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Opinion Article

Pathways and composition of dissolved organic carbon in a small agricultural catchment during base flow conditions

Alexander Eder[a,d,*], Gabriele Weigelhofer[b,c], Matthias Pucher[b,c], Alexandra Tiefenbacher[a], Peter Strauss[a], Martin Brandl[e], Günter Blöschl[d]

[a] Federal Agency for Water Management, Institute for Land and Water Management Research, Pollnbergstraße 1, 3252 Petzenkirchen, Austria
[b] University of Natural Resources and Life Sciences, Institute of Hydrobiology and Aquatic Ecosystem Management, 1180 Vienna, Austria
[c] WasserCluster Lunz - Biologische Station GmbH, 3293 Lunz am See, Austria
[d] Vienna University of Technology, Institute of Hydraulic Engineering and Water Resources Management and Centre for Water Resource Systems, Karlsplatz 13/222, 1040 Vienna, Austria
[e] Danube University Krems, Department for Integrated Sensor Systems, Dr.-Karl-Dorrek-Straße 30, 3500 Krems, Austria

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A B S T R A C T

The amount and composition of organic carbon are major controls on water quality and ecological processes in streams. In this study we explored the fate of the quantity of dissolved organic carbon (DOC) and the composition of dissolved organic matter (DOM) in an agricultural hillslope - stream network system. We conducted our study in the 66 ha HOAL (Hydrological Open Air Laboratory) in Lower Austria. We measured DOC of the soil eluates from different land use units, water samples from the stream and from seven tributaries, and estimated DOM components by fluorescent spectrophotometry and PARAFAC analyses. Soil DOC shows the highest concentrations in summer, but DOC concentrations in the tributaries are lower in summer than in winter by between 19% and 31%. DOM composition of the soil eluate differs between land use units. The forest site exhibits the largest fractions of humic-like fluorophores and less labile DOM. DOM composition in the tributaries is, in addition to DOC, controlled by soil moisture. We estimated the DOC import from the tributaries into the stream as 125 kg during base flow conditions in the period February to December 2017 and the instream DOC production as 38 kg, considering mass balance and exchange with groundwater. Six out of seven DOM components have a positive net production along the stream, only aliphatic DOM with low molecular weight is consumed (65 % of its input). These findings suggest that agricultural land use increases DOC input into streams and alters their DOM quality. Instream processes modify DOM quality over short distances.

1. Introduction

Agriculture delivers significant amounts of dissolved organic matter (DOM) to stream ecosystems, changing basic metabolic processes in the water and at the water-sediment interface, and affecting the ecological state and the health of aquatic systems (Fasching and Battin, 2012;

* Corresponding Author.
E-mail address: alexander.eder@baw.at (A. Eder).

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Findlay et al., 2001, 2003; Piscart et al., 2009; Rouhani et al., 2021). The amount and composition of terrestrial DOM influence benthic microbial growth and respiration as well as CO_2 emission from streams (Findlay et al., 2003; Piscart et al., 2009; Williams et al., 2010).

DOM is a mixture of various compounds with molecular weights ranging from simple carbohydrates to complex molecules of different aromaticity (Bolan et al., 2011). Dissolved organic carbon (DOC) typically represents ~67% of the elemental composition of DOM (Bolan et al., 2011) and, therefore, is often used as a proxy when quantifying DOM. Due to light absorbing chromophores and fluorescent fluorophores, DOM has distinct spectrophotometric properties in terms of both absorption and fluorescence (Baker et al., 2003; Chen et al., 2003; Hudson et al., 2007). UV-visible (200 – 800 nm) optical properties of DOM have been used to determine DOM characteristics such as aromaticity (SUVA254; (Weishaar et al., 2003a)) and molecular size (Dalrymple et al., 2010). Recent advances in fluorescent spectrophotometry have provided a new tool for rapidly identifying DOM fluorophores via excitation–emission matrices (EEM; wavelengths 200 – 500 nm, (Chen et al., 2003; Fellman et al., 2010)). An EEM identifies fluorescence peaks that can be attributed to various DOM components, such as humic-, fulvic- or protein-like fluorophores (Baker et al., 2003). Thus, fluorescence methods are useful for identifying anthropogenic DOM sources in streams (Hudson et al., 2007) and for distinguishing bioavailable from refractory DOM components, the relative abundance of which determines microbial activity and organic matter processing (Bolan et al., 2004; Findlay et al., 2001; Marschner and Kalbitz, 2003).

In natural streams, refractory DOM originating from terrestrial sources usually dominates over autochthonous, labile DOM from algal primary production (Osburn et al., 2017). Agricultural activities may significantly alter this DOM composition (Graeber et al., 2012). Both enhanced benthic primary production, resulting from increased nutrient supply and light penetration, and increased manure inputs with high amino acids contents may shift the composition towards the dominance of labile components (Fellman et al., 2009). Kalbitz et al. (2003) observed that pore-water DOM in agricultural soils showed lower molecular weights and less humicity than DOM in soils under native vegetation (see also Delprat et al., 1997). In addition, DOM aromaticity correlated positively with soil moisture, indicating that soil drainage may increase the export of labile DOM to streams (Brockett et al., 2012).

In contrast, other studies have found a higher proportion of humic-like, structurally complex DOM in agricultural streams than in pristine streams, which may be related to the disturbance of agricultural soils by tillage (Frank and Groffman, 2009; Kalbitz et al., 2000; Marschner and Kalbitz, 2003). Comparative studies of soil and stream DOM show contradictory results (Graeber et al., 2012) since the processes that drive the modifications are still largely unknown. The inconsistency of these findings may be related to differences in land use practices (e.g. fertilization, tillage, etc.) and environmental conditions (e.g. climate, vegetation, etc.), the significance of the different flow paths (surface runoff, soil pore water, drainage water), and different investigation methods. Xenopoulos et al. (2021) summarized, that climate, pollution, hydrology, soil properties, the intensity of human activities, and the extent of natural land covers define, how human altered landscapes produce DOM pools with diverging characteristics.

Past studies have generally followed one of four sampling strategies. Some studies focused on the DOM of soil eluate (water extractable organic carbon) from different land uses (Chantigny, 2003; Ghani et al., 2007; Zsolnay, 1996), its change with depth (Cronan and Aiken, 1985; Worrall and Burt, 2007) and the impact of land management (Kalbitz et al., 2000; Steenwerth and Belina, 2008; Sun et al., 2017). A second group of studies measured DOM in soil pore water, either directly in the field with suction cups (Vinther et al., 2006) or via percolation towards drainages from individual land use units such as pastures (Ghani et al., 2007). A third group focused instead on the streams and measured DOM within the stream system, relating the measured DOM quantity and composition to the proportion of different land uses (e.g. Ahearn et al., 2005; Graeber et al., 2012; Wilson and Xenopoulos, 2009) or soil types (Graeber et al., 2012). Another group estimated instream DOM processing via longitudinal sampling (Fellman et al., 2009) or addition studies (Pucher, 2021).

However, in order to understand the impacts of agriculture on DOM concentrations, composition and processing in streams, an approach is needed that combines measurements of soil DOM, the corresponding DOM in tributaries and changes in the instream DOM along stream reaches.

The aim of this study therefore is to link spatial and temporal variations of DOC and DOM quality in a stream to the potential terrestrial sources associated with agriculture, the delivery pathways and instream processes. Specifically, we explore (1) how DOM concentrations and composition change from the soil to the tributaries and along the stream to the catchment outlet and (2) which factors control the spatial patterns and seasonal dynamics of DOC and DOM quality of these different ecosystem components during base flow conditions.

The study is set in the Hydrological Open Air Laboratory (HOAL) Petzenkirchen (Blöschl et al., 2016), which has mainly agricultural land use, contains diverse flow paths (tile drainages, springs, saturation area flows) within a small area and is well instrumented. It is thus ideally suited for investigating the spatial and temporal variations of DOC concentrations and DOM quality from different land use units (arable, grassland, forest), the corresponding flow paths and instream DOC production. The focus is on base flow conditions as we were mainly interested in the seasonal pattern of instream DOM processing. Although rainfall runoff events certainly influence the seasonal pattern of instream processes, we decided to exclude those periods from our calculations as the temporal dynamic of DOC transport and metabolic processes during rainfall runoff events cannot be recorded sufficiently, their impact only temporarily superimpose the seasonal dynamics and they tend to have their implications further downstream.

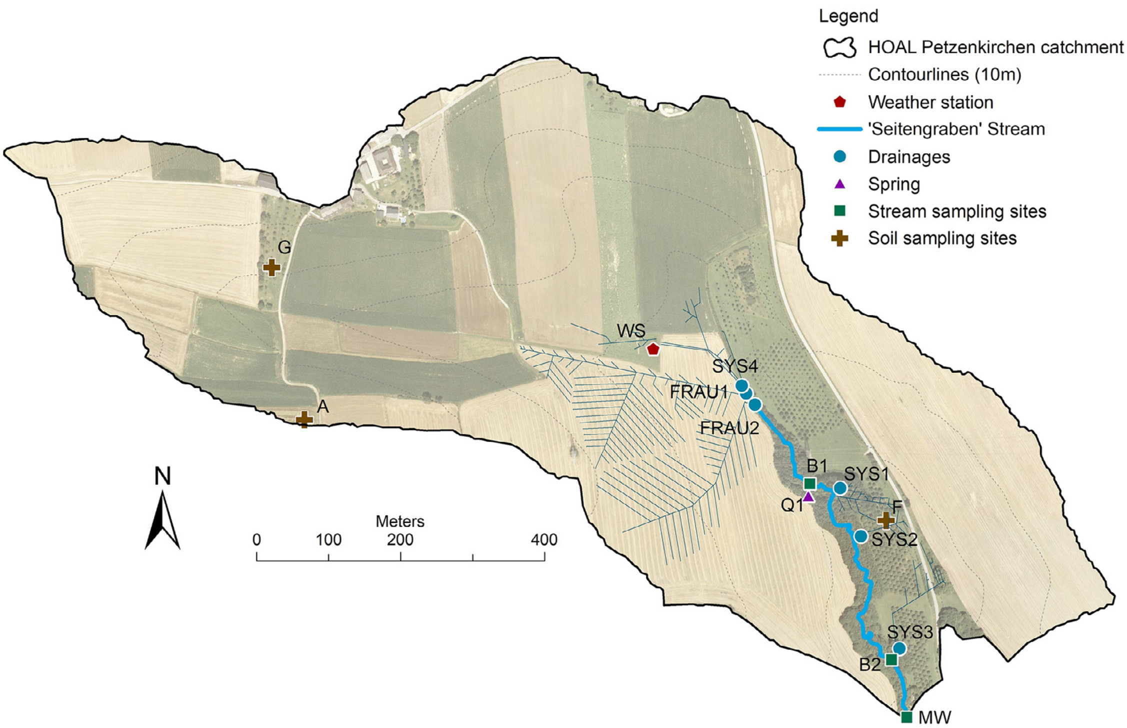

Figure 1. The Hydrological Open Air Laboratory (HOAL) Petzenkirchen with sampling locations. Water sampling sites: tile drains (blue dots), springs (purple triangular) and stream (green quadrats). Soil sampling sites (brown crosses) indicate different land use units (grassland – G; arable land – A; forest –F).

2. Material and Methods

2.1. Study area

The Hydrological Open Air Laboratory (HOAL) Petzenkirchen (Figure 1) is situated in the western part of Lower Austria (48°9' N, 15°9' E) and has a size of 66 ha. The catchment is drained by the Seitengraben stream, which is 620 m long and has an average flow of 3.93 L s^{-1} (1990-2020). The stream is sustained by eleven tributaries, five of which are perennial (Sys4, Q1, Sys1, Sys2 and Sys3) and two are ephemeral (Frau1, Frau2). The tributaries collect water from different pathways. These include tile drainages from arable areas (Frau1 and Frau2), tile drainages from mixed areas (arable, grassland and forest) (inlet Sys4, Sys3), a tile drainage from the forest (Sys2) and groundwater springs (Q1, Sys1). During low flow episodes, most of the stream water originates from Sys4, the main inlet of the stream, followed by deep aquifer water from spring Q1 and tile drain Sys1. The remaining tributaries contribute only 18 % of the total flow during low flow episodes (Széles et al., 2018). The stream itself interacts with the groundwater, which enables water and nutrient exchange (Exner-Kittridge et al., 2016) and results in diurnal fluctuations of stream flow, caused by transpiration from the riparian vegetation (Széles et al., 2018).

Overall, 87% of the catchment area is arable land, 5% is grassland, 6% is forested and 2% is paved. The dominant soil types are Cambisols (56% of the area), Planosols (21%) and Anthrosols (17 %) (IUSS Working Group WRB 2015). The climate is humid, with a mean annual temperature of 9.5°C and a mean annual rainfall of 823 mm yr^{-1} (1990–2014). Temperature, rainfall and rainfall intensity peak during summer. The elevation of the catchment ranges from 257 to 325m above sea level. The HOAL is jointly operated by the Federal Agency for Water Management and the Technical University of Vienna with the aim of studying catchment processes using data with high temporal and spatial resolution (Blöschl et al., 2016).

2.2. Sampling, preparation and analyses

A sampling campaign was conducted during the period January to December in 2017. The year was dryer than normal with a precipitation of 707 mm yr^{-1} compared to the long term mean of 785 mm yr^{-1} (1990 to 2019).

Stream flow has been measured by calibrated stream gauges (H-flumes and V-notch weirs) in combination with pressure transducers and/or ultra-sonic devices at all relevant tributaries to the stream and at the catchment outlet since 2010 (Figure 1) (Blöschl et al., 2016). Meteorological data are collected at a weather station located approximately in the centre of the catchment. Soil moisture is measured at 33 irregularly distributed sites at 10, 20, 30 and 50 cm depths; those nearest to the soil sampling sites within the same land use unit were used for the analyses.

The sampling strategy for the DOM analyses comprised three compartments. First, we took monthly soil samples from the top soil layer (0-5 cm) in three different land use units (arable, grassland and forest) to obtain information on the DOM sources. At each location we took three replicates, to minimise errors associated with the heterogeneous mixture of soil components and their non-uniform spatial distribution. The samples were immediately frozen and stored at -28°C before processing in the laboratory. Since the fluorescence-spectrometer analyses liquids, we produced an eluate from the soil samples after defrosting. Soil was sieved on a size below 4 mm and 40 ml of 0.5 mM K_2SO_4 were added to 20 g of soils and shaken for half an hour at 20°C. After hydro-extraction at 3000 rpm for 15 min at 20°C, the samples were filtered through pre-combusted 0.45 µm glass-fibre filters.

Soil organic carbon (SOC) content of the soil samples were calculated by subtracting inorganic carbon content (determined according to Scheibler), from total carbon content (measured with the Shimadzu SSM-5000A) after air-drying and sieving through 2 mm.

Second, monthly water samples during low flow conditions were taken from all tributaries to the Seitengraben stream and the catchment outlet (MW). Third, additional samples were taken from the stream itself at B1 and B2 to divide the stream into three sections (Sys4 to B1, B1 to B2 and B2 to MW).

All water samples were divided into two parts. One part was used for the DOC/DOM quality analyses, which was immediately filtered through pre-combusted glass-fibre filters with a pore size of 0.45 µm to minimize further microbial activity. The second part was used for the chemical analyses (total organic carbon (TOC), nitrate, ammonia, potassium, chloride, electric conductivity, pH-value and suspended sediment concentrations). The samples were stored at 4°C and processed not later than 3 days after collection.

For the DOM quality analyses, we used spectrophotometric and spectrofluorometric methods. The absorbance measurements was conducted with an UV-VIS spectrometer (UV1700 Pharma Spec, Shimadzu Corporation) with a scanning range from 200 to 700 nm (Chin et al., 1994). Samples were placed in a 5 cm quartz window cuvette (Hella Analytics). Fluorescence was measured with a fluorescence spectrophotometer (Hitachi F-7000, Hitachi High-Technology Corporation) in a range from 250 to 600 nm in 5 nm increments. Due to a scan speed of 1500 nm min^{-1} it took 15 min per sample to gather an emission-excitation matrix with a range of 200 to 450 nm for the excitation, and a range of 250 to 600 nm for the emission. Z-values of the matrix represent a light intensity, displayed in Raman Units. Each day, before the start of sample analyses, a sensitivity test with distilled water was performed (S/N Peak to Peak > 250, Drift <2 %). During the analyses, temperature was kept constant at 21°C.

The Fluorescence and absorbance spectra of DOM were analysed using the "staRdom" package of R (version 3.5; R Core Team, 2020) (Pucher et al., 2019). We conducted a PARAFAC analysis (Murphy et al., 2013; Pucher et al., 2019) and calculated fluorescence as well as absorbance indices to obtain DOM compositional parameters. We mainly used the relative contribution of the individual PARAFAC components to the total fluorescence gained from the PARAFAC model. The DOM quality analysis was complemented by determining the humification index (HIX; Zsolnay et al., 1999 - higher values indicate more humification) and the biological index (BIX, Huguet et al., 2009 - higher values indicate more autochthonous DOM production). Further we used the absorbance parameters SUVA254, which is defined as the UV absorbance of a water sample at the wavelength of 254 nm and normalized for dissolved organic carbon (DOC) concentration, as a surrogate for aromaticity (Weishaar et al., 2003b) and quantified average molecular size by the inverse relationship between DOM molecular weight and the peak ratio E2/E3, where E2 and E3 are the absorbance at 254 nm and at 365 nm respectively (Dalrymple et al., 2010).

In total, we analysed 384 samples (271 water samples of the tributaries and the stream and 36 soil samples). Inner-filter effects of the fluorescence analysis were corrected, the results were converted to Raman Units, and Raman and Rayleigh scattering of first and second order were removed and interpolated. In the PARAFAC model, seven outliers were removed based on their leverage and later reintroduced in the model with fixed emission and excitation loadings. We verified the PARAFAC model using a split-half analysis and compared the components by Tucker's congruence coefficient (TCC = 0.963; Tucker, 1951). Component spectra were visually checked for plausibility. The final PARAFAC model (R^2 = 0.996) resulted in 8 components (Table 1). The components' spectra were compared with findings from other studies using openfluor.org (Murphy et al., 2014).

2.3. Definition of base flow conditions

Since the focus of the study was on evaluating the seasonal patterns of instream processes during base flow conditions, such periods were identified with a recursive digital filter (Arnold et al., 1995; Nathan and McMahon, 1990), applied to the streamflow time series of MW on an hourly basis:

$$Q'_t = \beta \cdot Q'_{t-1} + \frac{1+\beta}{2} \cdot (Q_t - Q_{t-1}) \qquad (1)$$

where Q'_t is the filtered quick flow (event water) at time step t. Time steps with $Q'_t \leq 0$ are considered baseflow conditions. Q_t is the original stream flow of MW at time step t. The filter parameter β was set to 0.95 after visual data inspection, to reflect typical subsurface response of the catchment (Eder et al., 2010; Exner-Kittridge et al., 2016).

2.4. Exfiltration – Infiltration model

In order to estimate the DOC production in the stream, an infiltration model was setup that accounts for diffuse DOC inputs and losses due to water exchange with the subsurface. For each time step of one hour, DOC mass balance gives:

$$F_{prod} = F_{MW} - \sum_{i=1}^{n} F_i - F_{diff} \qquad (2)$$

where F_{prod} is the instream DOC production (g h^{-1}, positive if DOC is produced), F_{MW} is the measured DOC flux at the catchment outlet, F_i is the measured DOC input flux from tributary i, n is the number of tributaries (n=7), and

Table 1
Emission and excitation peaks (both in nm) of components with their interpretation according to the literature. The code is used in the further text in addition to component number for better readability.

Component	Emission peak (nm)	Excitation peak(s) (nm)	Description	Code	References
C1	500	<245 (365	humic-like fluorophore, derived from terrestrial material by photochemical degradation	hum	Murphy et al., 2014; Graeber et al., 2012
C2	436	<245 (340)	Humic-like, terrestial, identical to syringealdehyde, associated with waters with high organic matter loadings	hum-ter	Murphy et al., 2014; Lambert et al., 2016; Peleato et al., 2016
C3	414	<245	humic-like, terrestrial, recalitran, very likely was indicative of transformation and degradation of DOM within the lakes	hum-rec	Osburn et al., 2017; Osburn et al., 2011
C4	578	<245	Artifact from the fluorometer, has no ecologic implication	-	Murphy et al., 2006
C5	390	<245 (320)	humic-like, particularly at sites near terrestrial sources relatively fresh and potentially labile DOM, indicative of microbial activity	hum-mic	Murphy et al., 2014; Osburn et al., 2015
C6	340	300 (<245)	protein-like, similar to free and protein bound amino acids tryptophan-like, generated by both microbial communities, periphyton and leachates from higher plants	tryp	Stedmon et al., 2007; Murphy et al., 2006; Stedmon et al., 2007
C7	334	280	protein-like, tyrosine-like;	tyr	Murphy et al., 2006; Yu et al., 2015; Yamashita et al., 2011
C8	410	300 (<245)	microbial-derived, humic-like, relatively aliphatic, low molecular weight	hum-lab	Lambert et al., 2016; Podgorski et al., 2018

F_{diff} is the diffusive DOC flux from the groundwater to the stream.

The DOC input flux from the tributaries was estimated as the product of DOC concentrations and stream flow at a time interval of 1 minute. Since DOC concentrations were only measured 12 times during the study period while stream flow was measured every minute, we established a regression between DOC concentrations and the logarithm of flow for each tributary, in order to account for DOC variability between the sampling. These regressions included data from additional sampling during baseflow conditions (data not presented in this study) to extend the range of flow and avoid extrapolation.

The diffuse DOC flux F_{diff} was estimated as

$$F_{diff} = Q_{diff} \cdot C_{diff} \tag{3}$$

where Q_{diff} is the diffusive exchange water flux (positive when water infiltrates from the groundwater to the stream) at time step t, and C_{diff} is its DOC concentration. Water mass balance for each time step gives

$$Q_{diff} = Q_{MW} - \sum_{i=1}^{n} Q_i \tag{4}$$

where Q_{MW} and Q_i are the measured flows at the catchment outlet and at tributary i, respectively. Evaporation was neglected because most of the stream is shaded by trees. Estimates of daily evaporation from the stream surface were less than 1000 litre per day and thus less than 1.6 percent of daily stream flow on the day with the lowest flow. Infiltrating water ($Q_{diff} < 0$) was assumed to have the DOC concentration of the groundwater, i.e. $C_{diff} = C_{GW}$ which was set to the mean concentration measured at spring Q1. Exfiltrating water ($Q_{diff} > 0$) was assumed to have the average DOC concentration of the stream water which was estimated as the weighted mean of the DOC concentrations of the tributaries C_i as

$$C_{diff} = \frac{n}{\sum_{i=1}^{n} L_i \cdot \sum_{i=1}^{n} Q_i} \sum_{i=1}^{n} (Q_i \cdot C_i \cdot L_i) \tag{5}$$

The weighting was by flow Q_i as well as by the flow length L_i from the confluence of the tributary i with the stream to the catchment outlet.

For the calculation of net production of the individual components (C1-C8) the same model was used but DOC concentrations were replaced by Raman units (RU) of the components. Additionally, instead of a correlation between flow rate and concentration, mean values of the RU at each tributary were used because of the low correlations between flow rate and RU.

3. Results

3.1. Spatiotemporal variation of DOC

3.1.1. Soil

The lowest DOC values from soil eluate were measured at the arable land site with an annual mean of 0.9 mg L^{-1} and a standard deviation of 0.17 mg L^{-1} (Table 2) during the study period. Higher DOC concentrations were observed for the grassland site with a mean of 2.33 (±0.55) mg L^{-1}. The forest site soil eluate showed the highest DOC concentrations (4.36 (±1.34) mg L^{-1}) in line with the high organic carbon content of the forest soil. SOC contents were 2.0 (±0.35) g kg^{-1}, 4.1 (±0.76) g $kg^{-1}$and 9.2 (±0.88) g kg^{-1} for the arable land, grassland and forest sites, respectively, suggesting a clear relationship between soil eluate DOC and SOC with a linear regression coefficient of r=0.97.

Table 2
Mean concentrations of DOC and nitrate and mean values for DOM quality parameters (SUVA, HIX and BIX) including standard deviation for the individual sampling sites. Study period January to December 2017.

		DOC (mg L^{-1})	NO_3 (mg L^{-1})	SUVA (L mg^{-1} m^{-1})	E2/E3 (-)	HIX (-)	BIX (-)
Tributaries	Sys4	1.55 ± 0.44	42.5 ± 3.4	1.51 ± 0.77	7.3 ± 3.1	0.82 ± 0.13	0.89 ± 0.09
	Frau1	2.80 ± 0.71	57.5 ± 12.3	1.35 ± 0.17	7.0 ± 3.6	0.89 ± 0.01	0.90 ± 0.17
	Frau2	2.28 ± 0.67	31.2 ± 6.6	1.91 ± 0.62	7.6 ± 1.2	0.89 ± 0.03	0.89 ± 0.07
	Q1	1.50 ± 0.43	0.5 ± 0.3	3.16 ± 1.74	2.6 ± 1.4	0.84 ± 0.12	0.86 ± 0.05
	Sys1	1.87 ± 0.48	8.4 ± 3.3	2.08 ± 1.19	4.0 ± 1.5	0.84 ± 0.12	0.87 ± 0.11
	Sys2	1.59 ± 0.48	46.0 ± 3.1	1.61 ± 0.84	6.6 ± 1.9	0.83 ± 0.12	0.83 ± 0.05
	Sys3	1.92 ± 0.59	36.7 ± 6.0	1.57 ± 0.78	6.5 ± 2.3	0.79 ± 0.21	1.44 ± 1.68
	MW	2.08 ± 0.48	18.1 ± 4.0	1.96 ± 0.82	5.4 ± 1.7	0.79 ± 0.22	1.38 ± 1.58
Soil eluates	arable	0.90 ± 0.18		11.4 ± 12.7	4.8 ± 1.3	0.69 ± 0.15	1.04 ± 0.78
	grassland	2.33 ± 0.57		10.4 ± 11.5	4.6 ± 0.7	0.77 ± 0.08	0.75 ± 0.35
	forest	4.36 ± 1.41		4.8 ± 3.9	3.4 ± 1.8	0.79 ± 0.06	0.58 ± 0.13

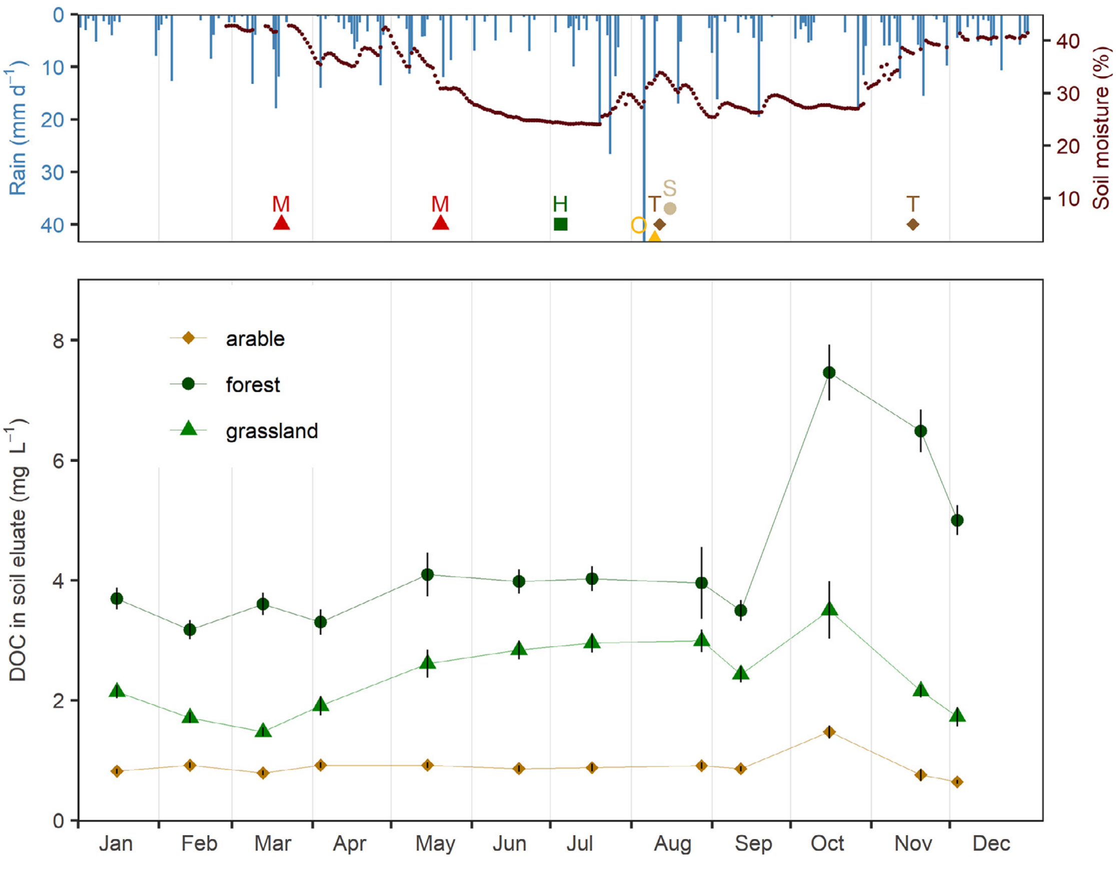

Figure 2. Time series of daily rainfall, soil moisture in 5 cm depth at the arable field and management activities at the arable field (upper panel; M – mineral fertilizer, H – Harvesting, O – organic fertilizer, T – soil treatment, S - seeding). Lower panel shows seasonal fluctuations of DOC concentrations of soil eluate from the three different land uses: arable land (brown diamonds), grassland (green triangles) and forest (dark green circles). Symbols represent the mean of 3 measurements, bars the standard deviations (estimated from both the spatial variability of 3 replicates and the measurement uncertainty of the laboratory device). The first three points (January to March) represent pooled samples, so bars show measurement error only.

In general, soil eluate DOC concentrations varied seasonally, showing slightly increased concentrations at the grassland and forest sites during summer, and high peaks in all soils in October (Figure 2). The peak was especially high in the forest, where DOC concentration almost doubled to the maximum DOC of 7.77 mg L^{-1} (Figure 2). This peak occurred at the onset of autumnal leaf fall.

In the arable field, monthly soil DOC changed little throughout the year. During the project period, winter barley was grown (seeding in October 2016) until the harvest in early July. In March and May, mineral fertilizer was applied (2 times 250 kg NAC ha^{-1}, which equals 2 times 62.5 kg N ha^{-1}). Pesticides were used in April (Husar: Iodosulfuron-Methyl-Natrium and Mefenpyr-Diethyl) and

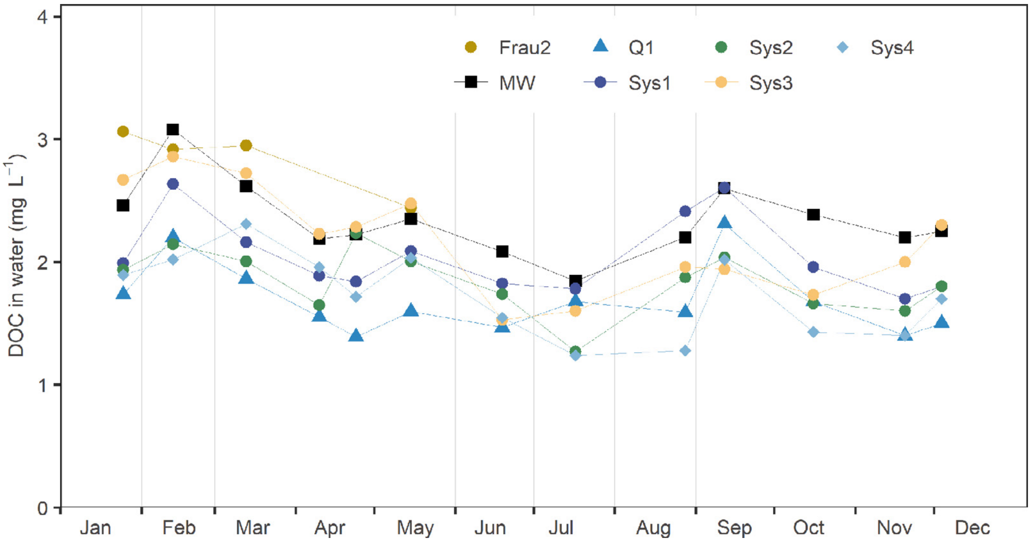

Figure 3. Seasonal fluctuations of DOC concentration for the tributaries and the catchment outlet (MW). The measurement error is 4%, thus is smaller than the symbols. Flow from tile drain draining the arable field (Frau2) only occurred from January to March and in May.

May (Aviator and Atlanil: Prothioconazol, Bixafen). At the end of August, pig slurry was distributed on the arable field and incorporated before the seeding of catch crops. These management procedures did, however, not change the soil DOC concentrations much. The higher value in October cannot be directly attributed to any documented management operation but it may be a delayed effect of the fertilization with pig slurry and its incorporation into the soil in August.

3.1.2. *Tributaries*

The DOC concentrations of the tributaries show an opposite seasonal variation compared to the soil eluates with the highest concentrations in winter (Figure 3). During base flow conditions, the DOC concentrations from the tributaries ranged between 1.5 and 4.9 mg L^{-1}. The highest concentrations were measured in the tributaries that drain the arable land with mean DOC concentrations of 2.8 ±0.71 mg L^{-1} (Frau1) and 2.3 ±0.66 mg L^{-1} (Frau2). DOC concentrations were lowest for the spring Q1 that is groundwater fed (1.50 ±0.43 mg L^{-1}) and Sys4 that has some groundwater contribution (1.55 ±0.44 mg L^{-1}). Surprisingly, the DOC concentrations of Sys2, which drains the forest with the highest DOC in soil eluate, were also low (1.59 ±0.48 mg L^{-1}). During the summer, the DOC concentrations in the tributaries decreased on average by 25% compared to the winter half year.

As mentioned earlier, the tributaries show a contrasting seasonal DOC pattern to those of the soil eluates. The flow paths and their sources are well known for the HOAL Petzenkirchen because of the detailed monitoring of all tributaries since 2010 (Blöschl et al., 2016) and additional, hypothesis-driven studies with focus on sediment transport (Eder et al., 2014, 2010), nitrogen transport including groundwater interactions (Exner-Kittridge et al., 2016) and transpiration effects during low flow conditions (Széles et al., 2018). Thus, flow paths of water within the HOAL Petzenkirchen catchment are well investigated and understood. Based on the results of these previous studies and historic drainage maps (Fig. 1), the drainages Frau1 and Frau2 can be attributed as drainages from the arable land use unit. While the soil sampling was not conducted in the same field because of logistic reasons, it was conducted in a field where both management and soil type are identical to those of the field drained by the tile drains. Also, the fields are spatially rather uniform in terms of soil characteristics. It was therefore assumed that the soil samples of the arable site are also representative of the area draining Frau1 and Frau2. Sys2 mainly drains the area around the forest on the left bank of the stream and also immediately responds to rainfall.

The comparison of the DOC concentrations of the arable and forest sites and the associated tributaries (arable associated with Frau1 and Frau2, forest associated with Sys2) shows that DOC concentrations in the soil are not aligned with those in the tributaries. At the arable site, the mean DOC concentration of the soil eluate was 0.87 mg L^{-1}, but 2.8 and 2.77 mg L^{-1} in the corresponding tributaries Frau1 and Frau2. In the forest, the mean DOC concentration of the soil eluate was 3.82 mg L^{-1}, but 1.84 mg L^{-1} in the corresponding tributary Sys2.

Overall, the DOC of the six tributaries (and the stream) were more similar to each other than the DOC of the three land use sites. The mean over the study period ranged between 1.3 and 3.5 mg L^{-1} for the tributaries, while it ranged between 0.5 and 4.5 mg L^{-1} for the three soil sites. The temporal standard deviations of the tributaries (maximum standard deviation at Frau1, ±0.7 mg L^{-1}) were also smaller than those of the soil sites (maximum standard deviation in the forest, ±1.4 mg L^{-1}). Both the spatial and temporal patterns of the tributaries show smaller variations than the soils, suggesting an important role of DOC turnover and buffering along the flow paths from the soil to the stream.

3.2. DOC: from the tributaries to the catchment outlet

3.2.1. Hydrology and identification of baseflow conditions

For evaluating budgets of water and DOC the period February 3rd to December 31st 2017 was used since streamflow data were missing in January 2017 due to frost damages of some pressure transducers.

The mean flow at the catchment outlet (MW) in this period was 2.32 L s-1 and thus less than its long term mean of 4.07 L s-1, indicating that the study period was drier than normal. The total flow volume was 85533 m³, of which 57570 m³ (67%) left the catchment during base flow conditions, which occurred 88% of the time.

Over the entire period, the contribution of the inlet (Sys4) to the total flow volume at MW was 29 %. The highest proportion of the water originates from the spring Q1 (40 %). The left bank drainage systems contributed 31% (Sys1: 29%, Sys2: 7%, Sys3: 7%) whereas the right bank drainage systems delivered only about 5% (Frau 1: 0.1%, Frau 2: 5%). During baseflow, the total flow volume contributed by the tributaries was 18 % higher than the total flow volume measured at the catchment outlet, suggesting an important exfiltration flux into the groundwater. This may be related to the relatively dry conditions during the study period (2017) with low groundwater tables. For the period 2013-2015, which was much wetter, Széles et al. (2018) found that 37 % of the total flow volume measured at MW during low flow periods enters the stream laterally. Simultaneous grab control measurements of flow in 2017 confirmed the exfiltration.

3.2.2. DOC mass balance

As mentioned earlier, the DOC loads of the tributaries were calculated using a regression between flow and DOC concentration. Although the correlation coefficients and the slopes of the regressions varied between tributaries, we found clear relationships for all sites (correlation coefficients between 0.76 and 0.97). Exceptions are the spring Q1 and Frau2, where the correlation coefficients were smaller than 0.5 due to the small flow variability in Q1 and hysteresis effects in Frau2. We therefore used the mean DOC concentrations to calculate loads at Q1 and Frau2.

Although the tributaries draining the arable sites (Frau1 and Frau2) had the highest concentrations, they only made a minor contribution (7%) to the total DOC input of 124 kg (during Feb 3rd to Dec 31st) into the stream due to their low flow volume (Figure 5). The highest DOC inputs into the stream occurred via the spring Q1 (35 kg DOC, 28 % of total DOC inputs) and Sys1 (34 kg, 28 %), because of their high discharge volumes (24 400 m³ and 16 400 m³, 36 % and 24 % of total flow). The calculated DOC loads clearly show that the DOC inputs were mainly controlled by the flow volume of the respective tributaries (Figure 4).

3.2.3. Instream DOC net production

Instream processes were evaluated by comparing the inputs from the tributaries and the outputs at the catchment outlet for both water volume and DOC loads. While over the period from February 3rd to December 31st 2017 a total loss of water of 10 300 m³ was measured, there was a DOC load surplus at the catchment outlet of 13.3 kg (Figure 5).

The exfiltration – infiltration model Eq. 2-(5) applied to the base flow data suggests that, from February 3rd to May 15th, 2017, 6900 m³ water infiltrated into the stream and imported 10.4 kg of DOC. On the other hand, the measured water loss during the rest of the year was 17 300 m³, which led to an estimated DOC exfiltration of 27.2 kg DOC. The seasonal patterns of water and DOC exchange and the resulting DOC net production are given in Figure 6. During the periods February 3rd to May 25th 2017 and November 20th to December 31st there was a DOC net production of 39 kg with a maximum production rate of 36 g DOC h^{-1}. On May 25th the net production turned negative with a minimum of -9 g DOC h^{-1}, indicating that more DOC was consumed (incorporated into microbial biomass or respirated), precipitated, flocculated or adsorbed than leached or secreted by algae within the stream. In July and August, the net consumption rate slightly increased to -4 g DOC h^{-1}, but showed a second low at the beginning of October similar to the one in June (-8 g DOC h^{-1}). On November 20th, the net production rate turned positive again. Whenever a rainfall runoff event occurred, it caused a temporary peak of DOC production, indicating an additional release of DOC.

3.3. Spatiotemporal variation of DOM quality

3.3.1. Soil

On average over all soil samples, 68% of fluorescence was caused by refractory, humic-like fluorophores (C1-C3), 18% by protein-like fluorophores (C6 and C7) and 14 % by labile, humic-like fluorophores (C5 and C8), characterised by low molecular weight. Both, land use and season affected the DOM composition (Figure 7). In summer, the forest site showed the highest proportion of refractory humic-like DOM (C1 to C3, 63%), followed by grassland (61%) and the arable site (57%). This decrease of the sum of these components from arable to forest is aligned with an increase of labile, humic-like fluorophores (C5 and C8). The proportion of labile humic-like DOM (C5 and C8) decreased from summer to winter for all land use units. The proportions of protein-like fluorophores (C6 and C7) were similar for all land use units in summer (15% to 16%), but in the winter half year, the mean contribution of C7 (protein-like, tyrosine-like) was 34%, while it was only 13% in summer.

To understand the differences of the DOM quality of soil eluates at different land use sites, Spearman's rank correlation coefficient between the individual components and DOC concentration, soil temperature and soil moisture were calculated. Significant correlations were found between hum (C7) and DOC (Spearman's rank correlation coefficient r_s=0.90, significance level of $p<0.001$), hum-lab (C8) and DOC (r_s=-0.78, $p<0.05$) and hum-mic (C5) and DOC (r_s=-0.73, $p<0.01$). Higher values for measured DOC in the soil eluate were associated with higher relative amounts of hum (C1), and lower relative amounts of hum-mic (C5) and hum-lab (C8) (Figure 8, Panel A).

Soil temperature and soil moisture did not show a significant correlation with any of the components (C1-C8). However, soil temperature was correlated with aromatic-

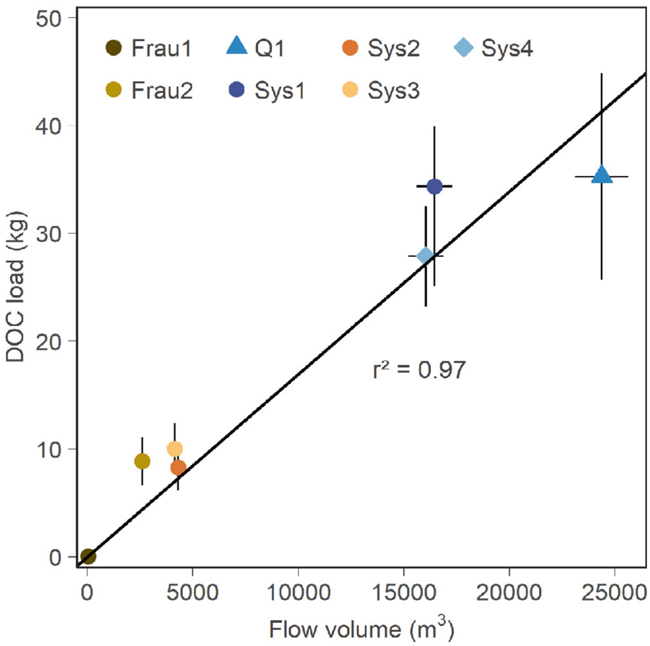

Figure 4. Relationship between DOC load and flow volume for the tributaries during baseflow conditions, February 3rd to December 31st, 2017. Horizontal bars represent the standard deviation of the flow measurements, vertical bars the uncertainty of the DOC load estimation based on the standard errors of the regression coefficients for each tributary.

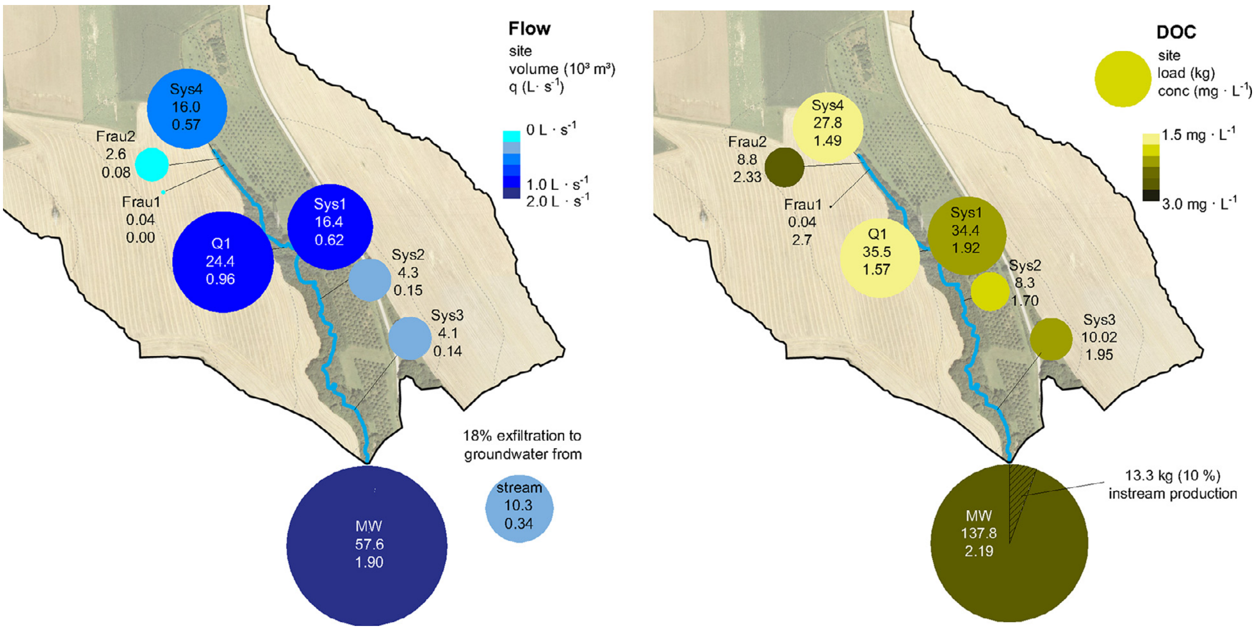

Figure 5. Mass balance of flow (left) and DOC (right) during base flow conditions from February 3rd to December 31st, 2017. Size of circles represents flow volume and DOC load, respectively. Colours indicate mean specific discharge q (flow per area) and mean concentration. The circles at the catchment outlet (MW) represent the measured flow volume (left) and DOC load (right) and the resulting differences due to exfiltration to groundwater and instream DOC production.

ity (SUVA, correlation coefficient r_s =-0.72, $p < 0.001$) and molecular size (E2/E3, r_s =0.50, $p < 0.01$), indicating that higher temperature has led to less aromatic DOM with low molecular weight.

The means of SUVA over the study period were highest at the arable site (11.4 L mg^{-1} m^{-1}), intermediate at the grassland site (10.35 L mg^{-1} m^{-1}), and lowest at the forest site (4.77 L mg^{-1} m^{-1}), but the standard deviation was high for all three land use units (Table 2). On average over the study period, the molecular size was highest at the forest site (E2/E3=3.4), intermediate at the grassland site (E2/E3=4.6) and lowest at the arable site (E2/E3=4.8).

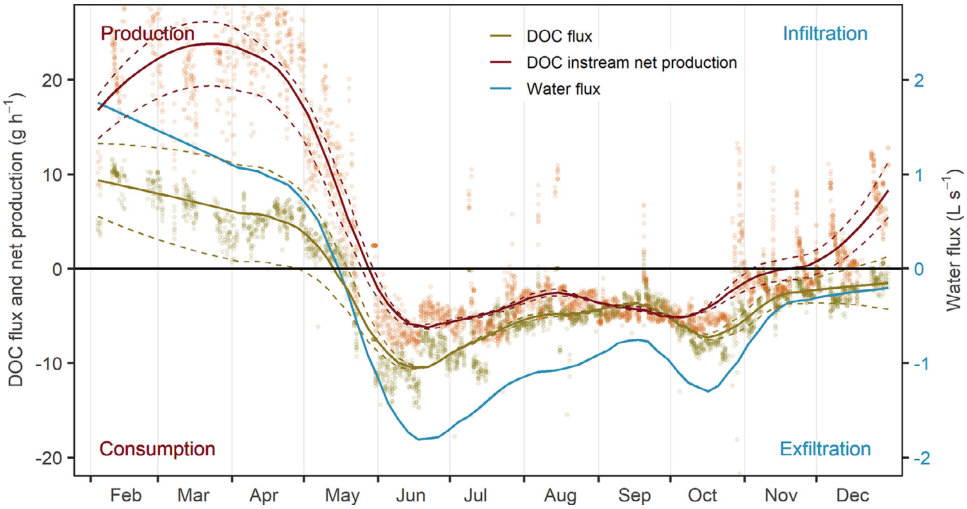

Figure 6. Seasonal patterns (lines) of diffuse infiltration from groundwater to the stream and exfiltration from the stream to groundwater for water (L s^{-1}, blue) and DOC (g h^{-1}, green) fluxes in 2017, from which instream DOC net production (g h^{-1}, red) was estimated. Dashed lines represent uncertainty estimations based on the standard error of the relationships between flow and DOC concentrations at the individual sites. The dots represent hourly values for DOC flux (green) and DOC net production (brown). The apparent scatter results from temporal variability.

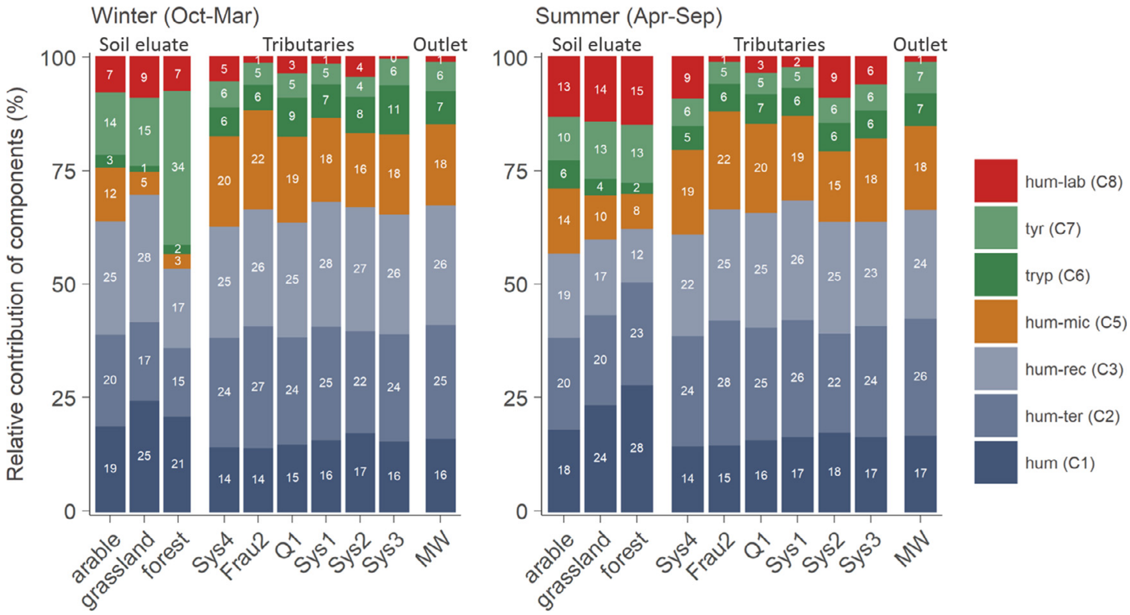

Figure 7. Mean relative contribution of the DOM components to total fluorescence of soil eluates and water samples for the winter (left) and summer (right) half year. Blue: refractory, humic-like (C1-C3); brown: microbial derived, labile, humic-like (C5); green: proteins (tryptophan (C6) and tyrosin (C7)); red (C8): aliphatic with low molecular weight, labile, humic-like.

3.3.2. Tributaries

At the tributaries, refractory humic-like fluorophores (C1 to C3) contributed between 62 % (Sys4) and 68 % (Sys1) to total fluorescence on average over the study period (Figure 7). Protein-like fluorophores (C6 and C7) accounted for 11 % to 12 % of fluorescence for all tributaries with minor differences between the tributaries. Microbial derived, humic-like fluorophores (C5) contributed between 16% (Sys2) and 22 % (Frau2). The remaining 1 % to 7 % were C8, which is described as microbially derived, relatively aliphatic, humic-like fluorophores with low molecular weight. Relevant seasonal changes occur for tryp (C6) and hum-lab (C8); tryp (C6) is lower in summer, while hum-lab (C8) is lower in winter.

We calculated Spearman's rank correlation coefficient between the DOM quality of the tributaries and environmental parameters, in a similar way as for the soil data, but included additional water quality parameters such as nitrate and phosphate concentration. The main explanatory variables of DOM composition were found to be soil moisture in the catchment the tributary is draining, availability of nitrate in the streamflow of the tributary and DOC

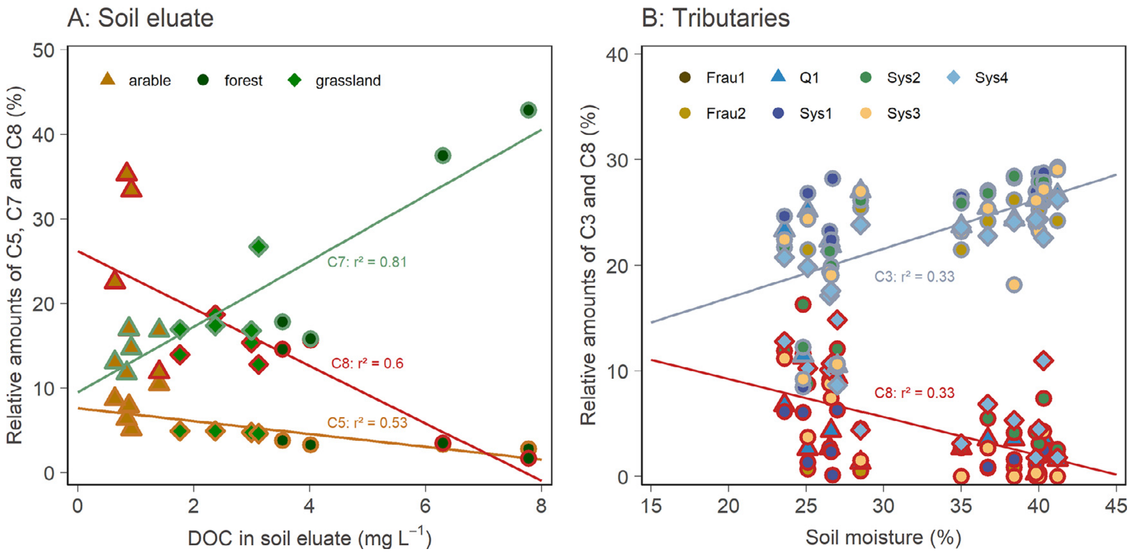

Figure 8. Relative amounts of DOM components in the soil eluate in relation to soil DOC concentration (Panel A) and relative amounts of DOM components in the tributaries in relation to catchment soil moisture (Panel B). Symbols and colour of fill indicate the land use unit and the pathway, respectively. Colour of the symbol borders and regression lines indicate the DOM component.

concentration. Soil moisture is positively correlated with the relative amounts of hum-rec (C3) and negatively with hum-lab (C8) of the tributaries (Figure 8, Panel B). Nitrate was positively correlated with hum-lab (C8) only (r_s=0.38, $p<0.01$), while higher nitrate concentrations are associated with lower aromaticity (SUVA, r_s=-0.36, $p<0.01$) and smaller molecular size of DOM (E2/E3, r_s=0.55, $p<0.001$). DOC concentration of the tributaries was positively correlated with hum-mic (C5, r_s=0.38, $p<0.01$) and negatively correlated with aromaticity (SUVA, r_s=-0.51, $p<0.001$). It appears that increasing DOC concentration has led to less aromatic, labile DOM.

3.4. DOM quality: from source to catchment outlet

3.4.1. Soil to tributaries

The DOM quality differs between soil eluate and tributaries. While the proportions of the more refractory components C1-C3 are comparable between eluates and tributaries (except for the forest soil in winter), the proportions of the more labile fractions vary. The tributaries showed a higher relative proportion of hum-mic (C5, +159%) and tryp (C6, +84%) and a lower proportion of tyr (C7, -62%) and hum-lab (C8, -63%) than the soil eluates (Figure 7). Besides, the seasonal variability of the DOM composition was much lower in the tributaries than in the eluates. Frau 2 (draining the arable field), Sys 1 (groundwater affected), and Sys3 (draining both arable and forested areas) showed lower proportions of hum-lab (C8) in winter than the other tributaries. The lowest seasonal variability occurs at the stream outlet (MW; Figure 7). Similar to Frau 2 and Sys 1, the outlet was characterized by relatively low proportions of hum-lab (C8).

The humification index (HIX) increased from an average of 0.75 in the soil eluate to 0.84 in the tributaries. The ratio E2/E3 was higher in the drainage Frau2 (7.6), Frau1 (7.0) and Sys 2 (6.6) than in the soil eluates of the corresponding arable site (4.8) and forest (3.4) (Table 2).

3.4.2. Tributary to catchment outlet

The instream processes of the individual DOM components were evaluated in an analogous way to DOC based on mass balance including exchanges with the aquifer due to exfiltration and infiltration. During the study period from February 3rd to December 31st, 2017, all DOM components apart from hum-lab (C8) showed a positive net production (Table 3). Only hum-lab (C8) was consumed, which almost completely disappeared at the catchment outlet.

In addition, changes of DOM quality along the stream were observed at two stream sections. The upstream section 1 was between Sys4 and B1 (190 m) and downstream section 2 between B2 and MW (96 m). For section 1 only periods without stream flow at Frau 1 and Frau 2 were compared. In both sections the relative contributions of hum (C1), hum-ter (C2), hum-rec (C3), tyr (C6) and tryp (C7) increased and hum-lab (C8) decreased according to the upper results provided in Table 3. Only hum-mic (C5) remained on the same level over the stream course. Molecular size (E2/E3) and aromaticity increased along the stream in both sections, indicating an increasing proportion of more refractory DOM components.

4. Discussion

4.1. Land use impacts on DOC and DOM quality

We observed a distinct impact of land use on the DOC concentrations in the soil eluate, showing a decrease from the forest to the grassland and the arable land. DOC concentrations were positively correlated with SOC as was also observed by others (Ghani et al., 2007; Khomutova et al., 2000; Ward et al., 2007; Zhang et al.,

Table 3
Measured flow volumes and calculated DOC and component loads (C1-C8) at the catchment outlet (MW) and as sum of all tributaries including standard deviation (±SD), and instream net production of DOC and the DOM components during the period of DOC net consumption (Mai 25th to November 20th) and during the period of DOC net production (February 3rd to May 24th and November 21st to December 31st, 2017) during baseflow conditions. The calculation of instream net DOC production includes inputs and losses due to water exchange with groundwater based on the Exfiltration-Infiltration model.

	MW		ΣTributaries		Instream production (+) and consumption (-)	
					period of net DOC consumption	period of net DOC production
Flow volume (m^3)	57582	(±3598)	67953	(±2133)	-	-
DOC load (kg)	138	(±14)	125	(±15)	-12	+42
C1, hum (RU m^3)	2462	(±165)	2359	(±77)	+183	+285
C2, hum-ter (RU m^3)	3719	(±355)	3728	(±129)	+220	+337
C3, hum-rec (RU m^3)	3627	(±664)	3790	(±458)	+143	+249
C5, hum-mic (RU m^3)	2666	(±490)	2885	(±111)	+74	+123
C6, tyr (RU m^3)	1064	(±319)	958	(±401)	+103	+154
C7, tryp (RU m^3)	971	(±670)	761	(±108)	+144	+202
C8, hum-lab (RU m^3)	97	(±155)	508	(±252)	-149	-211

2007; Zsolnay, 1996). Marschner and Kalbitz (2003) and Stutter and Billett (2003) suggested that DOC equilibrates between the mobile aqueous phase and the immobile solid phase, indicating that higher SOC leads to higher DOC in the soil. Land use is an important factor controlling the SOC content in the soil and thus also affects DOC concentrations in the soil eluate. The same pattern of decreasing DOC concentrations from forest floor over grassland (A horizon) to arable land (A horizon) was found by Chantigny (2003).

In general, the DOC concentrations in the tributaries measured in the present study area (the HOAL Petzenkirchen) are relatively low, compared to other studies. Vidon et al. (2008) found similar concentrations in tile drains from arable land (2.28 mg L^{-1}) but almost twice the values in groundwater (4.34 mg L-1 and 3.60 mg L^{-1}) and the streams (4.78 mg L^{-1} and 4.85 mg L^{-1}). (Graeber et al., 2012) found even higher DOC concentrations in streams of agricultural catchments (7.6 ±2.8 mg L^{-1}), but forested catchments had approximately the same mean DOC concentration (1.5 ±0.9 mg L^{-1}) as measured in Sys2 draining the forest in the HOAL. Kalbitz et al. (2000) reported that DOM is strongly adsorbed to clay minerals in the mineral soil, resulting in low DOC output from these soils. This process may explain the generally low DOC concentrations in the HOAL where the soil mainly consists of heavy clay material.

Surprisingly, DOC concentrations in the tributaries showed an opposite pattern to the corresponding soils, with increasing DOC concentrations from the tributary draining the forest to the tributary draining the arable field despite similar flow volumes (Sys2 and Frau2 in Figure 5). Higher DOC outputs from the arable fields may be caused by higher microbial degradation due to the surplus of nutrients by fertilization (Chantigny et al., 1999; Frank and Groffman, 2009) or due to soil treatments on the fields such as ploughing (Kalbitz et al., 2000; Steenwerth and Belina, 2008). Fertilizer application lead to a nitrogen surplus, increasing the decomposition rate of organic matter through an improved C/N ratio (Chantigny et al., 1999; Enowashu et al., 2009; Frank and Groffman, 2009) and thus the potential leaching. The laboratory leaching experiments with soils of the HOAL Petzenkirchen by Tiefenbacher et al. (2020) found that fertilization with both mineral and organic fertilizers reduced DOC leaching for a few weeks. Compared to sandy soils from other regions, less DOC was leached from the clayey soils.

Beside the C/N ratio, the oxygen supply is important for decomposition processes to occur. Bueno and Ladha (2009) found that cultivation and the turnover of soils accelerate the decomposition of plant residues in soils by providing oxygen, thereby resulting also in increased DOM leaching. Tile drains may intensify this process due to the direct linkage of agricultural soils to streams and less retention of DOC in the soil (Blann et al., 2009). This could have been the case in our study area as the field is regularly ploughed and drained.

In addition, an accumulation of organic matter in deeper soil layers during dry periods is possible. During subsequent rain events, this organic matter is leached and may lead to increased DOC concentrations in the corresponding drainage pipes Frau 1 and Frau 2.

In our study, the DOM composition of the soil was only poorly correlated with the DOM composition in the corresponding tributaries. Specifically, the labile DOM fractions (C5-C8) in the soil eluates showed higher proportions of the protein-like components tryp (C6) and tyr (C7) and of the humic-like low-molecular hum-lab C8, while the tributaries were characterised by a higher proportion of the humic-like low-molecular hum-mic C5. Graeber et al. (2012) concluded that seemingly contradicting results from soil and stream studies imply that only a low percentage of the soil organic matter (SOM) lost from agricultural soils is transported to the streams as DOM or that DOM originating from agricultural SOM is rapidly taken up in streams. Besides, the DOM from terrestrial sources is usually subject to a variety of biological, physical, and chemical processes in the soil, which alter its composition (Baldock and Skjemstad, 2000; Qualls and Richardson, 2003; Silveira, 2005). Especially the heavy, clayey soils in the HOAL Petzenkirchen increase the retention time of the soil pore water, thereby altering the DOM composition. Tiefenbacher et al. (2020) also observed differences in DOM composition depending on soil texture. The shift from proteins (C6, C7) and hum-lab (C8) to hum-mic (C5) indicates that hum-mic (C5) is probably a product of the degradation of one of the other components. Such relationships between the degradation of one component and the production of another component have also been observed elsewhere (Pucher et al., 2021 - submitted; Casas-Ruiz et al., 2017; Weigelhofer et al., 2020). The strong modification of DOM during the soil passage in our study is also indicated by the increase of HIX and the strong decrease of SUVA254 from soil to the tributaries. This is consistent with Fellman et al. (2009), who observed a decrease in SUVA254 values as DOM moved from soils to sub-catchment streams.

Another explanations for the different patterns of DOC and DOM quality in the soil eluate and the tributaries could be the fact that DOC concentrations of soil eluate represent a potential DOC (Tipping et al., 1999) rather than the material that is leached from the soil under natural conditions. The destruction of the soil aggregates during the analysis and the desorption of organic matter from mineral surfaces by K_2SO_4 stimulate the leaching of soil organic matter from the samples (Ewing et al., 2006; Ogle et al., 2005). Under conditions naturally met in the field, water from the fine pores is usually strongly bound and thus not available for transport.

4.2. Temporal variations of DOC and DOM quality

We observed no clear influence of agricultural practices on the DOC content of the arable soil eluate. The DOC content in the upper soil layer of the arable fields did not vary much, evidently caused by the limited SOC content (2.0 g kg^{-1}) compared to grassland (4.1 g kg^{-1}) and forest (9.2 g kg^{-1}). Although Kalbitz et al. (2000) found a direct impact of agrotechnical practices on DOC in the arable surface soil layer, causing more frequent fluctuations in the DOC content, we did not observe such changes on an about monthly sampling interval. Similarly, Rosa and Debska (2018) found no direct effect of the organic/natural fertilization on the DOC content in a 2 year arable soil sampling campaign in Poland, and Chantigny (2003) stated that changes in DOC resulting from management activities are generally of short duration. Shorter sampling intervals may provide more detailed insight into this question.

However, we observed clear seasonal patterns in the forest and the grassland, with increased DOC concentrations during the warm summer months and a pronounced DOC peak in late autumn. Again, this pattern was not reflected by the tributaries. In contrast, the tributaries showed a general decline in DOC concentrations during summer, with a small peak in late summer (coinciding with a small decline in the DOC concentrations of the soil eluates) and a larger peak in January and February. These patterns may have been mainly driven by precipitation. The dry weather in summer may have led to an accumulation of potentially leachable organic matter within the soils, resulting also in smaller exports from the terrestrial sources to the tributaries. With increasing rain fall and subsequent increasing moisture content in late summer, part of the accumulated soil organic matter was probably washed out, thereby increasing the DOC concentrations of the tributaries. This may also explain the correlation between soil moisture and DOC concentrations in the tributaries. Soil moisture affects the physical, chemical, and biological processes along the transport of DOM through soil and thus influences DOM export to subsurface and drainage waters (Tiefenbacher et al., 2021; Bolan et al., 2011). It appears that higher soil moisture also stimulates microbial activity (Brockett et al., 2012), leading to the consumption of humic-like fluorophores with low molecular weight (C8) and an increase of the relative amounts of terrestrial, recalcitrant, humic-like components (C3).

A relevant input of organic material and thus potentially leachable material is leaf litter in fall. This litter seems to have directly affected soil DOC concentration in the forest in addition to temperature induced seasonal variability. The same phenomenon with less intensity was also observed at the grassland site. These additional organic inputs seem to be immediately leachable and a metabolizable nutrition for microbes, leading to higher DOC concentrations of the soil eluate. In a long-term litter manipulation experiment Kalbitz et al. (2007) found that a doubling of litter input instantaneously doubled the DOC concentrations. The DOC peak in the forest eluates was accompanied by an increase in protein-like fluorescence from 15 % in summer to 36 % in winter. Fellman et al. (2009) observed similar patterns for protein-like fluorescence at three soils in Alaska, where the relative contribution on total fluorescence decreased from 8 and 10 % in May to approximately 5 and 3 % in July and August. The lower level of protein-like contribution compared to our results can be explained by the different climate in Alaska, with much colder temperatures and only 5 months of snow free season.

4.3. Main drivers of DOC at the catchment outlet

The annual DOC inputs from the tributaries into the stream are largely controlled by water flow, while the DOC source plays a secondary role. Blann et al. (2009) found that the catchment export of DOC was larger with drainages due to higher proportion of total annual precipitation discharged to surface waters relative to the amount that is stored in the soil during the year, evaporated or transpired. However, different land uses affected the DOC export to the stream. The tributaries draining the arable land exhibited higher DOC concentrations than the tributaries draining the mixed or forested land use units.

An important DOC source is the stream itself. During baseflow conditions within the period of positive net production from November to May, instream processes caused 37 % of the total measured DOC load at the catchment outlet. The seasonal patterns of instream DOC production can be explained by changes of temperature, light and availability of nutrients. In March and April, the stream shows a peak in net DOC production. During this time, algae growth and thus primary production are high due to increasing water temperatures and availability of light, thus contributing to instream DOC production (Fasching et al., 2016). Similar short periods of autotrophic production have been observed in other headwater streams (Weigelhofer et al., 2012). In May, the stream gets shaded, leading to a breakdown of algal biomass and a decrease of primary DOC production. High water temperatures and nutrient availability control and stimulate bacterial activity, leading to an increase of instream net consumption due to carbon incorporation into microbial biomass and respiration (Demars et al., 2011; Hill et al., 2000; Rosemond et al., 2014). Interestingly, the stream becomes net productive again already in November, at a time when autotrophic activities are still low. We believe that this net DOC production in winter is mainly due to an increased leaching of leaves within the stream or at the banks (lateral DOC inputs not measured) and generally low heterotrophic activities due to low water temperatures.

Short rainfall runoff events in summer can lead to temporary peaks of net production during a period of general net consumption (shown in Figure 6 by individual positive dots during summer). Such temporary peaks are probably due to lateral inputs of DOC from inundated bank areas and/or resuspension and mixing of stream bed material, encouraging instream leaching. In the same catchment, Eder et al. (2014) found that a small rise of stream water level increased transport capacity and caused the resuspension of bed sediments, which likely affects organic matter leaching. A rise of water level will also increase the water contact area for leaching.

Instream processes also alter DOM composition especially during baseflow (Fasching et al., 2016; Raymond et al., 2016). Hum-lab (C8) almost completely disappeared after 600 m of flow length. Molecular size (E2/E3) and aromaticity (SUVA254) increased along the stream indicating bacterial uptake of aliphatic, low molecular weight DOM. This is consistent with the findings of Fellman et al. (2009) for two rivers in Alaska where the protein-rich, labile fraction was selectively removed with passage downstream.

During the period February 3rd to December 31st, 2017, only small rainfall runoff events occurred and thus DOC instream balances were only calculated for baseflow. During high rainfall runoff events, import by tributaries, diffuse lateral inputs from the floodplain, and resuspension will gain in importance, while instream processes will be less significant (Fasching et al., 2016; Raymond et al., 2016). Besides, terrestrial DOM sources for the stream may change in importance.

5. Summary and Conclusions

Based on a sampling campaign conducted during 2017 in the HOAL Petzenkirchen in Lower Austria we draw the following conclusions:

The DOC concentrations of the soil eluates correlate positively with the SOC contents and are 5 and 1.5 times higher at the forest site and the grassland site, respectively, than at the arable land site. In summer, the soil eluate DOC concentration increases probably due to increased microbial activity and the related faster decomposition of organic material. Additional inputs of organic material such as leaf litter in autumn also increase the DOC concentrations in the soil eluate. In contrast to the soil eluate, the DOC concentrations of the tributaries are lower in summer, probably due to the lower hydraulic connectivity from the source to the tributaries. The strong temporal correlation between DOC load and total flow volume of all seven tributaries (r=0.91) indicates that total DOC inputs into the stream are determined by hydrology (i.e. the water fluxes) and land use plays only a secondary role.

Land use and season affect the DOM quality of soil eluate. Leaf litter in winter causes an increase of protein-like DOM. At the tributaries, the impacts of land use and season on the DOM composition are neglectable as processes in the soil alter the DOM quality during transport from the terrestrial source to the stream. Soil moisture correlates with DOM quality, indicating that moisture drives organic matter processing and transport in the soil. High soil moisture leads to an increased share of refractory DOM components and a lower contribution of protein-like and labile humic-like components.

The study also demonstrates that methods of DOC and DOM quality sampling and processing in the soil and the stream are not necessarily comparable. While soil eluates are easy to obtain, they only represent a DOC and DOM quality potential. Even soil pore water collected in the field or from percolation experiments may not represent the DOC and DOM components actually entering the stream, as they are likely modified along the flow path.

Although the catchment of this study is small, relatively homogeneous and dominated by agriculture, the monitoring of the tributaries shows that small forest patches in the immediate vicinity of the stream may play a significant role in the DOC supply. Since flow volumes tend to vary more in space and time than DOC concentrations, the former are more important for determining total DOC loads. Thus, relationships between DOC and DOM quality in the stream and the dominating land use is hard to detect and probably do not fully represent the actual drivers of DOC input into streams. Furthermore, time lags between activities in the catchment and responses in the aquatic DOC need to be accounted for.

Our study also reveals the significance of instream processing of DOC and DOM components, including both production and degradation, complicating the detection of land use impacts and agricultural practises on aquatic carbon characteristics further. In the study period, instream processes increased total DOC export from the catchment by 24 % compared to the DOC inputs from the tributaries. From May 25th to November 20th, 2017, instream net DOC consumption was observed, leading to a loss of 12 kg DOC probably due to bacterial uptake and respiration. Instream processes also alter the DOM quality. The labile humic-like component C8 almost completely disappeared after 600 m of flow length. Molecular size (E2/E3) and aromaticity increased along the stream indicating bacterial uptake of aliphatic, low molecular weight DOM.

Future work may be directed towards rainfall runoff events and their impact on DOC inputs from the fields into the stream and the consecutive stimulation of instream processes. Preliminary results from two observed rainfall runoff events indicate higher DOC inputs from the individual tributaries during high flow compared to base flow and a stimulation of the instream DOC release. Alternative methods for characterising soil DOC and DOM quality may allow the establishment of more direct links across scales. Furthermore, it would be of interest to examine the role of varying levels of DOC loads associated with different land uses for instream DOM processes in streams of different sizes and shapes.

Ethical Statement

The research was done according to ethical standards.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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