range of 147–1,000 mass-to-charge ratio (m/z). FT-ICR-MS data were initially recorded in magnitude mode and subsequently transformed to absorption mode using FTMSprocessing (v 2.2.0), which increased the resolution of mass spectra (Da Silva et al., 2020).

All spectra were internally calibrated with a reference mass list of known NOM masses ($n = 188$; $250 < m/z < 640$) and the mass accuracy after linear calibration was better than 0.2 ppm ($n = 101$). Peaks were considered if the signal-to-noise ratio (S/N) was greater than 2. Reference DOM samples (Suwannee River fulvic acid, SRFA) and quality control samples (e.g., pooled aliquots of all the samples included in the run) were repeatedly measured to check instrument performance across measurement days. Extraction and solvent blanks were also included in all runs.

2.5.3. Data Processing

Molecular formulas were assigned to mass peaks within ±0.5 ppm in the range of 150–1000 m/z according to published rules using element ranges $C_{1\text{-}180}H_{1\text{-}198}N_{0\text{-}3}O_{0\text{-}40}S_{0\text{-}1}$ (Koch et al., 2014). All molecular formulas assigned to blank (solvent and extraction) peaks were removed from the samples. Multiple assignments accounted for less than 1% of all assigned peaks and were removed. Isotopologue formulas (^{13}C, ^{34}S) were used for quality control but removed from the final data set as they represent duplicate chemical information. Chemical constraints were further applied to the assigned molecular formulas: $0.3 \le H/C \le 3.0$, $0 \le O/C \le 1.0$, $0 \le N/C \le 1.5$, $0 \le DBE \le 25$ (double bound equivalent, $DBE = 1 + 1/2\,[2C - H + N]$) (Koch et al., 2014), $-10 \le DBE\text{-}O \le 10$ (Herzsprung et al., 2014), and element probability rules proposed by Kind and Fiehn (2007). Due to the high degree of spectral similarity between samples (47% of the mass peaks were present in at least 75% of all samples), detailed data evaluation was based on normalized intensities. Relative peak intensities (RI) were calculated based on the sum of intensities of all assigned peaks in each sample. The RI is a semi-quantitative measure of the contribution of formulas to the overall DOM in the sample, accessible by this method. The RI also allow the comparison of peak intensities across samples, with an increase in RI indicating an enrichment of the respective compounds contributing to the overall DOM. Throughout the manuscript, we refer to an assigned DOM molecular formula as compound, although a DOM molecular formula potentially represents multiple isomers (Han et al., 2021).

To calculate the probability of the existence of aromatic structures, the modified aromaticity index (AI mod) was used (Koch & Dittmar, 2006, 2016). The AI mod assumes that half of oxygen forms a C–O double-bond and is an index applied for identification of aromatic (0.5 > AI mod > 0.67) and condensed aromatic structures (AI mod ≥ 0.67) from FT-ICR-MS data (Koch & Dittmar, 2006, 2016). The intensity-weighted average

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($_{wa}$) of elemental ratios (H/C, O/C, N/C, S/C) and of AI mod was also calculated and used as aggregated DOM molecular descriptors. For molecular weight, the average *m/z* was used instead of intensity-weighted average because the highest peaks are located around 400 *m/z*.

2.6. Statistical Analysis

Analysis of variance (ANOVA) was used to test for differences in group means (DOC concentration, absorption quality indices, seasons, and aggregated DOM molecular descriptors) followed by a Tukey's test to determine which groups were significantly different. The *t*-test was used to test for significant differences in discharge values (two groups only). The coefficient of variation (CV) was also applied to describe the relative variability of absorption quality indices. The separation of sampling sites into zones was also evaluated by ANOVA and principal component analysis (PCA). PCA is a nonsupervised ordination method used to detect patterns in a multivariate data set. PCA was performed with the aggregated DOM molecular descriptors (H/C_{wa}, O/C_{wa}, N/C_{wa}, S/C_{wa}, m/z_{mean}, and AI mod_{wa}) calculated from the shared formulas between the samples within each of the three zones ($n = 98$ samples in total). All variables were centered and scaled before the PCA was calculated. In order to analyze the spatial patterns of DOM composition, the relationship between RI of compounds and DOC concentration was tested in the subset of compounds shared within samples of the same zone and for each zone separately. Pearson's correlation was used to test whether the relationship between RI and DOC concentration was significantly ($p < 0.05$) positive or negative. To control the false discovery rate of multiple testing, *p*-values were adjusted using Benjamini and Hochberg "BH" method (Benjamini & Hochberg, 1995) before the nonsignificant correlated formulas were filtered out. To better compare the intensity distribution among DOM source samples, intersample rank was applied to the normalized intensity (RI) calculated for the shared compounds among the three samples (Herzsprung et al., 2012). All statistical analyses were performed using R (R-Core-Team, 2017).

3. Results

3.1. Spatial Patterns of Mobilized DOM in the Große Ohe Catchment

Over the period of study (June–November 2018 and April--November 2019), baseflow conditions were identified at 26% and 25% of the time at MGL and at HSL, respectively (Table S1). In 14% of the time baseflow conditions were simultaneously identified in both locations and, based on this, baseflow conditions were inferred at HSU. The average DOC concentration retrieved from the spectrophotometers during baseflow conditions was very similar among MGL, HSU, and HSL (2.6 ± 0.3 mg L^{-1}, 2.6 ± 0.5 mg L^{-1}, and 2.6 ± 0.6 mg L^{-1}, respectively, Figure 2a), with no significant difference (ANOVA one way, $p = 0.57$). However, mean specific discharge was significantly (*t*-test, $p < 0.001$) higher at MGL (17.1 ± 15.8 L s^{-1} km^2) compared to HSL (14.1 ± 9.7 L s^{-1} km^2) (Figure 2b). Moreover, at each continuous monitoring site, DOC concentration was not significantly different between summer and fall at baseflow conditions, while discharge was significantly different (ANOVA one-way, $p < 0.001$) between all seasons (Figure S3). During spring, however, DOC concentration was significantly higher ($p < 0.001$) compared to the other seasons. In accordance with the high resolution DOC data from the spectrophotometers, DOC concentration in all grab samples used for FT-ICR-MS analysis was not significantly different between the three defined zones (ANOVA one-way, $p = 0.07$).

As indicators of DOM quality, SUVA and E_2:E_3 were used. The range of SUVA values during the study period (from 4 to 8 L m^{-1} mg-C^{-1}) was in the range as reported for other small forested catchments in Germany (e.g., Broder et al., 2017; Werner et al., 2019). The highest median SUVA and E_2:E_3 values were recorded at HSL, followed by MGL and HSU (Figures 2c–2d). The coefficients of variation of SUVA and E_2:E_3 were also higher at HSL (8.1% and 13.6%, respectively) as compared to HSU (5.9% and 7.5%, respectively) and MGL (7.1% and 6.6%, respectively). SUVA and E_2:E_3 were significantly different between the monitoring sites (ANOVA one-way, $p < 0.001$). Regarding season, SUVA was only significantly different between fall and spring (ANOVA one-way, $p < 0.001$) and between fall and summer (ANOVA one-way, $p < 0.001$), while E_2:E_3 was only significantly different between spring and fall (ANOVA one-way, $p < 0.001$) and between spring and summer (ANOVA one-way, $p < 0.001$) (Figure S3). Spectral slopes as $S_{275-295}$ has also been widely used to assess DOM molecular weight (Helms et al., 2008). $S_{275-295}$ showed highest variability at HSU, but

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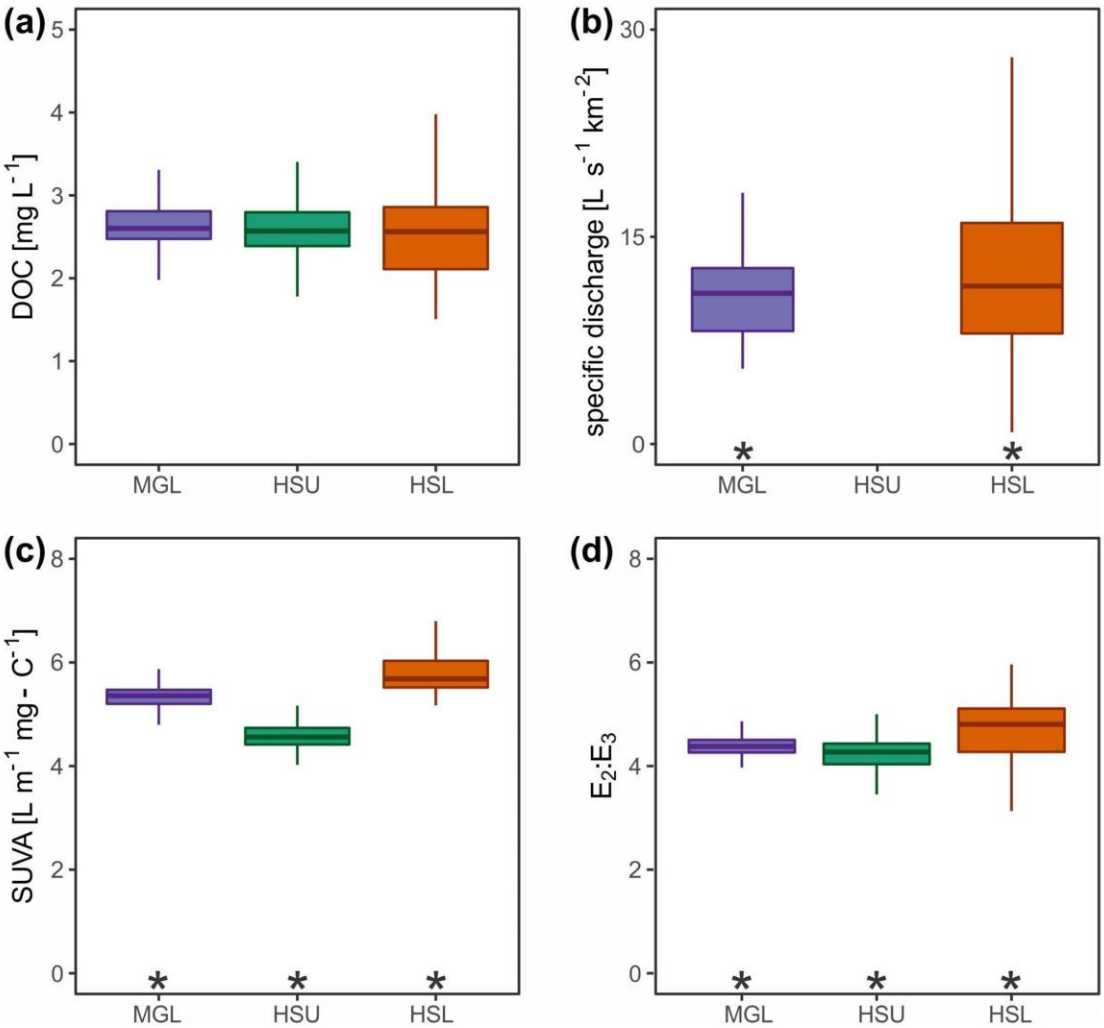

Figure 2. Boxplot of spectrophotometer data recorded at baseflow conditions during the study period for (a) dissolved organic carbon (DOC) concentration, (b) specific discharge, (c) specific ultraviolet absorbance (SUVA), and (d) E_2:E_3. Bold horizontal line represents median value and asterisks indicate a significant ($p < 0.05$) difference between zones. Outliers are not displayed.

in general a similar trend was shown by $S_{275\text{-}295}$ and E_2:E_3 (Figure S4). Overall, DOM quality described by absorption indices showed higher variability, but also a more aromatic and low MW DOM in the HSL zone, which is less steep and covers a larger portion of hydromorphic soils, compared to the upstream zones (HSU and MGL).

Detailed molecular composition of the DOM from almost a hundred collected samples (11 sampling campaigns) during the study period (1.5 years) could be derived from the FT-ICR-MS analysis. In total, 23,712 unique molecular formulas were assigned to DOM compounds in this data set with a comparable number of compounds identified in each sample (Table 1). Yet, there is a significant difference in the RI of compounds shared between the three zones (ANOVA, $p = 0.004$). Tukey's test revealed that the RI of compounds at MGL was significantly different from HSL ($p = 0.02$), but not between HSU and HSL ($p = 0.17$) or between MGL and HSU ($p = 0.29$). Moreover, samples of the same zone have a high degree of compositional similarity

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Table 1
DOC Concentration and FT-ICR-MS Data for all Grab Samples Used in This study

	MGL	HSU	HSL	Shallow groundwater	Riparian soil groundwater	Riparian zone surface water
Samples	32	33	33	1	1	1
DOC concentration (mg L^{-1})	3.4 ± 0.8	3.3 ± 0.8	3.8 ± 1.3	0.4	25.2	10.2
Identified compounds	6537 ± 644	6692 ± 705	6746 ± 600	7973	6932	6266
CHO %	50 ± 2	51 ± 3	52 ± 2	46	50	53
CHNO %	38 ± 2	37 ± 1	38 ± 1	39	35	35
CHOS %	9 ± 1	9 ± 1	9 ± 1	9	10	8
H/C_{wa}	1.08 ± 0.01	1.09 ± 0.01	1.09 ± 0.01	1.18	1.04	1.02
O/C_{wa}	0.45 ± 0.01	0.45 ± 0.01	0.46 ± 0.01	0.43	0.50	0.45
N/C_{wa} ($\times 10^{-2}$)	1.22 ± 0.08	1.15 ± 0.07	1.13 ± 0.06	1.21	1.05	1.14
S/C_{wa} ($\times 10^{-3}$)	1.60 ± 0.26	1.56 ± 0.25	1.60 ± 0.24	1.78	3.04	1.47
AI mod_{wa}	0.36 ± 0.01	0.36 ± 0.01	0.36 ± 0.01	0.31	0.38	0.40
m/z_{mean}	474.39 ± 11.26	474.92 ± 10.75	477.29 ± 13.12	494.2	486.5	476.2
Shared compounds among all samples	2970	3021	2972	4440*	4440*	4440*
Mean RI of shared compounds	81	81	82	91*	92*	90*

Note. For MGL, HSU, and HSL, values are represented as mean ± standard deviation calculated for all samples collected at each zone.
*Represent shared compounds and mean RI of shared compounds between the DOM source samples ($n = 3$).
Abbreviations: AI, aromaticity index; DOC, dissolved organic carbon; HSL, lower Hinterer Schachtenbach; HSU, upper Hinterer Schachtenbach; MGL, lower Markungsgraben; RI, relative peak intensities.

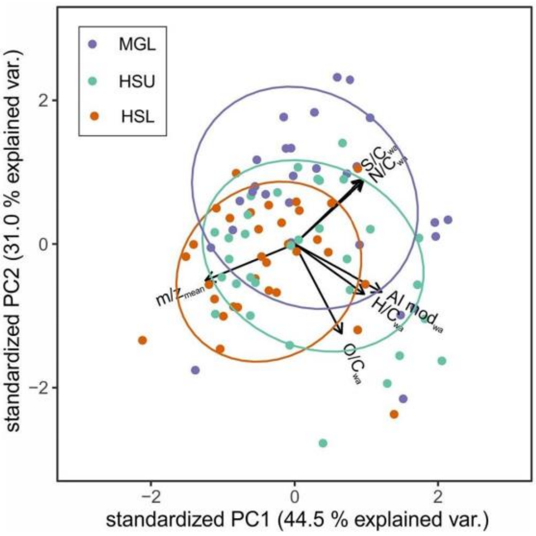

Figure 3. Biplot of principal component analysis (PCA) analysis of aggregated dissolved organic matter (DOM) molecular descriptors (H/C_{wa}, O/C_{wa}, N/C_{wa}, S/C_{wa}, m/z_{mean}, and AI mod_{wa}) derived from FT-ICR-MS data. PCA analysis includes all stream samples ($n = 98$) collected at the three different zones, represented by different colors. An ellipse with 95% confidence interval was drawn based on the normal distribution of data from each zone.

between them (45% of the peaks are shared between all samples from the same zone, comprising >80% of the RI in each spectrum), with minor contribution of unique peaks to the overall DOM composition (Table 1). Therefore, in the further analysis, only the compounds shared between samples from the same zone were considered.

Nevertheless, PCA revealed subtle differences in aggregated DOM molecular descriptors between MGL, HSL, and HSU (Figure 3). The first principal coordinate (PC 1) explains 44.5% of the total variation in the data set and the variables that most contribute to it are m/z_{mean}, AI mod_{wa} and H/C_{wa} (Table S2). Accordingly, O/C_{wa}, S/C_{wa}, and N/C_{wa} contribute the most to PC 2, explaining 31.0% of the total variation. Overall, PCA showed a slight ordination of samples from MGL to HSL. MGL samples tended to have higher N/C_{wa} and S/C_{wa}, while samples collected at HSL tended to have higher m/z_{mean} and O/C_{wa} (ellipses on Figure 3). HSU samples where distributed between HSL and MGL samples, indicating a transition between the steep and flat zone. Moreover, no apparent gradient for DOC concentration or sampling campaign evolving from the PCA was identified (result not shown). However, testing the difference in the aggregated DOM molecular descriptors used in the PCA via ANOVA resulted in no significant differences between zones ($p = 0.54$), suggesting that using less aggregated parameters, such as the distinct RI of the underlying individual compounds, may be better suited to reveal DOM composition differences along a small environmental gradient. Furthermore, the longitudinal profile of aggregated DOM molecular descriptors only show significant (negative) trend for N/C_{wa} and S/C_{wa} from upstream toward downstream and no apparent trend evolving from season (Figure S5).

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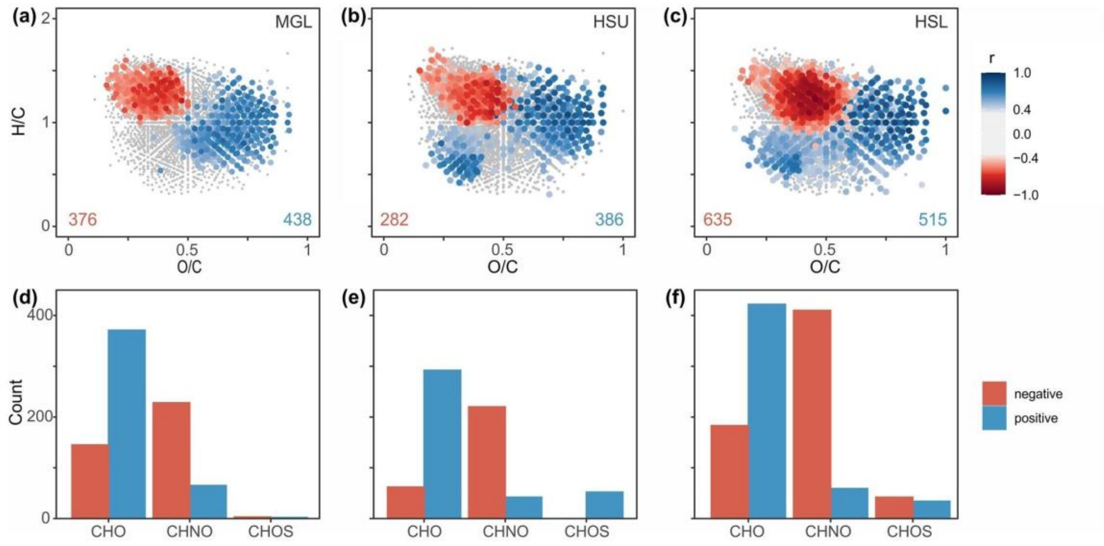

Figure 4. Van Krevelen diagram of formulas in (a) lower Markungsgraben (MGL), (b) upper Hinterer Schachtenbach (HSU) and (c) lower Hinterer Schachtenbach (HSL) color coded according to the Pearson's correlation coefficient (*r*) of relative peak intensity with dissolved organic carbon (DOC) concentration (top) and the respective number of formulas per formula class negatively/positively correlated in (d) MGL, (e) HSU, and (f) HSL. In (a-c) the grey dots represent formulas for which the Pearson's correlation coefficient was not significant and the numbers on the bottom right and left represent the total number of compounds significantly positively and negatively correlated, respectively.

3.2. Molecular Composition of the Mobilized DOM Under Baseflow Conditions

Due to the high degree of compositional similarity among the samples of the same zone (even before the filter of shared samples), the significant difference in the RI of compounds between the zones and the gradient evolving from PCA, the relationship between RI of compounds and DOC concentration was tested for each zone separately. At HSL, the percentage of formulas with RI significantly ($p < 0.05$) correlated with DOC concentration (39%) was higher as compared to HSU (22%) and MGL (27%). From the total number of compounds for which RI was significantly correlated with DOC concentration, 12% were positively correlated in all three zones. Similarly, 13% were negatively correlated in all three zones. For all zones, the negatively correlated compounds were characterized by high H/C and low O/C (Figures 4a–4c), and were predominantly of the CHNO formula class (Figures 4d–4f). In contrast, the chemical characteristics of the positively correlated compounds differed between zones. At MGL, the positively correlated compounds with DOC concentration were oxygen-rich (high O/C ratio), while at HSU and HSL there was a second cluster of compounds characterized by both low O/C and low H/C. The positively correlated compounds at high O/C ratio were mainly of CHO formula class, while the cluster at low O/C and low H/C was characterized by CHOS and CHO formula classes (Figure S6). This resulted in an overall larger contribution of CHOS formulas to the significantly correlating formulas at HSL as compared to MGL. Overall, formulas positively correlated with DOC concentrations were oxygen rich and less saturated, indicating that elevated stream water DOC values were associated with more aromatic and polar DOM.

3.3. Composition of DOM Sources in the Catchment

Three possible sources in the catchment contributing to stream DOM were sampled during the period of study as representative of shallow groundwater (spring), riparian soil groundwater (~65 cm, piezometer) and riparian zone surface water DOM (puddle). Each DOM source was sampled one time and, therefore, there is an uncertainty associated with the temporal variability of these sources. However, the number of compounds shared between 2 (for shallow groundwater) and 3 (for each riparian soil groundwater and riparian zone surface water) samples of the same source and the distribution of the CV values of the RI of

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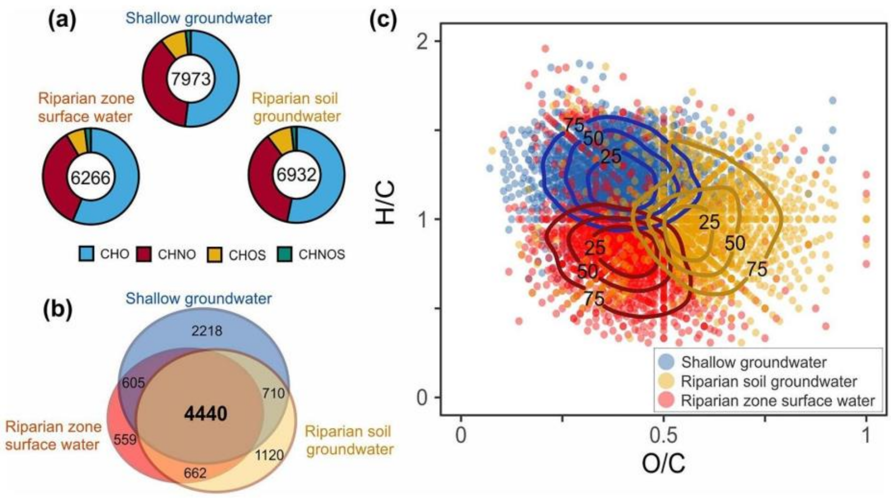

Figure 5. (a) Distribution of formula classes of all formulas present in each dissolved organic matter (DOM) source sample, (b) shared and unique formulas assigned to three DOM source samples shallow groundwater (blue), riparian soil groundwater (yellow) and riparian zone surface water (red), and (c) van Krevelen diagram of formulas shared between the DOM source samples ($n = 4{,}440$) colored according to the source in which the compound presented the relative highest relative intensity (i.e., lowest inter-sample rank) among the source samples. In (a) the value in the center is the total number of formulas assigned and in (c) the density contours include 25%, 50%, and 75% of the formulas in each sample.

these compounds showed less variability than DOM in stream samples (Figure S7). Thus, we assume here that at baseflow conditions the composition of DOM sources are more stable during seasonal changes than the composition of DOM in the stream, which is subject to varying hydrologic conditions. The source DOM samples also displayed some unique compounds (~40% of all formulas assigned in each sample), which can represent characteristic fingerprints of those sources. However, as the unique compounds represent less than 10% of the total intensity in each mass spectrum and a detailed molecular characterization of DOM sources is outside of the scope of this study, the unique compounds identified in the source samples will not be discussed further. The variation in the DOC concentration between the DOM source samples was larger than the variation observed in the stream samples (Table 1). The DOC concentrations in the riparian zone surface water and riparian soil groundwater were higher than the ones sampled in the stream, while the shallow groundwater had the lowest DOC concentration of all samples during the period of study. Among the source samples, shallow groundwater had the largest number of formulas assigned, followed by the riparian soil groundwater and riparian zone surface water (Figure 5a). The formula class distribution in the DOM source samples was similar between them and the stream samples, with a predominance of CHO, typical for terrestrial DOM. However, the average *m/z* of the DOM source samples (shallow groundwater and riparian soil groundwater) was higher than the average in stream samples (Table 1).

In total, 4,440 compounds were shared between all three DOM source samples (accounting for 63% of all assigned formulas on average), representing 90% of total intensity (Figure 5b). The intersample rank analysis revealed distinct differences in the molecular composition between them (Figure 5c). The shallow groundwater DOM was characterized by the relative higher RI of compounds with high H/C and low O/C, being attributed as mostly aliphatic and saturated compounds. For the riparian zone surface water DOM, the relative most intense peaks were characterized by unsaturated and aromatic formulas having low O/C and low H/C values. The riparian soil groundwater DOM also had a relative intense signal in high O/C ratio and variable H/C ratio.

In total, 96% of the compounds positively/negatively correlated with DOC concentration in the stream samples (Figures 4a–4c) were also present in the three DOM source samples (Figure 6). Most of the formulas with relative higher RI in samples from the riparian soil groundwater and from the riparian zone surface

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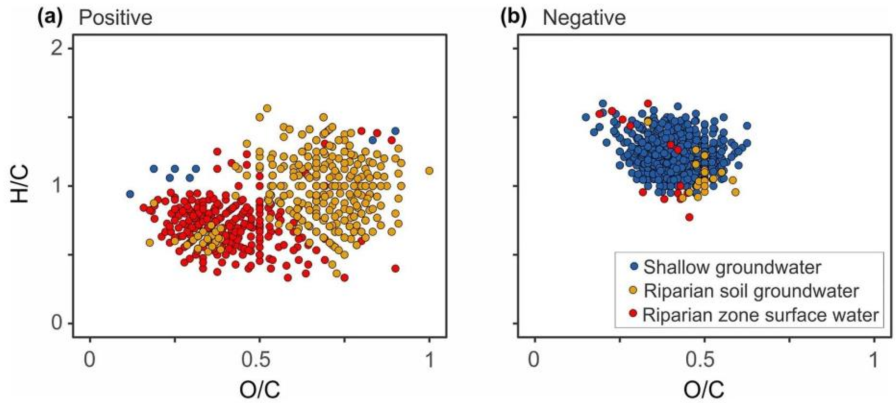

Figure 6. Van Krevelen diagram showing the compounds present in the stream samples of the three zones (lower Markungsgraben [MGL], upper Hinterer Schachtenbach [HSU], and lower Hinterer Schachtenbach [HSL]) for which the relative intensity is significantly (a) positive or (b) negative correlated with dissolved organic carbon (DOC) concentration and also present in the dissolved organic matter (DOM) source samples. Dots are colored according to their lowest inter-sample rank (i.e., highest relative intensity) among the DOM source samples.

water (48% and 49%, respectively) corresponded to the compounds positively correlated with DOC concentration in the stream samples at the three zones, while most of the compounds (94%) with relatively high RI in the shallow groundwater DOM agreed with the ones that were negatively correlated with DOC concentration (Figure 6).

4. Discussion

4.1. Mobilization of DOM Under Baseflow Conditions

The variation in DOC concentrations over base and event flow recorded during the period of study is in the range reported in the literature for other German forested catchments (Beudert et al., 2012; Werner et al., 2019) and the baseflow concentrations are also similar to those reported for a forested catchment in the USA (Singh et al., 2015). The comparatively low DOC concentrations at baseflow conditions observed in our study are expected since, at baseflow conditions, DOM percolates through the mineral soil profile, which has generally low DOC concentrations (Inamdar, Finger, et al., 2011; Kaiser & Guggenberger, 2000). However, similar to northern catchments (Monteith et al., 2007), a significant increase in DOC concentration has been observed in the past 20 years in the Große Ohe catchment (Beudert et al., 2012). Moreover, it is difficult to isolate single factors driving this increase (Roulet & Moore, 2006). In this respect, a better understanding of the linkages between discharge and DOM dynamics is essential to assess changes in the terrestrial carbon cycle (Ledesma et al., 2015; Roulet & Moore, 2006).

In our study, DOC concentration showed no significant spatial variation (Figure 2a). However, the variability of DOC concentration and discharge is especially higher for HSL. Additionally, significantly higher DOC concentration and lower apparent MW were observed in spring for all zones (Figure S3), indicating that the wetter conditions of the system may hydrologically connect DOM sources, especially from shallower layers of the soil, which are more conductive (Bishop et al., 2004; Ledesma et al., 2015) and export less microbially degraded DOM (Roth et al., 2019). However, at a lower temporal scale, no clear seasonal pattern was observed in the aggregated molecular descriptors of DOM composition (Figure S5).

In contrast to the DOC concentration, DOM quality derived from the high-frequency UV-Vis data showed significant variability among the zones (Figures 2c–2d). However, the pattern observed in SUVA was not found in the AI mod_{wa} values derived from the FT-ICR-MS data. The disagreement between SUVA and AI mod_{wa} may be due to numerous reasons, like the high level of aggregation applied to the calculation of AI mod_{wa}, the distinct frequency of sampling, or the fact that SUVA only captures the UV-active part of the

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DOM, while the mass spectrometry technique captures also the UV-inactive part. Considering the aggregated molecular descriptors derived from molecular information, the large number of chemical parameters were able to separate the zones according to N/C_{wa}, S/C_{wa}, O/C_{wa}, and m/z_{mean} in the PCA analysis. Samples collected at MGL showed overall higher N/C_{wa} and S/C_{wa} compared to HSU and HSL (Figure 3, Figure S5). High N/C ratios in terrestrial DOM is used as a marker for DOM derived from microbial origin and often attributed to DOM mobilized in the deep layers of the soil (Kaiser et al., 2004; Malik et al., 2016). The sources of sulfur (S) in terrestrial and aquatic DOM are not fully constrained yet (Kaiser et al., 2001; Ksionzek et al., 2016). For example, the presence of S in DOM sampled in soil or surface water in forested catchments can be originated from atmospheric deposition (Vestreng et al., 2007), degradation of living tissues (Mangal et al., 2016), abiotic sulfurization (Poulin et al., 2017), and/or bacterial dissimilatory reduction (Kang et al., 2014). PCA revealed that the most pronounced compositional difference in our data set was that samples collected at the lower part of the Große Ohe catchment (HSL) represented DOM with a higher O/C_{wa} ratio and higher m/z_{mean} compared to the upper, much steeper part of the catchment (MGL). Although these differences are numerically small, they can be seen as significant given that DOM composition in rivers is quite similar around the world (Wagner et al., 2015). Moreover, the spectrophotometers also captured the signal of generally more aromatic DOM in the lower part of the catchment (Figure 2). High m/z, aromaticity, and O/C ratio indicate the input of fresh plant-derived material (Seifert et al., 2016). The pronounced difference in DOM composition between MGL and HSL and the more microbially processed DOM fingerprint in the upper part of the catchment also indicates that, in general, the water is flowing through deeper layers of the soil in the upper part of the catchment compared to the floodplain area. Since no in-stream or photo degradation processes are expected to substantially alter DOC concentration or DOM quality in our study area, as water residence time in the catchment is low, we conclude that the contribution of different DOM sources may be the main drivers for the observed changes in DOM quality and composition along the stream (Singh et al., 2015). The wetter conditions at the floodplain area may favor the connection and contribution of more superficial layers of the soil DOM in constrast to the steep terrain at the upper part of the catchment.

4.2. Identification of DOM Sources

In the first- and second-order streams, a similar number of compounds were assigned and no clear trend was observed in the unique compounds in the samples (Table 1). Consequently, shifts in RI rather than presence and absence better describe the DOM dynamics. The correlation between RI of compounds and DOC concentration showed that the amount and composition of DOM were connected even under baseflow conditions in the Große Ohe catchment (Figure 4). Whereas a negative correlation between DOC concentration and RI of compounds indicates a relative decrease in the contribution of these compounds to the overall DOM composition, an increase indicates enrichment of them. Compounds of which the RI was negatively correlated with DOC concentration were similar between all three zones, indicating their large contribution to the background DOC exported at low DOC concentrations. These compounds can be described as carboxylic-rich alicyclic molecules and lipid-like (Lam et al., 2007), but the high structural diversity present in DOM limits the assignment of these formulas to more refined molecular categories (Hertkorn et al., 2008; Patriarca et al., 2020). Moreover, the compounds for which RI is inversely correlated with DOC concentration in the stream samples are mostly representative of CHNO (Figure 4). This compound class has also higher contribution in the shallow groundwater sample (Table 1). At the three locations, most of the compounds negatively correlated with DOC concentration correspond to the relatively most intense compounds in the shallow groundwater sample (Figure 6). The low DOC concentration, high nitrogen content, and high contribution of aliphatic compounds in the shallow groundwater sample are in line with the composition ascribed to groundwater DOM flowing through deep flow paths (Inamdar, Singh, et al., 2011; Kaiser & Kalbitz, 2012). The agreement between the negatively correlated compounds and the shallow groundwater is an indication that at low DOC concentration the stream water samples, independently of the location, may have higher contributions of deep groundwater inputs (Peralta-Tapia et al., 2015). The also higher m/z_{mean} values in the shallow groundwater indicates that the low MW compounds become less abundant at deeper layers of the soil as a result of the consumption by microorganisms (Roth et al., 2019).

On the other hand, compounds positively correlated with DOC concentration changed between zones, indicating the contribution of distinct sources at different zones (Figure 4). We assume that the similar pattern

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observed between HSU and HSL and distinct from MGL is not mainly caused by the flow of KS into HS, but rather a change in DOM sources from upstream to downstream parts of the catchment. In all zones, the compounds enriched at high DOC concentrations are mostly characterized by high O/C ratio and variable H/C ratio and may be attributed to lignin and tannin degradation products. These compounds are markers for DOM mobilized from superficial layers of the soil (Kaiser & Kalbitz, 2012; McDonough et al., 2020). In the MGL zone, the compounds significantly positively correlated with DOC concentration share compositional features with the compounds most characteristic for the riparian soil groundwater source sample (as observed from the intersample ranks, Figure 5). The riparian soil groundwater DOM source sample was characterized by the highest O/C ratio and relative high aromaticity among the DOM sources sampled, matching the description of riparian soil groundwater DOM, which is younger and less processed compared to deep groundwater (Ledesma et al., 2018; McDonough et al., 2020). Furthermore, the comparably high contribution of CHNO molecular formula in both the riparian soil groundwater and the shallow groundwater samples indicates that DOM is more biologically processed in both samples compared to the riparian zone surface water DOM source sample (Longnecker & Kujawinski, 2011). In addition, in the HSL and HSU, the positively correlated compounds also overlap with the characteristic compounds in the riparian zone surface water sample (low H/C and low O/C ratios) (Figure 6). The riparian zone surface water DOM source was sampled in a puddle in the terrain, a feature which was only observed in the floodplain area in HSL. Thus, it is expected that their signal will not be found in the upper parts of the catchment. Moreover, the riparian zone surface water sample had the highest AI mod_{wa} recorded and relatively high DOC concentration. In fact, these pools may represent a very important DOC source for small headwater streams, when hydrologically connected to the stream (Ploum et al., 2020). Moreover, all DOM sources were sampled at the lower part of the HS catchment, which may under represent the sources contributing at the upper part of the catchment, especially at MG. Overall, although DOC concentration was not significantly different between zones at baseflow conditions, the relationship between RI of compounds and DOC concentration is indicative of different sources of DOM being activated under baseflow conditions upstream compared to downstream.

Interestingly, formulas being enriched at higher DOC concentration at baseflow conditions reflect the findings discussed in the literature regarding rain event-based changes in DOM composition, with changes in DOM character from more aliphatic-like to more aromatic-like (Wagner et al., 2019). At comparatively higher DOC concentration during baseflow and peak discharge during storm events, more aromatic- and humic-rich DOM are exported to the stream compared to lower discharge values (Hood et al., 2006; Inamdar, Singh, et al., 2011). However, the contribution of terrestrial sources and amplitude of the changes in DOM composition during baseflow conditions are smaller compared to the ones reported for DOM mobilized during storm events.

5. Conclusions

Dominant trends in DOC concentration and DOM quality were captured by spectrophotometer probes in the stream, while discrete FT-ICR-MS data allowed to specifically characterize DOM molecular composition and link the findings from in-stream samples with specific DOM sources. Remarkably, nuances in DOM composition could be distinguished from the FT-ICR-MS data, highlighting the applicability of the ultrahigh-resolution technique for studying DOM dynamics. The detailed molecular level view of DOM composition could also elucidate the contribution of different DOM sources in the catchment to the mixed signal in-stream. As described in the River Continuum and River as Chemostat concepts, we were able to demonstrate the major contribution of terrestrial DOM sources and the importance of riparian and wetland areas for DOM dynamics at headwater streams even during baseflow conditions.

The information regarding DOM sources contributing to baseflow DOM concentration and composition along the stream is important in the construction of models of DOC export, improving our ability to predict hydrological and biogeochemical responses to environmental change and providing insights into changes in water sources. The elucidation of DOM sources in the Große Ohe catchment is also important given the increasing trend in DOC concentration in the catchment, the impact of DOC concentration in macroinvertebrate communities, and the possible changes in the hydrological conditions of the system in the context of climate change.

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Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Data from this article can be found at Figshare (da Silva et al., 2021): da Silva, M. P.; Blaurock, K.; Beudert, B.; Fleckenstein, J. H.; Hopp, L.; Peiffer, S.; Reemtsma,T.; Lechtenfeld, O. J. (2021): Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments. Figshare. Dataset (https://doi.org/10.6084/m9.figshare.14495175.v1).

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Supporting Information for

Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments

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Text S1. Calibration of spectrophotometers

During the monitoring period the spectrophotometers were installed on June 12th, 2018 and stayed in the field until November 14th, 2018 when they were removed and remained disconnected during winter season. On April 8th, 2019 the same instrument was installed in the same place at each location. Yet, a small increase in DOC concentration between 2018 and 2019 can be observed for all three instruments (Figure S2). The increase, observed comparing the minimum values recorded each year, is systematic for all locations (0.7 mg L^{-1}), with minimum values of 1.7 (MGL), 0.7 (HSU) and 1.3 (HSL) mg L^{-1} in 2018, and 2.4 (MGL), 1.4 (HSU) and 2.0 (HSL) mg L^{-1} in 2019. In contrast to the minimum DOC concentration, the annual median of DOC concentration during baseflow in 2018 for MGL (2.7 mg L^{-1}), HSU (2.5 mg L^{-1}) and HSL (2.4 mg L^{-1}) is similar to the annual median of baseflow DOC concentration in 2019 for the same location (MGL=3.4 mg L^{-1}, HSU=3.1 mg L^{-1}, and HSL= 3.0 mg L^{-1}). However, DOC concentration is strongly influenced by the wetness state of the system and by the number and amplitude of storm events in each year. Moreover, the difference in the minimum value between the two years is small and the fit of calibration curve is not perfect for all locations (r^2= 0.91, 0.98 and 0.95 at MGL, HSU and HSL, respectively), but still in the range reported in literature (Hoffmeister et al., 2020). Additionally, monthly samples were taken and DOC concentration was measured in lab to calibrate the field measurements. The calibration was done for both years together, during the processing of the data and after all data were recorded. Using the available data, we cannot draw conclusions about systematic bias in the spectrophotometer data coming from the setup of the sensors based on the minimum or median values. Thus, we decided to use the spectrophotometer data without further correction of the inter-annual variability. Nevertheless, the spectrophotometers data as used in this manuscript are highly aggregated and discussed as variability between zones (where we observed a consistent shift between years) using robust metrics, without emphasis on inter-annual trends.

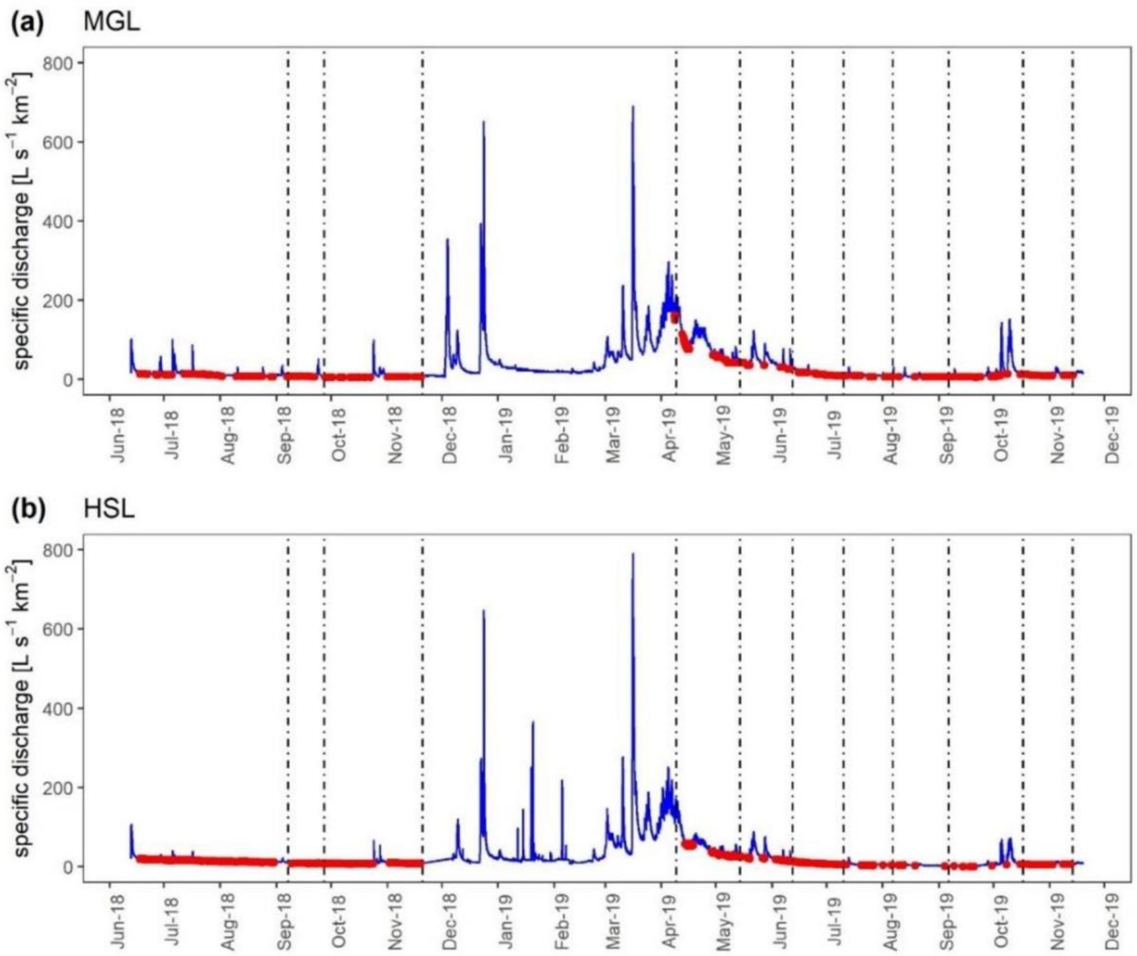

Figure S1. Discharge recorded between June 2018 and December 2019 (in blue) and identified baseflow conditions (in red) at (a) MGL and (b) HSL during the studied period from June 2018 to November 2018 and from April 2019 to November 2019. Vertical dashed lines indicate days of sampling campaigns to collect samples for FT-ICR-MS analysis.

3

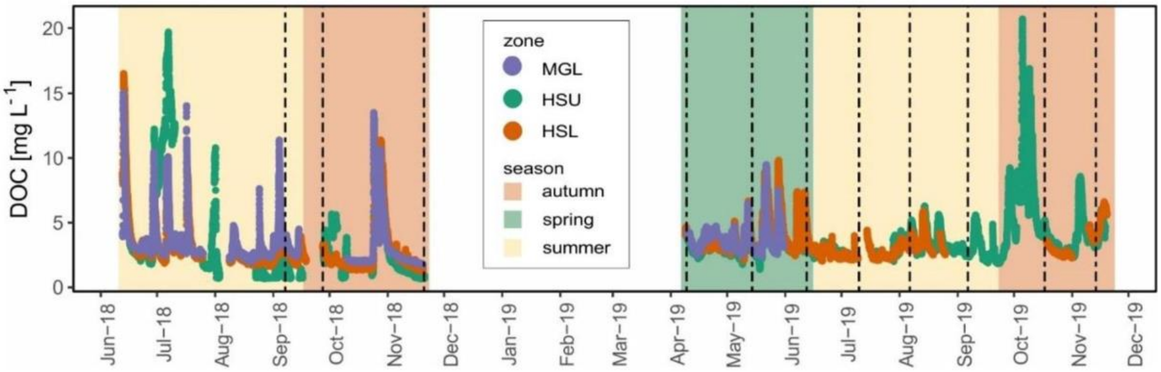

Figure S2. DOC concentration derived from spectrophotometers for all discharge conditions. During winter months (December-March) the spectrometers were removed from the field. Other gaps in the time series are caused by the failure of the sensors. Vertical dashed lines indicate days of sampling campaign to collect samples for FT-ICR-MS analysis and background color indicates season.

4

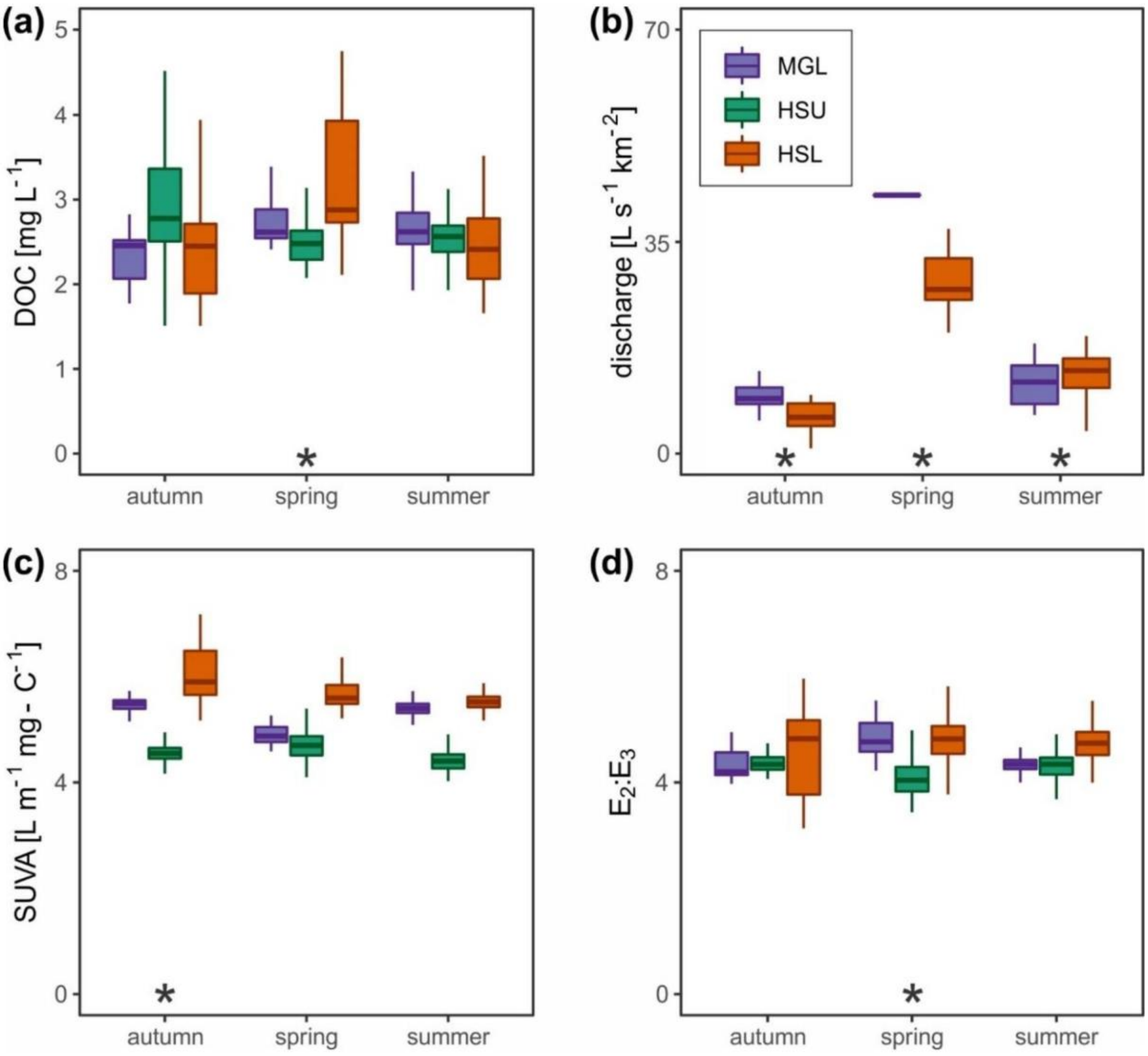

Figure S3. Boxplot of data recorded by the spectrophotometers for (a) DOC concentration, (b) specific discharge, (c) SUVA and (d) E_2:E_3. Bold horizontal line represents median value and asterisks indicate a significant ($p<0.05$) difference between seasons. Outliers are not displayed.

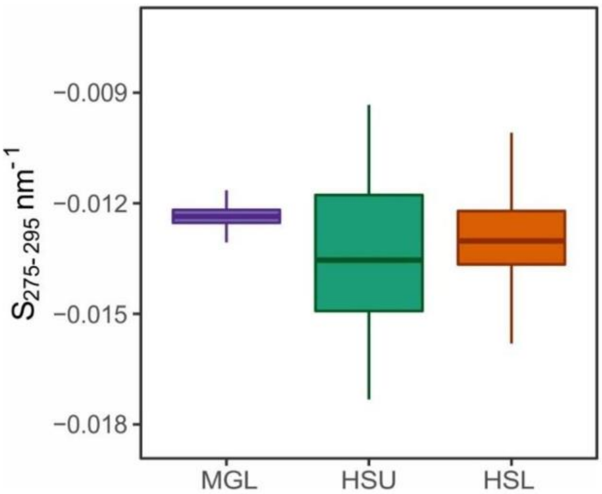

Figure S4. Boxplot of spectral slope calculated between 275 and 295 nm according to Helms et al. (2008). Outliers are not displayed.

6

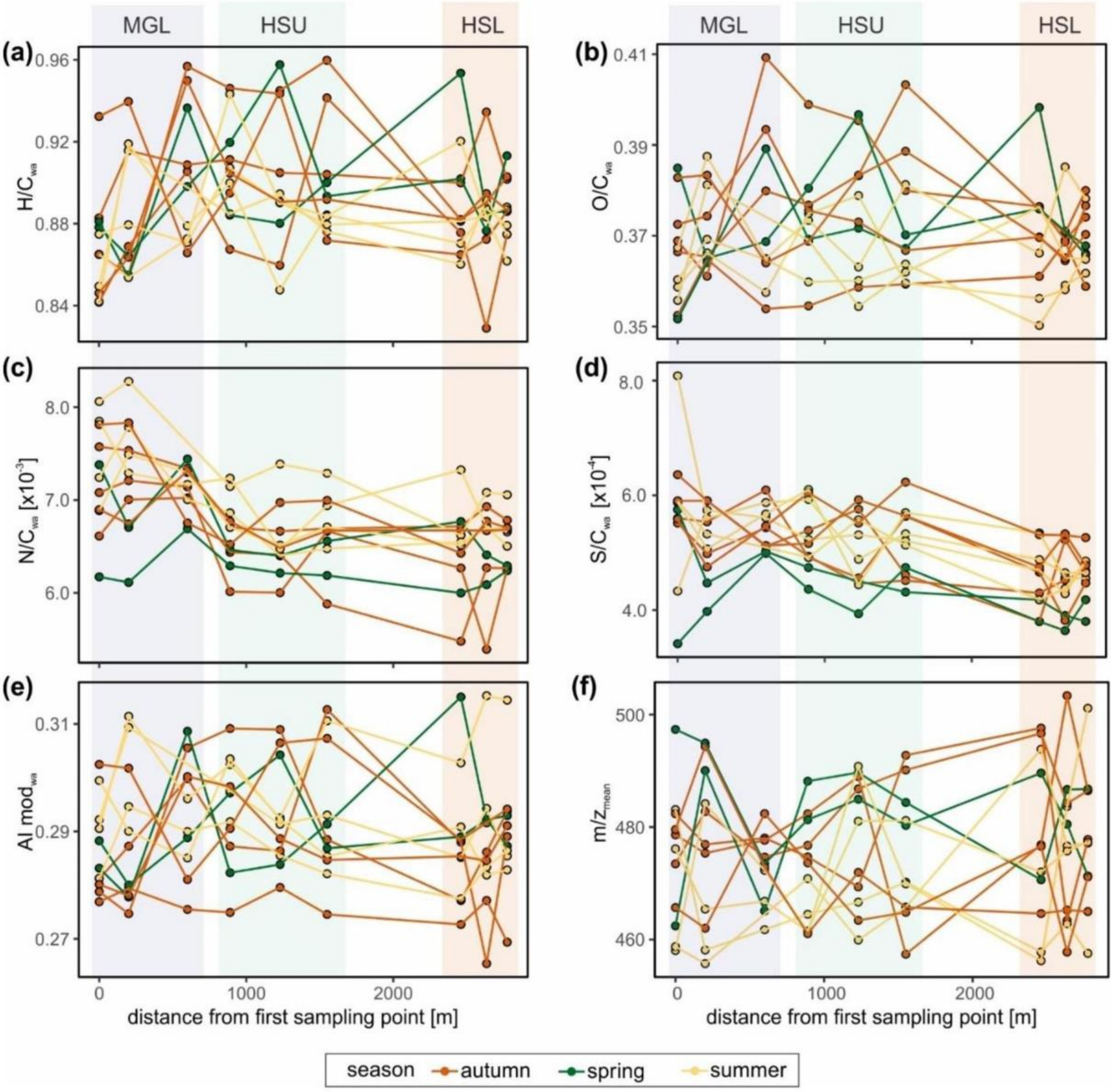

Figure S5. Longitudinal profile of (a) H/C_{wa}, (b) O/C_{wa}, (c) N/C_{wa}, (d) S/C_{wa}, (e) AI mod_{wa} and (f) m/z_{mean} calculated from the shared compounds between samples of the same zone and colored according to the calendar season. The distance was calculated linearly from the sampling point further upstream towards downstream. A significant (ANOVA one-way, $p<0.05$) longitudinal trend was observed only for N/C_{wa} and S/C_{wa} with higher values sampled upstream compared to downstream.

7

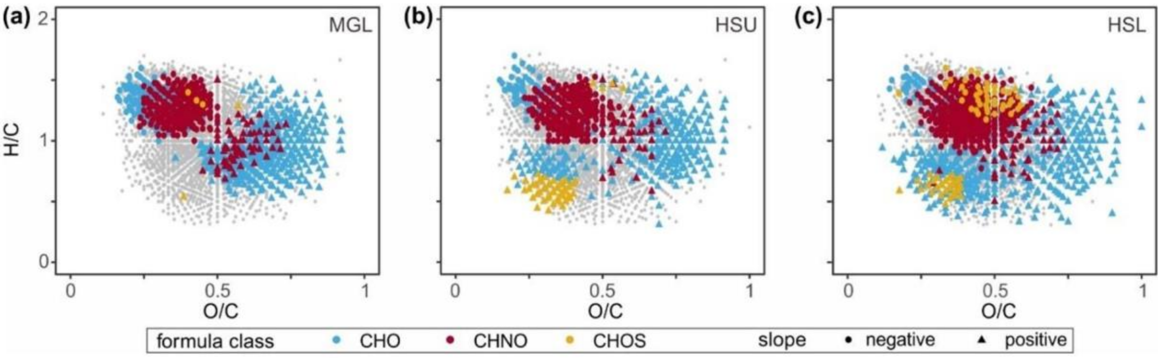

Figure S6. Van Krevelen diagrams of compounds which relative intensity is significantly correlated with DOC concentration with the respective formula class in the stream samples at (a) MGL, (b) HSU and (c) HSL. Grey points represent the formulas present in all samples within zone, but not significantly correlated with DOC concentration.

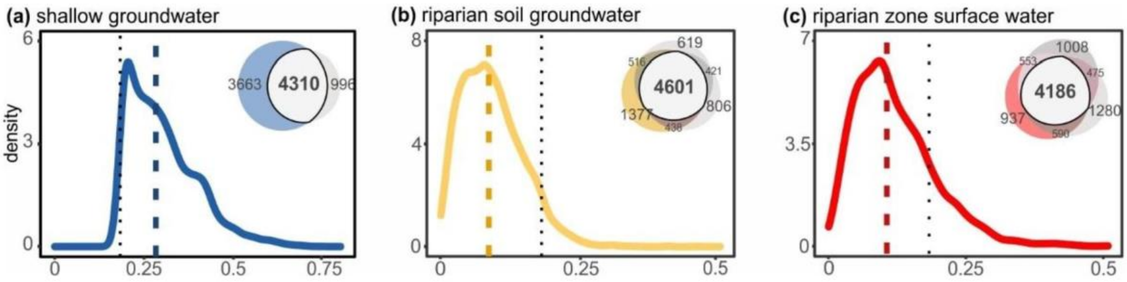

Figure S7. Density plot of coefficient of variation (CV) of the relative intensity for (a) two samples collected in the spring (shallow groundwater), (b) three samples collected from the piezometer (riparian soil groundwater) and (c) three samples collected on puddles (riparian zone surface water) and the respective Venn diagram of shared compounds between the samples on top right. Dashed line represent the mean CV of the samples from the same DOM source and dotted line the mean CV from all stream water samples (i.e. 11) collected at one sampling site at HSU (closer to the sources location, see Figure 1). The colored segment in each Venn diagram represent the sample used in the main text for comparison with the stream water data. Samples shown here were collected at different dates during the study period (June-November 2018 and April-November 2019).

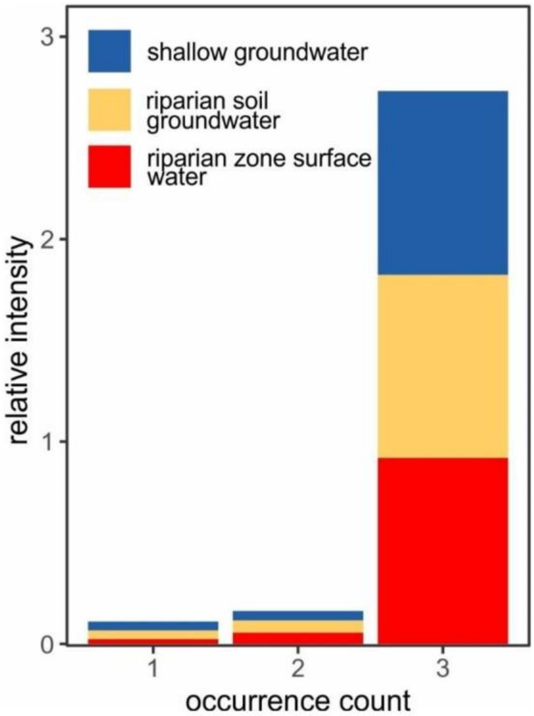

Figure S8. Sum contribution of relative intensity of compounds present in 1, 2 and 3 DOM source samples. Three source samples were analyzed: shallow groundwater, riparian soil groundwater, and riparian zone surface water.

Table S1. Number of data points recorded at the monitoring sites (MGL, HSU and HSL) for discharge and for the spectrophotometers (DOC concentration, SUVA and E_2:E_3) during the studied period, and number of data points after baseflow separation and filtering for consistency between all location. Baseflow conditions at HSU (*) were assumed when baseflow conditions were identified at MGL and HSL simultaneously.

Parameter	Data set	MGL	HSU	HSL
Discharge	All data recorded	36456	-	36456
	Identified baseflow conditions	9315	-	9461
	Baseflow conditions in all locations	5263	5263*	5263
DOC concentration	All data recorded	16240	26902	26589
	Baseflow conditions in all locations	2425	2260	3507
SUVA	All data recorded	16240	25278	20124
	Baseflow conditions in all locations	2344	1262	1510
E_2:E_3	All data recorded	16240	18806	20124
	Baseflow conditions in all locations	2345	1265	1687

Table S2. Contribution (%) of each variable to the four principal components resulted from the principal components analysis (PCA).

Variable	PC 1	PC2	PC3	PC4
H/C_{wa}	16.6	14.0	37.2	7.2
O/C_{wa}	11.2	25.4	4.2	20.8
N/C_{wa}	16.0	18.0	15.1	12.8
S/C_{wa}	15.4	18.6	2.1	36.3
m/z_{mean}	20.6	10.3	19.3	13.7
$AI\ mod_{wa}$	20.2	13.7	22.1	9.2

List of publications

Published:

Blaurock, K., Garthen, P., da Silva, M. P., Beudert, B., Gilfedder, B. S., Fleckenstein, J. H., Peiffer, S., Lechtenfeld O. J., Hopp, L. (2022). Riparian microtopography affects event-driven stream DOC concentrations and DOM quality in a forested headwater catchment. Journal of Geophysical Research: Biogeosciences, 127, e2022JG006831. ttps://doi.org/10.1029/2022JG006831

Blaurock, K., Beudert, B., Gilfedder, B. S., Fleckenstein, J. H., Peiffer, S., Hopp, L. (2021): Low hydrological connectivity after summer drought inhibits DOC export in a forested headwater catchment. Hydrology and Earth System Sciences, 25(9), doi:10.5194/hess-25-5133-2021

Da Silva, M. P., Blaurock, K., Beudert, B., Fleckenstein, J. H., Hopp, L., Peiffer, S., Reemtsma, T., Lechtenfeld, O. J. (2021): Delineating Source Contributions to Stream Dissolved Organic Matter Composition Under Baseflow Conditions in Forested Headwater Catchments. Journal of Geophysical Research: Biogeosciences, 126(8), doi:10.1029/2021JG006425

Von Fumetti, S.; Blaurock, K. (2018): Effects of the herbicide Roundup® on the metabolic activity of Gammarus fossarum Koch, 1836 (Crustacea; Amphipoda). Ecotoxicology, 27(9), doi:10.1007/s10646-018-1978-5

In preparation:

Blaurock, K., Beudert, B., Hopp, L.: High-resolution DOC measurements indicate seasonal differences in the contribution of three nested forested subcatchments to DOC export

Munir, M. U., Blaurock, K., Frei, S.: Impact of local climate change on groundwater resources and surface water availability in headwater catchments

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