

Experimental evidence reveals impact of drought periods on dissolved organic matter quality and ecosystem metabolism in subalpine streams

Astrid Harjung ^{1*} Elisabet Ejarque ^{2,3} Tom Battin,⁴ Andrea Butturini,¹ Francesc Sabater,^{1,5}
Masumi Stadler,⁶ Jakob Schelker^{2,3}

¹Department of Evolutionary Biology, Ecology and Environmental Sciences, University of Barcelona, Barcelona, Spain

²WasserCluster Lunz GmbH, Lunz am See, Austria

³Department of Limnology and Oceanography, University of Vienna, Vienna, Austria

⁴Stream Biofilm and Ecosystem Research Laboratory, School of Architecture, Civil and Environmental Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

⁵Centre de Recerca Ecològica i Aplicacions Forestals (CREAF), Cerdanyola del Vallès, Spain

⁶Département des sciences biologiques, Université du Québec à Montréal, Québec, Montréal, Canada

Abstract

Subalpine streams are predicted to experience lower summer discharge following climate change and water extractions. In this study, we aimed to understand how drought periods impact dissolved organic matter (DOM) processing and ecosystem metabolism of subalpine streams. We mimicked a gradient of drought conditions in stream-side flumes and evaluated implications of drought on DOM composition, gross primary production, and ecosystem respiration. Our experiment demonstrated a production and release of DOM from biofilms and leaf litter decomposition at low discharges, increasing dissolved organic carbon concentrations in stream water by up to 50%. Absorbance and fluorescence properties suggested that the released DOM was labile for microbial degradation. Dissolved organic carbon mass balances revealed a high contribution of internal processes to the carbon budget during low flow conditions. The flumes with low discharge were transient sinks of atmospheric CO₂ during the first 2 weeks of drought. After this autotrophic phase, the metabolic balance of these flumes turned heterotrophic, suggesting a nutrient limitation for primary production, while respiration remained high. Overall our experimental findings suggest that droughts in subalpine streams will enhance internal carbon cycling by transiently increasing primary production and more permanently respiration as the drought persists. We propose that the duration of a drought period combined with inorganic nutrient availability are key variables that determine if more carbon is respired in situ or exported downstream.

Mountainous regions are estimated to provide more than 30% of the global water runoff from the continents to the oceans (Meybeck et al. 2001). At the same time, these regions are predicted to be strongly affected by climate change, as more precipitation will fall as rain rather than snow (Barnett et al. 2005), resulting in a potential loss of stream flow during spring and summer (Berghuijs et al. 2014). In addition, streams in the European Alps are subject to direct human impacts on the hydrological regime, such as water extractions and hydroelectric power production (Maiolini and Bruno

2008). Hence, there is an increasing need to understand the implications of hydrological regime change and in particular, the occurrence of droughts, on alpine stream ecosystem functioning (Hannah et al. 2007; Ulseth et al. 2017).

Subalpine streams are considered net heterotrophic (Uehlinger and Naegeli 1998; Fellows et al. 2001; Hall et al. 2015), with ecosystem respiration (ER) exceeding gross primary production (GPP) resulting in a negative net ecosystem production (NEP). Net heterotrophy is also reported for most other fluvial ecosystems (Mulholland et al. 2001; Hoellein et al. 2013) where high ER is maintained by a steady supply of particulate and dissolved organic matter (POM and DOM) from the terrestrial ecosystem (Battin et al. 2008). The DOM supply from the surrounding catchment is determined by the availability of DOM in soils (Schelker et al. 2013) and its transport with surface runoff and subsurface flow into the main channel (Aitkenhead-Peterson et al. 2003). Hence, heterotrophy largely depends on the hydrological connectivity of soils and streams.

*Correspondence: astridharjung@msn.com

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

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

Autochthonous DOM has been found to contribute less than 5% of the DOM pool of headwater streams (Mulholland 1997).

The effects of hydrological variation on DOM quantity have been well studied in the context of stormflow events. For example, several studies report that DOM quantity increases with discharge (Ågren et al. 2008; Wiegner et al. 2009; Bass et al. 2011; Guarch-Ribot and Butturini 2016). DOM quality changed toward a terrestrial, more humified composition, with probably lower biodegradability for heterotrophic metabolism (Saraceno et al. 2009; Fasching et al. 2016; Raymond et al. 2016). However, little is known about how extended periods of reduced flow may affect DOM quantity and quality, particularly in humid regions (Larned et al. 2010).

Streams regularly subject to flow intermittency, such as those of the Mediterranean biome, show distinct patterns of DOM processing. DOC concentrations have been found to increase with decreasing discharge during summer drying (Von Schiller et al. 2015). Although this DOC increase during drying is less prominent than during storm events, the former is paralleled with a change in DOM composition toward labile characteristics (Vázquez et al. 2011; Butturini et al. 2016; Ejarque et al. 2017). Additionally, some Mediterranean and semiarid streams have been characterized to transiently shift to net autotrophy (Webster and Meyer 1997; Velasco et al. 2003), acting as sources of aquatic DOM. Phases of net autotrophy are partly explained by high water temperatures that enhance GPP (Busch and Fisher 1981; Acuña et al. 2004). Similarly, Proia et al. (2016) report higher autochthonous carbon loads in a Mediterranean river during summer low-flow associated with longer water residence times.

To identify the potential effects of drought conditions on subalpine stream ecosystem functioning, we designed an experiment in stream-side flumes. We recreated six hydrological conditions, ranging from baseflow to drought, and evaluated changes in DOM quantity and quality, as well as in whole-flume metabolism. We expected the ecosystem response to drought to be similar to the responses reported for drier regions (Jones et al. 1996; Mulholland et al. 2001; Velasco et al. 2003) and predicted that discharge reduction will increase water residence time and water temperature. Following these alterations, we expected higher in-stream DOC production and an increase of autochthonous DOM in the flumes with low discharges, as well as an increase in autotrophic metabolic pathways.

Methods

Experimental setup

This study consisted of simulating decreasing flow conditions from base flow to drought in six streamside flumes located in the subalpine region of lower Austria (47° 15'N 15°04'E). All flumes were fed with stream water of the "Oberer Seebach," a pristine, second-order stream draining a karst catchment of 25 km² located between 600 m and 1900 m above sea level (Schelker et al. 2016). Previous studies have identified

hydrological conditions as a major driver of dissolved CO₂ concentrations (Peter et al. 2014). Generally low production and high respiration result in a low autotrophic contribution to the carbon budget (Ulseth et al. 2017). DOC concentration ranges from 1.11 mg C L⁻¹ to 5.43 mg C L⁻¹ and increases with discharge. DOM composition is typically terrestrially derived and humic-like, with some autochthonous imprints during base flow (Fasching et al. 2016). Summer stream water temperature ranges from 6.6°C to 15.0°C, inorganic nutrient concentrations (mean ± SD) are generally low (N-NO₃ = 1197 ± 261 μg L⁻¹; N-NO₂ = 0.8 ± 0.5 μg L⁻¹; N-NH₄ = 10 ± 8 μg L⁻¹; P-PO₄ = 5 ± 2.5 μg L⁻¹) and the stream is commonly supersaturated in O₂ (12.1 ± 0.8 mg L⁻¹) (Müllner and Schagerl 2003).

The flumes (40 m length, 0.4 m width) were filled with a mixture of sand (d_{50} = 0.2–0.4 mm) and leaf-litter (*Fagus sylvatica* and *Acer pseudoplatanus*), representing the streambed sediment containing a typical source of POM of terrestrial origin. We chose a total organic carbon to sediment ratio of ~ 1.5 g C kg⁻¹ that is within the range of 0.8–2.1 g C kg⁻¹ found in the bed sediments of "Oberer Seebach" (Leichtfried 1996). The sand-leaf-litter mixture was distributed as a series of dunes (2 m long, maximum height of 0.15 m and minimum height of 0.05 m above the bottom of the flumes) in order to create a sequence of pools and riffles (Fig. 1a–d). A thin layer of gravel was added the tops to avoid erosion.

The experiment was performed during August and September of 2015 and consisted of three phases: First, a 2-week pretreatment phase with constant discharge (2.65 L s⁻¹) in all flumes to allow colonization by bacteria and establishment of biofilms. Second, a 3-week treatment phase with different levels of decreased discharge (Table 1) in each flume, except for the control flume (F6) remaining with the initial discharge. Third, a reflow phase where all flumes received pretreatment discharge levels for 3 d.

Flume ecosystem monitoring

We used a combination of high-frequency monitoring with sensors and grab sampling. Light intensity and temperature were measured continuously in each flume over the whole duration of the experiment by a HOBO Pendant Temperature/Light 64K Data Logger (Onset Computer Corporation). Dissolved oxygen concentrations were recorded continuously during treatment and reflow with one HOBO Dissolved Oxygen Data Logger at the end of each flume, as well as at the inlet of control flume F6. A UV-Vis probe (Spectro:lyser, S::can Messtechnik GmbH) was installed in a flow through cell, measuring absorbance spectra from the water at the outflow of each flume (once per hour) and from the inflow (twice per hour) during the last week of the treatment phase. From UV-Vis spectral data hourly DOC and NO₃ concentrations were estimated using the manufacturer's algorithms. Surface water was sampled manually every 3 d during pretreatment and during treatment, and every day during the reflow phase. Temperature and dissolved oxygen concentration were measured at

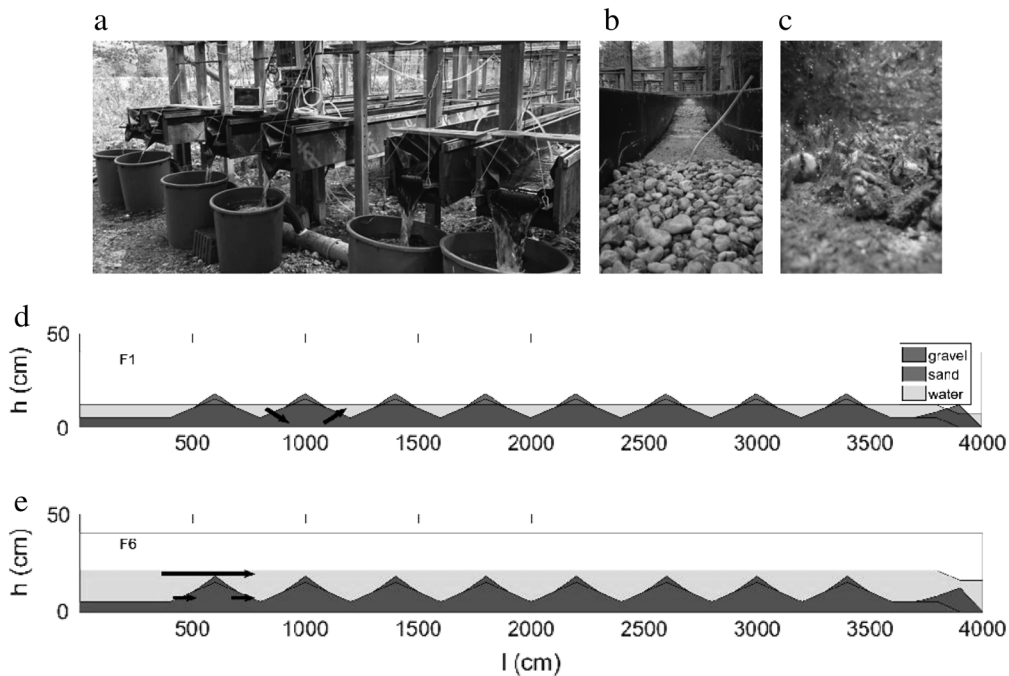


Fig. 1. (a) Flume outlets with discharge ascending from the left (F1) to the right (F6). (b) Set up of flumes before water flow and (c) underwater photo of biofilm after 2 weeks of treatment (17th of September 2015). (d) Scheme of F1 during treatment with black arrows indicating the enforced water flow through the stream bed. (e) Scheme of F6 during treatment with black arrows indicating the water flow predominantly above the stream bed.

every manual sampling at the inflow and the outflow with a FiresStingO2 optical oxygen meter (Pyro Science GmbH). Manual measurements of dissolved oxygen agreed well with automated measurements ($r^2 = 0.94$; slope = 0.99, y -intercept = 0.27; data not shown). Discharge was measured volumetrically at the inflow and at the outflow. Salt slug injections were used to measure flow velocity during treatment. Samples, collected with three replicates at the inflow and one at each outflow for DOC and optical properties were stored in borosilicate vials, which were prepared by soaking in 0.1 N HCl, rinsing with MilliQ water and combusting at 450°C for 4 h. Inorganic nutrient samples were collected into sterile conical base centrifuge tubes. All manual samples were filtered with 0.7 μm Whatman GF/F filters directly in the field. Manual

samples for dissolved gases (CO_2 and CH_4) were collected in clear glass serum bottles with unfiltered stream water without a headspace and closed with a gas-tight rubber septum.

Laboratory analyses

We analyzed for DOC, N- NO_3 , N- NO_2 , N- NH_4 , and P- PO_4 concentrations and measured DOM fluorescence and absorbance. DOC concentration was measured on a TOC analyzer with an inorganic carbon removal unit (GE-Sievers 900). DOM absorbance spectra over 200–700 nm wavelength were obtained from an UV-Vis spectrophotometer (Shimadzu UV 17000), using 5-cm cuvettes and MilliQ water as a blank. Fluorescence intensities were measured on a Hitachi F-7000 spectrofluorometer with 1-cm quartz cuvettes at excitation wavelengths ranging from 240 nm to 450 nm and emission wavelengths from 250 nm to 550 nm. N- NO_3 , N- NO_2 , N- NH_4 , and P- PO_4 concentrations were measured on a continuous flow nutrient analyser (Alliance Instruments). Dissolved gas (CO_2 and CH_4) partial pressure of manual gas samples was measured in a manually generated headspace on a Cavity RingDown Spectrometer (CRDS) G2310 (Picarro cooperation).

Table 1. Discharge (Q), flow velocity (v), water residence time (WRT), water volume (WV), and the percentage of water volume being interstitial water (IW) in flumes during treatment.

Flume	Q (L s^{-1})	v (cm s^{-1})	WRT (min)	WV (m^3)	IW (%)
F1	0.03	0.19	351	0.63	100
F2	0.10	0.34	196	1.18	63
F3	0.35	1.11	66	1.39	54
F4	0.73	2.27	29	1.29	58
F5	1.45	4.07	16	1.39	53
F6	2.65	6.67	10	1.59	47

DOM spectroscopic data treatment

DOM quality was investigated using its specific fluorescence and absorbance characteristics as described in the following. Excitation-emission-matrices were subtracted by MilliQ water blanks to remove Raman scattering (Goletz et al. 2011) and were corrected for the inner filter effect using

corresponding absorbance spectra (Lakowicz 2006). Raw fluorescence data was converted into Raman units by dividing by the area of the Raman peak of a MilliQ sample measured on the same day of analysis. All fluorescence measurements were corrected for wavelength-dependent lamp inefficiencies using manufacturer's built-in functions. From absorbance and fluorescence measurements the following parameters were determined (Table 2): Specific ultra violet absorbance (SUVA₂₅₄) was calculated as absorbance measured at 254 nm, divided by the cuvette path length and normalized to the DOC concentration and is reported in units of mg C m⁻¹ L⁻¹. Higher SUVA₂₅₄ has been found to correspond to higher aromaticity of DOM (Weishaar et al. 2003). Spectral slope ratio (SR) was calculated as described by Helms et al. (2008), attributing an increase of this ratio to photodegradation. Fluorescence index (FI) was calculated as the ratio of excitation at 370 nm of intensities emitted at 470 : 520 nm (Cory and McKnight 2005); lower values are considered to be of terrestrial origin and higher values correspond to an autochthonous origin (McKnight et al. 2001). Biological index (BIX), the ratio of emission 380 nm and 430 nm at excitation 310 nm, was used to describe freshness (higher values refer to more recent production) of DOM (Huguet et al. 2009). The humification index (HIX), an index increasing with humification, was calculated using the area under the emission spectra 435–480 nm divided by the peak area 300–345 nm from the spectra at excitation 254 nm (Ohno 2002). Parallel factor analysis (PARAFAC) components were calculated with the MATLAB toolbox drEEM by Murphy et al. (2013). A 4-component model was validated using split-half analysis with four

random split combinations (Murphy et al. 2013). PARAFAC components are expressed as relative fluorescence intensities (ΣCi) using, %Ci = $Ci \setminus \Sigma Ci \times 100\%$.

Statistical analyses

To focus on the net changes in water chemistry occurring within each flume, rather than on the variability in the incoming water, data are reported relative to the inflow as

$$\eta X = \frac{X_f - X_{in}}{X_{in}} \times 100 \quad [\%], \quad (1)$$

where ηX is the percentage of change of the parameter at the outlet of the flume X_f compared to the mean value of three replicates of the inflow X_{in} .

The effects of hydrology (discharge, 6-level factor) on ηX were tested using nonparametric Kruskal–Wallis tests, followed by Tukey–Kramer post-hoc analysis when significant differences were found. Specifically, we compared discharge levels from F1 to F5 during treatment with the control discharge (2.65 L s⁻¹) that covered data from F6 during the whole experimental period and from F1 to F5 during pretreatment and reflow. The flumes were subject to the prevailing light conditions. Therefore we performed Kruskal–Wallis tests, followed by Tukey–Kramer post-hoc analysis with the daily sum of light intensity as the response variable and flume as the main effect. F1 showed a higher light intensity, while all the other flumes were not significantly different ($p > 0.1$). This was the same for all three experimental phases (pretreatment, treatment, and reflow). Hence, we assume that any trends seen

Table 2. Description of abbreviations of absorbance and fluorescence optical indices for dissolved organic matter used in this study.

Parameter	Abbreviation		Description		Units	Literature
Specific ultraviolet absorbance	SUVA ₂₅₄		Higher absorbance at 254 nm divided by DOC concentration indicates higher aromatic carbon content		mg-C L ⁻¹ m ⁻¹	Weishaar et al. (2003)
Spectral slope ratio	SR		Generally increases with DOM being subjected to irradiation			Helms et al. (2008)
Fluorescence index	FI		Indicates the relative contributions of allochthonous vs. autochthonous DOM			Mcknight et al. (2001)
Humification index	HIX		Increasing with humification of DOM			Ohno (2002)
Biological index	BIX		Indicates freshly produced DOM in the aquatic environment			Huguet et al. (2009)
Parallel factor analysis	PARAFAC	Excitation/emission	Peak	Description	%	Murphy et al. (2013)
Component 1	C1	<240, (350)/476	Peak C	Ubiquitously humic-substances, associated with predominately terrestrial sources		Coble (1996), Yamashita et al. (2010)
Component 2	C2	300/396	Peak M	Low molecular weight, biological activity		Lapierre and Del Giorgio (2014), Cory and Mcknight (2005)
Component 3	C3	275/342	Peak T	Amino acids, free or bound in proteins, may indicate intact proteins		Cory and Mcknight (2005), Yamashita et al. (2010), Lapierre and Del Giorgio (2014)
Component 4	C4	<240, (275)/314	Peak B	Tyrosine-like fluorophore, amino acids, free or bound in proteins		Yamashita et al. (2011)

during treatment, but not during pretreatment or reflow are a sole result of differences in discharge and that difference in light availability between the flumes had a negligible impact on the variability in ηX . Linear trends of variables over time and with discharge were tested with nonparametric Mann-Kendall test using MATLAB with the curve fitting toolbox (MATLAB 2016). Variables which were found to be affected by the drought treatment with the Kruskal–Wallis test ($p < 0.01$), were also tested with a two-way ANOVA on the influence of two independent variables (discharge and days of treatment) and the interaction of these two. Normality of residuals was evaluated with the Shapiro–Wilk test (significance level $\alpha = 0.01$) and with histograms. Data not fulfilling normality were power transformed with the most suitable exponent to meet the assumptions (Helsel and Hirsch 2002; post-transformation histograms see Supporting Information Fig. S2). Whereas no transformation was required for ηDOC (Shapiro–Wilk test $p = 0.77$), ηNO_3 (post-transformation $p = 0.07$) was transformed to the power of 2, ηC_3 (post-transformation $p = 0.07$) and ηSUVA_{254} (post-transformation $p = 0.02$) to the power of -2 . This analysis was performed with the R-package car (R Team Development Core 2008).

Estimation of net ecosystem production

NEP was estimated from continuous diel dissolved oxygen measurements (Odum 1956). Estimates were based on 5-min interval by taking the change in dissolved oxygen from the inflow (represented by dissolved oxygen measurements at the inflow of F6) and the outlet of each flume. Reaeration coefficient k was calculated with Bayesian models, using the R toolbox “streamMetabolizer” (Appling et al. 2017) and in addition with the nighttime regression method by taking the slope between the rate of change and the deficit of dissolved oxygen during each night. Both methods gave k -values in the same range (Supporting Information Table S1). For simplicity, we decided to only use the robust k 's of the Bayesian models with the best fit.

We used the two-station-method to account for the short reach length of the flumes. According to Reichert et al. (2009) the minimal reach length depends on flow velocity and the reaeration coefficient. This criterion was not fulfilled for flumes F5 and F6. Hence, NEP was only calculated for flumes F1 to F4 during treatment. The change of dissolved oxygen ($\text{DO}_{\text{outflow}} - \text{DO}_{\text{inflow}}$) was divided by the travel time (t_t) of each flume and subtracting the temperature corrected reaeration coefficient (k_t) multiplied with the oxygen deficit (D) (Odum 1956; Bernot et al. 2010)

$$\text{DO}_{\text{net}} = \frac{\text{DO}_{\text{outflow}} - \text{DO}_{\text{inflow}}}{t_t} - k_t D \quad [\text{mg O}_2 \text{ L}^{-1} \text{ min}^{-1}] \quad (2)$$

From this corrected oxygen net rate (DO_{net}) the mean values of each night were taken and temperature-corrected with the following formula after Demars et al. (2016), centring the values around the overall average temperature T_{all} of 10.26°C , representing the ER at every minute.

$$\text{ER} = \text{mean}(\text{DO}_{\text{net,night}}) \times \exp \left[E \times \left(\frac{1}{\text{Bk} \times T_{\text{all}}} - \frac{1}{\text{Bk} \times T_{\text{mean}}} \right) \right] \quad [\text{mg O}_2 \text{ L}^{-1} \text{ min}^{-1}] \quad (3)$$

where E is the apparent activation energy (0.57 eV) for respiration taken from Yvon-Durocher et al. (2012) for rivers and Bk is the Boltzmann constant ($8.62 \times 10^{-5} \text{ eV K}^{-1}$). The $\text{GPP}_{\text{daily}}$ was then calculated by adding the absolute values of ER to the corrected net rate and integrating the resulting values over time in order to obtain $\text{mg O}_2 \text{ L}^{-1} \text{ d}^{-1}$.

Estimation of DOC mass balance

To illustrate carbon fluxes at different discharge levels, we estimated carbon mass balances for 24 h at the end of the treatment (17th day). This day was chosen because of the availability of sensor and laboratory measurements and stable light conditions during that day. DOC generated from the flumes ($\eta\text{DOC}_{\text{gen}}$) was calculated with DOC estimates from absorbance spectra as:

$$\eta\text{DOC}_{\text{gen}} = Q_f \times \int_{t_2}^{t_1} (\text{DOC}_f - \text{DOC}_{\text{in}}) dt \quad [\text{mg C d}^{-1}] \quad (4)$$

where t_1 is the time before sunrise and t_2 the same time on the next day; DOC_f the DOC concentration at the outflow of each flume and DOC_{in} the mean DOC concentration at the inflow measured by the UV–Vis probe ($\text{DOC}_{\text{in,r1}}$ and $\text{DOC}_{\text{in,r2}}$). As some inaccuracies in optical measurements can occur (e.g., by particles blocking the optical path), data treatment included the removal of out-of-range values, whereby only $(\text{DOC}_f - \text{DOC}_{\text{in}})$ values which were higher than $\max|\text{DOC}_{\text{in,r1}} - \text{DOC}_{\text{in,r2}}|$ were included in Eq. 4. Further, DOC mass exports since the beginning of the treatment until the day of the DOC balance were quantified as the following: First, ηDOC was interpolated for every day. Second, $\eta\text{DOC}_{\text{gen}}$ was calculated by multiplying ηDOC with a correction factor accounting for reduced DOC release during nighttime. This correction factor (0.833 and 0.64 for F1 and F2, respectively) was estimated as the ratio of manually measured $\eta\text{DOC}_{\text{gen}}$ calculated from daytime DOC concentrations and $\eta\text{DOC}_{\text{gen}}$ from continuous measurements (UV–Vis probe) for the entire day as presented in Eq. 4. Third, DOC mass exports [g] were then calculated by summing up daily $\eta\text{DOC}_{\text{gen}}$.

NEP estimations were converted into carbon concentrations by multiplying them with the molar ratio of CO_2 and

Table 3. Concentrations of DOC and nutrients and DOM optical properties during the treatments (means \pm standard deviation). Bold letters indicate that the main effect of discharge (Q) was significant in the Kruskal–Wallis test. Daggers indicate the results of the post-hoc analysis. Asterisks indicate if the interaction of Q and treatment duration was significant in the two-way ANOVA.

	F1	F2	F3	F4	F5	F6	Inflow
Q (L s ⁻¹)	0.03	0.10	0.35	0.73	1.45	2.65	
DOC ($\mu\text{g L}^{-1}$) *	1517$\dagger$$\pm$196	1488$\dagger$$\pm$331	1299$\dagger$$\pm$359	1272\pm359	1261\pm328	1249\pm358	1240\pm346
N-NO ₃ ($\mu\text{g L}^{-1}$) *	892$\dagger$$\pm$96	930$\dagger$$\pm$53	986\pm40	1000\pm37	1006\pm34	1013\pm29	1019\pm37
N-NH ₄ ($\mu\text{g L}^{-1}$)	10 \pm 5	11 \pm 5	10 \pm 13	11 \pm 10	7 \pm 8	7 \pm 7	6 \pm 3
P-PO ₄ ($\mu\text{g L}^{-1}$)	0.1 \pm 0.0	0.1 \pm 0.0	0.2 \pm 0.3	0.2 \pm 0.2	0.2 \pm 0.2	0.1 \pm 0.1	0.3 \pm 0.4
C1 (%)	51.7 \pm 2.5	52.5 \pm 3.3	54.2 \pm 2.2	54.3 \pm 2.3	54.4 \pm 2.9	54.5 \pm 2.1	53.9 \pm 2.4
C2 (%)	37.0 \pm 1.6	37.5 \pm 1.6	38.6 \pm 1.0	39.2 \pm 0.7	39.5 \pm 0.7	39.1 \pm 0.7	39.4 \pm 0.8
C3 (%)	5.4$\dagger$$\pm$1.8	4.7\pm1.3	3.3\pm0.8	2.7\pm0.9	2.3\pm0.7	3.2\pm1.0	2.3\pm0.9
C4 (%)	5.9 \pm 3.6	5.3 \pm 3.7	3.9 \pm 2.5	3.8 \pm 2.6	3.9 \pm 2.9	3.2 \pm 1.8	4.4 \pm 2.1
SUVA ₂₅₄ (mg-C L ⁻¹ m ⁻¹)	2.48$\dagger$$\pm$0.17	2.59$\dagger$$\pm$0.20	2.78\pm0.19	2.79\pm0.17	2.81\pm0.26	2.86\pm0.23	2.82\pm0.14
S _R	0.92\pm0.04	0.90\pm0.04	0.86\pm0.04	0.84\pm0.03	0.85\pm0.02	0.86\pm0.05	0.83\pm0.04
HIX	0.86 \pm 0.03	0.87 \pm 0.03	0.90 \pm 0.03	0.91 \pm 0.02	0.91 \pm 0.02	0.90 \pm 0.02	0.90 \pm 0.02
BIX	0.68 \pm 0.02	0.69 \pm 0.02	0.68 \pm 0.02	0.69 \pm 0.02	0.68 \pm 0.03	0.70 \pm 0.03	0.69 \pm 0.02
FI	1.75 \pm 0.06	1.71 \pm 0.03	1.73 \pm 0.05	1.69 \pm 0.02	1.74 \pm 0.07	1.68 \pm 0.07	1.71 \pm 0.04

with the photosynthetic quotient PQ of 1/1.2 for GPP and the respiration coefficient RQ of 1/0.85 for ER (Dodds et al. 1996). The concentration was converted into mass by multiplying them with the water volume (WV) of each flume as

$$\text{GPP}_{\text{daily}} = \frac{12}{32} \times \text{PQ} \times \text{WV} \times \text{GPP}_{\text{daily}} \quad [\text{mg C d}^{-1}] \quad (5)$$

and

$$\text{ER}_{\text{daily}} = \frac{12}{32} \times \text{RQ} \times \text{WV} \times \text{ER}_{\text{daily}} \quad [\text{mg C d}^{-1}] \quad (6)$$

Finally, for the mass balance MB_{daily} we assumed that GPP_{daily} would be equal to the amount of carbon respired (ER_{daily}) and exported ($\eta\text{DOC}_{\text{gen}}$).

$$\text{MB}_{\text{daily}} = \text{GPP}_{\text{daily}} - (\text{ER}_{\text{daily}} + \eta\text{DOC}_{\text{gen}}) \quad [\text{mg C d}^{-1}] \quad (7)$$

If the MB_{daily} was negative, we assumed that DOC was supplied by autotrophs or by leaf litter in the sediment.

Results

Drought effect on nutrient concentrations and DOM composition

Drought impacted DOM and nutrient composition (Fig. 2, Table 3). Low discharge levels (0.03 L s⁻¹ in F1 ($n = 5$) and 0.1 L s⁻¹ in F2 ($n = 5$) during treatment) resulted in significantly higher ηDOC ($\chi^2 = 41.1$, $\text{df} = 5$, $p < 0.01$), lower ηNO_3 ($\chi^2 = 36.9$, $\text{df} = 5$, $p < 0.01$) and lower ηSUVA_{254} ($\chi^2 = 29.7$, $\text{df} = 5$, $p < 0.01$) compared to the control discharge during the whole experimental period (2.65 L s⁻¹, $n = 53$). Additionally, PARAFAC component ηC3 in F1 ($\chi^2 = 17.7$, $\text{df} = 5$, $p < 0.01$)

and ηDOC in F3 ($Q = 0.35 \text{ L s}^{-1}$, $n = 5$) during treatment were significantly higher compared to the control discharge. Overall, the variation of ηDOC with the six discharge levels could be best described by an exponential function, where average $\eta\text{DOC}(\%) = 41 \times e^{-5.6 \times Q}$ (linear model with $\log(Q)$: $r^2 = 0.90$, $p < 0.01$, $n = 6$). Water residence time showed a positive, linear relationship with average ηDOC ($r^2 = 0.98$, $p < 0.01$, $n = 6$), as well as $\eta\text{water temperature}$ with all ηDOC values during the whole treatment phase ($r^2 = 0.75$, $p < 0.01$, $n = 30$). By contrast, ηSR , ηHIX , ηBIX , and ηFI and the PARAFAC components ηC1 , ηC2 , and ηC4 did not show significant differences between discharge levels.

Moreover, we found that ηDOC was also significantly related to the interaction between discharge level and treatment duration (two-way ANOVA, $F_{(5,8)} = 56.2$, $p < 0.01$). Over time, flumes with the lowest discharge (F1 and F2) showed a continuous increase in ηDOC (Fig. 2a), reaching values of almost 50% in F1 ([DOC] = 1513 $\mu\text{g L}^{-1}$, compared to the inflow [DOC] = 1034 $\mu\text{g L}^{-1}$) by the end of the treatment. In F1 and F2, variation over time followed a significant linear trend (Mann-Kendall test, both $p = 0.02$) where the increase in F1 had a steeper slope (slope = 1.5) than in F2 (slope = 1.2). ηNO_3 was also related to the interaction between discharge and treatment duration ($F_{(5,18)} = 7.2$, $p < 0.01$). ηNO_3 declined by 25% in the beginning of the treatment in F1, but gradually returned to pretreatment levels (Fig. 2d). The interaction effect of treatment duration and discharge was not significant for DOM indices ηC3 ($F_{(5,18)} = 0.2$, $p = 0.9$) and ηSUVA_{254} ($F_{(5,18)} = 0.6$, $p = 0.7$), indicating that the quality of the released DOC did not follow an overarching temporal change. During treatment, protein-like ηC3 was on average (\pm SD) +160 (± 98)% and +135 (± 105)% in F1 and F2, respectively.

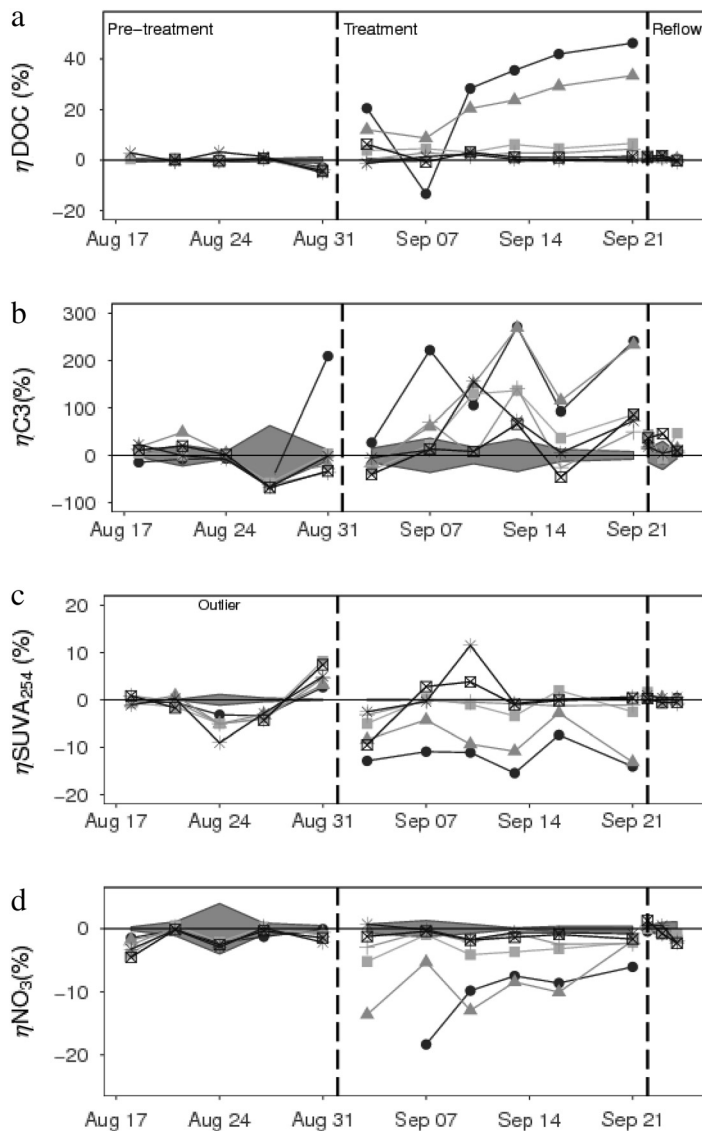


Fig. 2. η values for (a) DOC concentration, (b) $SUVA_{254}$, (c) C3 (peak T, labile), and (d) $N-NO_3$ concentrations in the flumes F1 (red circle), F2 (orange triangle), F3–F6 (light to dark blue squares and crosses) relative to the inflow (the SD replicates of the inflow as gray area) over the whole experimental period. Dashed lines indicate the start and the end of the treatment.

In contrast, $SUVA_{254}$ was $-12\% \pm 3\%$ and $-8\% \pm 4\%$ in these flumes.

Drought effect on water temperature

During pretreatment and reflow, $\eta_{\text{water temperature}}$ was less than $\pm 10\%$. Discharge reduction increased water residence time, resulting in a high positive $\eta_{\text{water temperature}}$ and diurnal variability (maximum daily range of water temperature between 9°C and 18°C in F1 compared to 8°C and 11°C in F6). During the treatment phase, the flumes with the lowest discharge (F1 and F2) had a significantly higher $\eta_{\text{water temperature}}$ ($\chi^2 = 24.1$, $df = 5$, $p < 0.01$) than the control

discharge over the whole experimental period. The highest $\eta_{\text{water temperature}}$ observed in F1 was $+77\%$ (equals to $\sim 20^\circ\text{C}$).

Gas concentrations and metabolic balance

Flume gas concentrations of O_2 and pCO_2 showed strong variation over time and with treatment. During pretreatment, ηpCO_2 decreased continuously to $\eta pCO_2 -50\%$, whereas ηO_2 remained near zero (Fig. 3). During treatment, ηpCO_2 increased in all flumes with a more pronounced increase in F1, F2, and F5 and reached values of up to 120% in F1 at the end of the treatment. With the beginning of reflow ηpCO_2 immediately dropped to 0% in all flumes which coincided with a rapid reduction in water temperature from 10°C to 7.5°C (Fig. 3c). The temporal dynamics of ηO_2 consisted of a strong increase in the beginning of the treatment phase in F1 and F2 and a decrease over time (Fig. 3b). Dissolved Oxygen went up in F1 ($\eta O_2 = 35\%$) immediately after the beginning of the treatment phase and in F2 by 40% by the end of the first week. After that, ηO_2 declined to negative ηO_2 values in both flumes after 3 weeks of treatment.

The dynamics of the dissolved gases were reflected in the dynamics of the production-respiration-ratio (P/R ratio, Fig. 3d). In F1 and F2, the P/R ratio reached values above 2 in the first week of treatment but declined to values below 1 during the third week. By contrast, the P/R ratio in F3 and F4 remained close to 1 (0.9 ± 0.4 and 1.1 ± 0.4 , respectively), indicating that no process (production or respiration) was dominating. In F1, GPP showed a significant negative linear trend with treatment duration (Mann-Kendall test, $p < 0.001$). However, ER did not follow this trend, indicating a decoupling of GPP and ER during treatment.

DOC mass balance

The reduction of discharge had a pronounced effect on sources and sinks of carbon, as exemplified by DOC mass balances integrating carbon fluxes of 24 h at the end of the experiment. Hourly UV–Vis sensor data revealed that ηDOC and ηNO_3 in F1 and F2 followed clear diel cycles during treatment, which disappeared immediately with reflow (Fig. 4). The ηDOC estimated from the absorbance spectra peaked during daytime at $+48\%$ in F1 (8 pm) and at $+34\%$ in F2 (5 pm). At nighttime, ηDOC decreased to 10% in F1 and to 5% in F2. In terms of production rate per day ($\eta\text{DOC}_{\text{gen}}$), we estimated a $\eta\text{DOC}_{\text{gen}}$ of $\sim 1.0 \text{ g C d}^{-1}$ from F1 and 1.8 g C d^{-1} from F2. When we calculated $\eta\text{DOC}_{\text{gen}}$ for the same day by extrapolating the lab measurement of one grab sample taken during daytime, $\eta\text{DOC}_{\text{gen}}$ from F1 (1.2 g C d^{-1}) and F2 (2.8 g C d^{-1}) were notably higher. This demonstrates that omitting diel cycles alters estimations of daily DOC exports.

F1 never reached positive NEP on the day of the DOC mass balance but released relatively more DOC coming from either autotrophic production or previously stored DOC than F2. In F1, 35% more DOC than inflowing was exported (Fig. 5a),

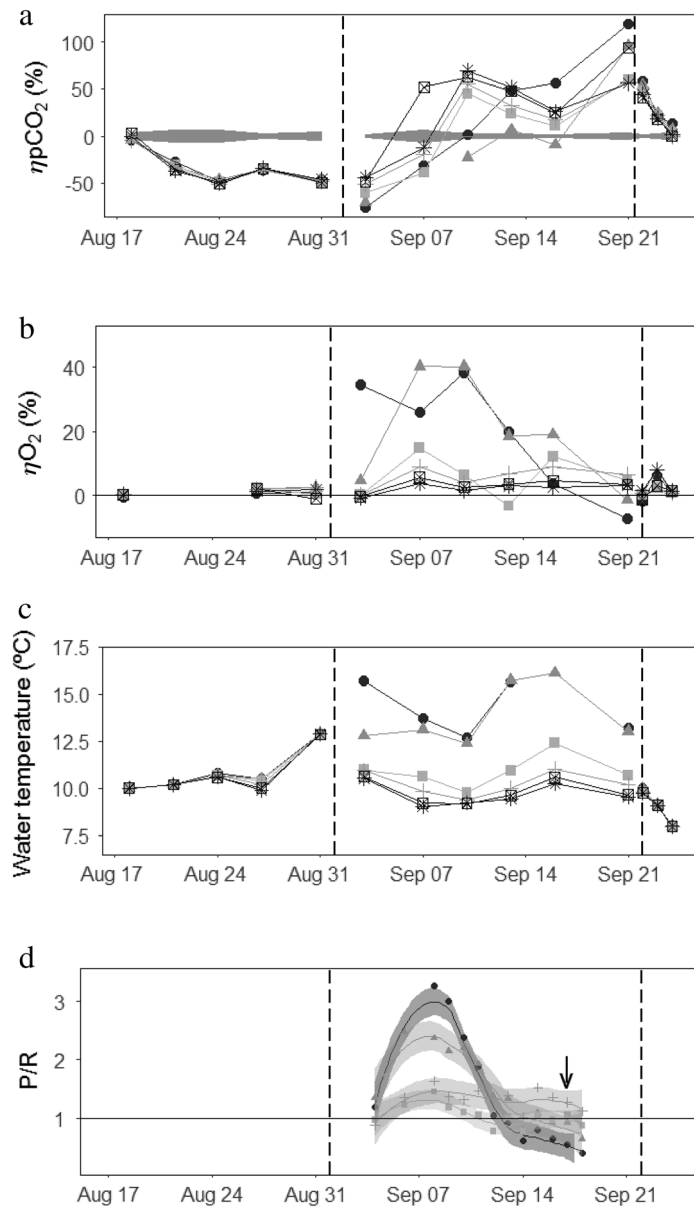


Fig. 3. (a) Shows the $\eta p\text{CO}_2$ relative to the mean of the inflow (the SD of all six inflows as gray shaded area). (b) O_2 measured at the outflow of each flume compared to inflow as η values for F1 (red circles), F2 (orange triangles), and F3–F6 (light to dark blue squares and crosses) over the whole experiment period. (c) Water temperature ($^{\circ}\text{C}$) at the outflow of flumes (same scheme as in a, b) and inflow (black line). (d) Daily P/R values for flumes F1 (red circles), F2 (orange triangles), F3 (green squares), and F4 (cyan crosses) during the treatment period. Arrow indicates the day of the mass balance. Dashed lines indicate the start and the end of the treatment.

while this export was only 21% in F2 (Fig. 5b). Moreover, we found that there was almost three times as much carbon respired (5.8 g C d^{-1}) than incorporated by photosynthesis in F1 (2.1 g C d^{-1}). In general, GPP and ER were important fluxes in the carbon budget of F1 and F2, while in flumes with

higher discharge these fluxes were relatively lower. For example in F1, GPP and ER represented 72% and 200% of the DOC mass entering the flume, whereas in F4 these fluxes only represented 13% and 15%, respectively (Fig. 5c).

Since daily NEP was negative in F1 on the day of the DOC mass balance, the export and respiration of carbon was supported by DOM from a surplus of GPP stored since the onset of drought or from microbial processing and leaf litter. We estimated a surplus of biomass originating from NEP of 1.9 g in F1 and 5.6 g in F2 that could maintain excess $\eta\text{DOC}_{\text{gen}}$ and ER. However, a rough estimation of $\eta\text{DOC}_{\text{gen}}$ since the beginning of the treatment suggested that 7.5 g and 15.2 g were already exported during the same time period from F1 and F2, respectively. This estimation demonstrates that export and respiration of DOC relied on leaf litter as a carbon source and that the microbial utilization of this source was likely higher in the flumes with low discharge than in the others.

Discussion

Our experiment demonstrated an increase of DOC concentration with discharge reduction that originated from autochthonous sources (high C3 and low SUVA_{254}) with assumingly high availability for heterotrophic metabolism. The change in DOM bioavailability during drought was paralleled by an initial phase of increased GPP that was superimposed with high ER. The latter persisted until the end of the experiment, despite a decline in GPP. These findings show that summer droughts in subalpine streams might enhance in-stream carbon processing and that longer drought periods can facilitate the decomposition of organic matter stored in stream sediments.

Potential drivers of labile DOM increase during low flow

We found net DOC releases ($\eta\text{DOC}_{\text{gen}}$) of up to $65 \text{ mg C m}^{-2} \text{ d}^{-1}$ and $113 \text{ mg C m}^{-2} \text{ d}^{-1}$ for F1 and F2, respectively. These values are in the same range as the net DOC export from GPP reported from a desert stream ($70\text{--}209 \text{ mg C m}^{-2} \text{ d}^{-1}$; Jones et al. 1996). Similarly, DOC mass balances from a Mediterranean river have revealed pulses of net DOC release of up to $800 \text{ mg C m}^{-2} \text{ d}^{-1}$ during a low-flow period (Butturini et al. 2016). Nutrient-rich, urban streams were even found to exceed these values with DOC releases of up to $1344 \text{ mg C m}^{-2} \text{ d}^{-1}$ (Sivirichi et al. 2011). In our experiment, ηDOC had a positive, linear relationship with water residence time and water temperature, suggesting that these two factors were the main drivers of DOM release and composition change.

GPP has been found to be affected by water residence time and water temperature. For example, rivers with high flow velocities and resulting bottom shear stress sustain GPP by benthic algae, whereas in large and slow flowing rivers plankton and long filamentous algae dominate (Larned et al. 2004; Hall et al. 2015). We do not have explicit information on the autotrophic community structure in our experiment but observed floating, filamentous algae only in F1 and F2.

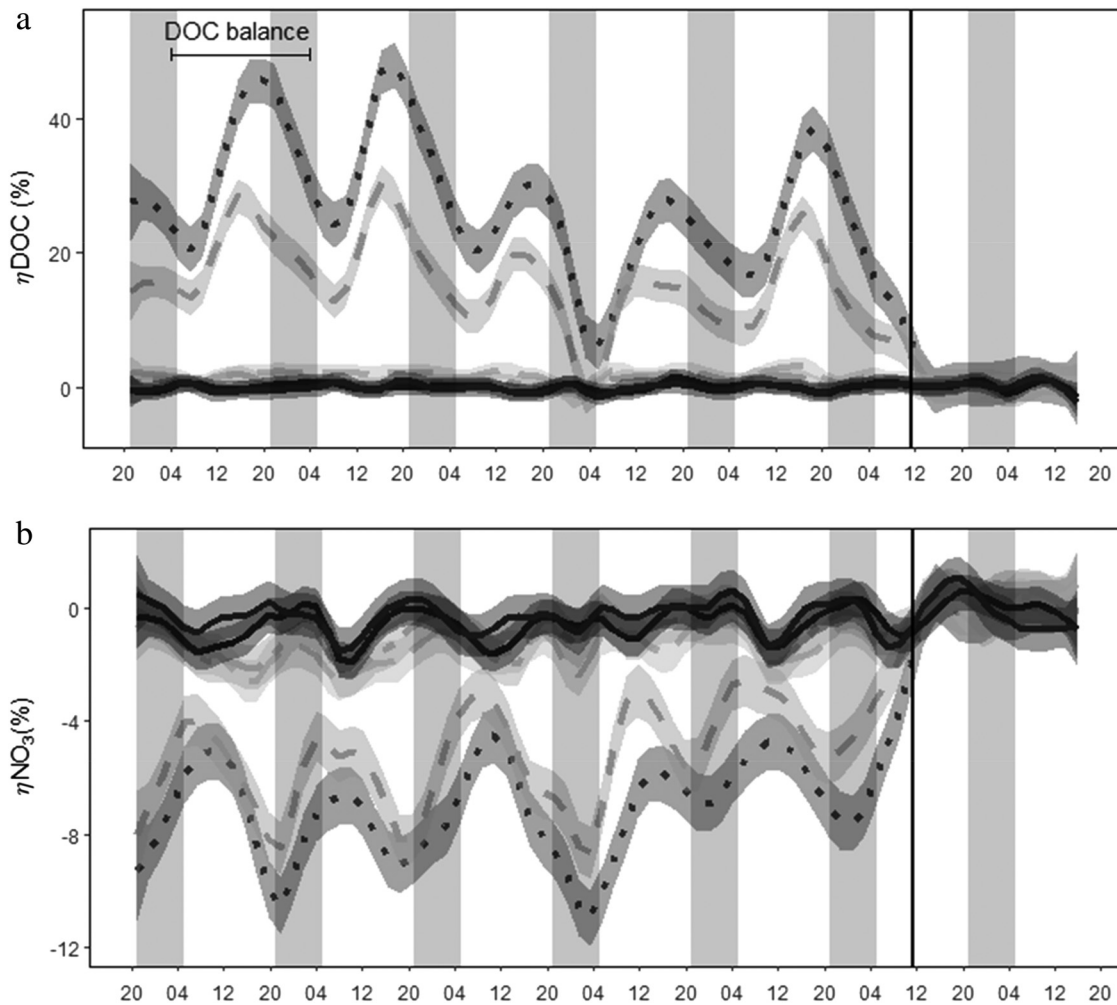


Fig. 4. Diel cycles of (a) η DOC with the time of the DOC mass balance indicated at the top and (b) η NO₃ in the flumes F1 (red, dotted), F2 (orange, dashed), F3–F6 (light to dark blue, longdash to solid line). Dynamics of η DOC and η NO₃ were determined from hourly measurements of the UV–Vis sensor beginning 5 d before the end of the treatment phase. The solid vertical line marks the initiation of reflow; gray vertical shading indicates night time. The x-axis denotes the hour of the day.

Similarly, Müllner and Schagerl (2003) reported from the “Oberer Seebach” that pioneer-algae communities of *Synurophyceae* and *Bacillariophyceae* dominated at riffle sections and during high flow conditions. Under intermediate and stable flow conditions, growth of filamentous *Chlorophyta* and *Cyanoprokaryota* was common. Algae community and the velocity of algal colonization can also change with water temperature (Villanueva et al. 2011), whereby higher water temperature increases GPP when light is not a limiting factor (Murphy 1998). We assume that light was not limiting in our setting because measured light availability was higher than the light saturation threshold of $90 \mu\text{E m}^{-2} \text{s}^{-1}$ suggested by Acuña et al. (2004) during most days. This assumption is further corroborated by the GPP curves showing a steep increase with sunrise followed by the formation of a plateau in the morning, while light availability further increased.

Diurnal increases in DOC similar to those observed in this study occur in desert streams, with high DOC releases from algal production (Jones et al. 1996). Kaplan and Bott (1982) reported daily increases of DOM by 40% in a piedmont stream, which is similar to the increase observed in F1. They showed in microcosm experiments using carbon isotopes that this gained DOM was composed of exudates of benthic algae modified by heterotrophic bacteria. Furthermore, Fasching et al. (2016) observed DOC concentrations to peak before sunset in the “Oberer Seebach” during summer baseflow. This daily increase was found to vary as a function of light availability, water temperature, and time span since the last storm event. In this study, we identified similar environmental controls of daily DOC variation under controlled experimental conditions. Specifically, our observed increases of daily DOC release with treatment time highlights the influence of time span since the last hydrological disturbance.

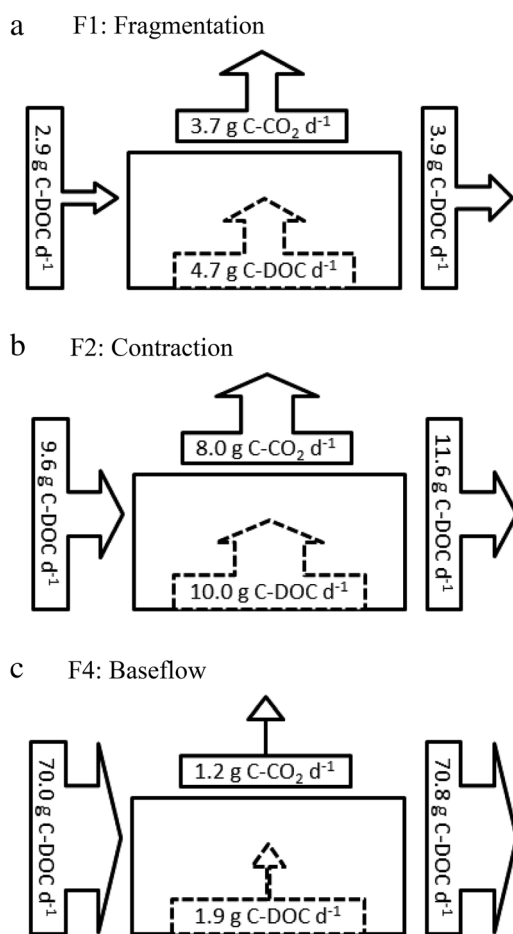


Fig. 5. Mass balances for F1 (a), F2 (b), and F4 (c) on the 17th day of treatment, where numbers represent daily carbon flux in g. Horizontal arrows represent inflow and outflow, solid vertical arrow NEP and dashed vertical arrow missing carbon, originating from the flume.

Higher temperatures enhance microbial activity, as for example the enzymes that catalyze the oxidation of phenolic compounds to quinines, thereby increasing the transformation rate from POM to DOM (Freeman et al. 2001; Kane et al. 2014). This mechanism was reported from experiments using POM from peatlands, where an increase of 10°C in water temperature resulted in an increase of 33% of DOC concentration (Freeman et al. 2001). The results are similar to our observations of a 40% increase in DOC concentration with a temperature difference between inflow and outflow of up to 8°C. DOM quality was also observed to change as a function of temperature, in the form of a decrease in SUVA₂₅₄ and aromaticity (Kane et al. 2014) due to enhanced microbial activity (Kim et al. 2006). Therefore, the low SUVA₂₅₄ detected in F1 and F2 might be related to microbial activity favored by increased stream temperature.

Diel cycles of η DOC that were mirror-inverted with η NO₃ (see Fig. 4) and the inverse trend of η NO₃ and GPP over the whole drought period suggests that NO₃ concentration was

controlled by the uptake by autotrophs. At high GPP, up to 25% of the available NO₃ was taken up, suggesting that at some point during the day the primary production was nutrient limited. We suspect that this limitation was caused by the lack of inorganic P, because of the high nitrogen to phosphorus ratio (> 100 : 1) and the fact that P-PO₄ concentrations were continuously below the detection limit in F1. Nutrient limitation is often present when inorganic nutrients are not supplied from the surrounding soils or groundwater (Roberts et al. 2007). Further, high light to nutrient ratios have been found to stimulate the release of algal carbon exudates as DOM because nutrient uptake is unable to keep pace with carbon fixation (Sterner et al. 1997; Lyon and Ziegler 2009). This supports our idea that algal exudates substantially contributed to increased DOC fluxes.

As a secondary pathway, the availability of algal exudates might have favored the degradation of complex organic matter. This effect known as “priming” is a process, where inputs of bioavailable organic matter (e.g., algal exudates) can increase the rate at which microbes consume more stable organic matter (e.g., POM) (Guenet et al. 2014; Hotchkiss et al. 2014). While the process is well documented for soil microbial communities (Wolfaardt et al. 1994), the existence of the priming effect in stream ecosystems is currently questioned (Bengtsson et al. 2015; Wagner et al. 2017). However, the steady gain of labile DOM parallel to the increase of CO₂ and ER in this study, lead us to suggest a potential contribution of at least “apparent priming” (Catalán et al. 2015) and thereby enhanced degradation of sediment leaf litter during drought.

Shift in metabolic balance

Streams are generally assumed to be net heterotrophic (Hoellein et al. 2013), but exceptions are reported, mainly from desert and Mediterranean streams (Busch and Fisher 1981; Velasco et al. 2003). The DOC mass balance indicated that F1 and F2 had a higher contribution of GPP to their carbon budget than the other flumes even after the *P/R* ratio of F1 and F2 remained below 1. The phase of net autotrophy in F1 and F2 enabled to store and export carbon that was generated within the flumes. However, the excess DOC stored during the first week of the experiment was rapidly respired or exported from the flumes during the third week. The quantity of ER and η DOC_{gen} even suggests that more of the sediment leaf litter had to be degraded in F1 and F2 than in the other flumes.

The increase of ER and the decrease of GPP indicate a decoupling of these two metabolic rates. GPP can decline or even collapse due to light or nutrient limitation. Light limitation in streams is not only caused by riparian vegetation but also by organic matter accumulation (e.g., dead algal mats) in the stream that can lower the performance of the underlying autotrophs (Acuña et al. 2004). Sabater et al. (2008) report that algal biomass increased until spring in

an intermittent stream and reduced with summer drying. In this stream, floods washed away the overlying materials and algae could grow again readily, when light availability to the bed surface was restored. Apart from that, bacterial growth and the availability of DOM was observed to lead to higher ratios of bacterial biomass to algal biomass in lakes when light to nutrient ratios rose (Elser et al. 2003). However, this shift was not confirmed in a flume experiment that simulated streams with a flow velocity of 10 cm s^{-1} (Hill et al. 2011). Taking into account that this flow velocity is ten times higher than the velocity present in F2 during treatment, we suggest that the metabolism of flumes with high water residence time might include mechanisms more commonly found in lakes than in lotic systems.

Coupling between ER and biofilm growth has been reported in experimental flumes (Singer et al. 2010; Haggerty et al. 2014), which may explain the rise of ER and $\eta p\text{CO}_2$ over time in all flumes. In our study, the consistent increase in ER and ηDOC in F1 and F2 may be explained by increased primary production and release of labile DOM leading to high $\eta p\text{CO}_2$. However, ER (and resulting $p\text{CO}_2$) remained high even after primary production declined. Following this observation, we propose that high ER is fueled by the added allochthonous POM in the sediment, rather than DOM from primary production.

Microbial respiration of newly moistened leave litter is described to peak after 20 d (Suberkropp 1998). This time-frame would approximately coincide with the time period of the shift in metabolic balance in F1 and F2 that took place 3 weeks after the start of the water flow in the flumes. Additionally, the second and third week were characterized by warmer streamwater temperatures than the first week. Temperature affects ER more than GPP because of the higher apparent activation energy for ER (Sand-Jensen et al. 2007; Acuña et al. 2008; Yvon-Durocher et al. 2012). Consequently, Skoulikidis et al. (2017) identified a threshold temperature of 22°C for respiration dominating over production. Certainly, the highest water temperature observed in this study was lower ($\sim 20^\circ\text{C}$). However, such a threshold could well be reduced for microbial communities of subalpine streams that are adapted to a different temperature regime.

Finally, in carbonate rich karst streams, high rates of photosynthesis can cause CO_2 contributions from carbonate precipitation (de Montety et al. 2011). We cannot discriminate such a contribution to stream $p\text{CO}_2$ from those of ER in our study. However, given that neither calcite nor aragonite precipitation was observed at the sediment surface or on in situ sensors, we assume this contribution to be minor in our experiment.

Overall, we suggest that a superposition of the drivers (biofilm growth and subsequent labile organic matter availability, leaf litter decomposition, temperature increase with associated modification of the balance of ER and GPP) caused the increase of ER and thereby the shift in the metabolic balance of F1 and F2.

From a flume experiment to stream ecosystem functioning

Mimicking the drying phase of an intermittent stream with flumes poses challenges, at the same time as it provides the opportunity to study the effects of hydrological variability beyond the range naturally present in the past. Our selected range of discharge covered the stages of baseflow (F4–F6) and drying, namely contraction (F2 and F3) and fragmentation (F1), while complete desiccation was not recreated. Natural drying of intermittent streams includes receding of wetted perimeters and the gradual weakening of connectivity between laterals and the main channel (McDonough et al. 2011). We argue that a summer drought period, when reaches only receive water from upstream sections, can be well represented within a flume experiment. By contrast, we did not recreate the gradual decrease of lateral and groundwater inputs in the experiment. Likewise, our experimental design mimicked streams with a shallow permeable streambed constrained by concrete, bedrock, or clay soils and therefore neglects a larger hyporheic zone. Hyporheic respiration can contribute more than half of the total respiration of mountainous streams, depending on the vertical exchange (Uehlinger and Naegeli 1998; Fellows et al. 2001). Further, we acknowledge that this experiment simulated only low gradient stream reaches. Higher slopes could have decreased water residence time substantially and thus would have likely changed the exponent of the relationship of ηDOC with discharge. In fact, it shall be noted, that streams of this area often have steeper slopes than the ones present in the experiment, increasing their gas exchange velocity and flow velocity (Schelker et al. 2016). Another difference between our flumes and a natural stream may be the enhanced exposure of the flumes to air temperature, potentially causing additional warming. However, high water temperature and enhanced daily amplitudes, especially in isolated pools, are found commonly in intermittent streams during drought conditions (Ward and Stanford 1982). Also, high amplitudes of water temperature have been reported from some alpine intermittent streams (Robinson et al. 2016). Nevertheless, all these aspects have to be taken into account when extrapolating our findings to natural subalpine streams.

Our experimental results expand earlier work on carbon cycling during baseflow in the “Oberer Seebach” (Fasching et al. 2016). In the light of climate change, our objective was to experimentally extend a baseflow situation of the “Oberer Seebach” to a summer drought. We found our results in agreement with studies of Mediterranean and desert streams; this refers specifically to the increase in labile DOM and the shift to autotrophy. Contrary to our initial hypothesis, this trophic state did not persist throughout the treatment phase. In fact, a large portion of the accumulated biomass was respired and a smaller portion exported downstream. Putting our findings into the context of climate change, this would suggest that flow intermittency can lead to enhanced carbon fixation in the remaining surface water, but only for a limited period of

time. Consequently, the gain of aquatic respiration with increasing temperature might not be countered by photosynthesis as suggested previously in the literature (Demars et al. 2016), if the streams are affected by drought. The fate and pathways of newly fixed carbon then depend on the light to nutrient ratio in a stream reach, a ratio that, together with water temperature might have caused the shift of the metabolic balance in this study. Low inorganic nutrient concentration in subalpine streams could limit GPP substantially even with otherwise favorable conditions for high GPP under climate change, meaning more carbon would be respired or exported downstream. After all, the time span until reflow, that is, the event when the organic material will be flushed downstream to fuel downstream reaches appears crucial. If this time span is long, a large proportion of the freshly produced biomass will likely be respired and might also enhance respiration of allochthonous organic matter stored in sediments.

The recently introduced “pulse-shunt concept” (PSC) (Raymond et al. 2016) proposes that DOC routing in stream networks may be described by a gradient between two main flow conditions. During high flow, headwater streams are assumed to act as pipes delivering terrigenous DOC downstream with little removal, whereas pronounced DOC uptake is considered in upland streams at low flows. Following our results, we propose that this concept remains incomplete under the conditions of a drought. Then, small streams produce DOC and favor the decomposition of sediment POM that may otherwise not be accessible for microbial degradation. The gained DOC may then be partially respired by heterotrophic organisms, but a relevant fraction is to be rerouted into the stream network at reflow. This will likely create events of disproportionately high C-mineralization downstream following droughts and reflow. We suggest, that this additional C-pathway from primary production and sediment POM may become more relevant in stream networks, if the frequency of large storms (providing sediment POM and nutrients) and droughts (remobilizing sediment POM and producing DOC) is increased by climate change.

References

- Acuña, V., A. Giorgi, I. Munoz, U. Uehlinger, and S. Sabater. 2004. Flow extremes and benthic organic matter shape the metabolism of a headwater Mediterranean stream. *Freshw. Biol.* **49**: 960–971. doi:[10.1111/j.1365-2427.2004.01239.x](https://doi.org/10.1111/j.1365-2427.2004.01239.x)
- Acuña, V., A. Wolf, U. Uehlinger, and K. Tockner. 2008. Temperature dependence of stream benthic respiration in an Alpine river network under global warming. *Freshw. Biol.* **53**: 2076–2088. doi:[10.1111/j.1365-2427.2008.02028.x](https://doi.org/10.1111/j.1365-2427.2008.02028.x)
- Ågren, A., M. Jansson, H. Ivarsson, K. Bishop, and J. Seibert. 2008. Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. *Aquat. Sci.* **70**: 21–29. doi:[10.1007/s00027-007-0943-9](https://doi.org/10.1007/s00027-007-0943-9)
- Aitkenhead-Peterson, J. A., W. H. McDowell, and J. C. Neff. 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters, p. 25–70. *In* S. E. G. Findlay and R. L. Sinsabaugh [eds.], *Aquatic ecosystems*. Elsevier.
- Appling, A. P., R. O. Hall, M. Arroita, and C. B. Yackulic. 2017. streamMetabolizer: Models for estimating aquatic photosynthesis and respiration. Available from <https://github.com/USGS-R/streamMetabolizer>
- Barnett, T. P., J. C. Adam, and D. P. Lettenmaier. 2005. Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature* **438**: 303–309. doi:[10.1038/nature04141](https://doi.org/10.1038/nature04141)
- Bass, A. M., M. I. Bird, M. J. Liddell, and P. N. Nelson. 2011. Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment. *Limnol. Oceanogr.* **56**: 2282–2292. doi:[10.4319/lo.2011.56.6.2282](https://doi.org/10.4319/lo.2011.56.6.2282)
- Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater. 2008. Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* **1**: 95–100. doi:[10.1038/ngeo101](https://doi.org/10.1038/ngeo101)
- Bengtsson, M. M., K. Wagner, N. R. Burns, E. R. Herberg, W. Wanek, L. A. Kaplan, and T. J. Battin. 2015. No evidence of aquatic priming effects in hyporheic zone microcosms. *Sci. Rep.* **4**: 5187. doi:[10.1038/srep05187](https://doi.org/10.1038/srep05187)
- Berghuijs, W. R., R. A. Woods, and M. Hrachowitz. 2014. A precipitation shift from snow towards rain leads to a decrease in streamflow. *Nat. Clim. Chang.* **4**: 583–586. doi:[10.1038/nclimate2246](https://doi.org/10.1038/nclimate2246)
- Bernot, M. J., D. J. Sobota, R. O. Hall, P. J. Mulholland, W. K. Dodds, J. R. Webster, J. L. Tank, and L. R. Ashkenas. 2010. Inter-regional comparison of land-use effects on stream metabolism. *Freshw. Biol.* **55**: 1874–1890. doi:[10.1111/j.1365-2427.2010.02422.x](https://doi.org/10.1111/j.1365-2427.2010.02422.x)
- Busch, D. E., and S. G. Fisher. 1981. Metabolism of a desert stream. *Freshw. Biol.* **11**: 301–307. doi:[10.1111/j.1365-2427.1981.tb01263.x](https://doi.org/10.1111/j.1365-2427.1981.tb01263.x)
- Butturini, A., A. Guarch, A. M. Román, A. Freixa, S. Amalfitano, S. Fazi, and E. Ejarque. 2016. Hydrological conditions control in situ DOM retention and release along a Mediterranean river. *Water Res.* **99**: 33–45. doi:[10.1016/j.watres.2016.04.036](https://doi.org/10.1016/j.watres.2016.04.036)
- Catalán, N., A. M. Kellerman, H. Peter, F. Carmona, and L. J. Tranvik. 2015. Absence of a priming effect on dissolved organic carbon degradation in lake water. *Limnol. Oceanogr.* **60**: 159–168. doi:[10.1002/lno.10016](https://doi.org/10.1002/lno.10016)
- Coble, P. G. 1996. Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy. *Mar. Chem.* **51**: 325–346. doi:[10.1016/0304-4203\(95\)00062-3](https://doi.org/10.1016/0304-4203(95)00062-3)
- Cory, R. M., and D. M. McKnight. 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. *Environ. Sci. Technol.* **39**: 8142–8149. doi:[10.1021/es0506962](https://doi.org/10.1021/es0506962)

- de Montety, V., J. B. Martin, M. J. Cohen, C. Foster, and M. J. Kurz. 2011. Influence of diel biogeochemical cycles on carbonate equilibrium in a karst river. *Chem. Geol.* **283**: 31–43. doi:[10.1016/j.chemgeo.2010.12.025](https://doi.org/10.1016/j.chemgeo.2010.12.025)
- Demars, B. O. L., G. M. Gíslason, J. S. Ólafsson, J. R. Manson, N. Friberg, J. M. Hood, J. J. D. Thompson, and T. E. Freitag. 2016. Impact of warming on CO₂ emissions from streams countered by aquatic photosynthesis. *Nat. Geosci.* **9**: 758–761. doi:[10.1038/ngeo2807](https://doi.org/10.1038/ngeo2807)
- Dodds, W. K., R. E. Hutson, A. C. Eichen, M. A. Evans, D. A. Gudder, K. M. Fritz, and L. Gray. 1996. The relationship of floods, drying, flow and light to primary production and producer biomass in a prairie stream. *Hydrobiologia* **333**: 151–159. doi:[10.1007/BF00013429](https://doi.org/10.1007/BF00013429)
- Ejarque, E., A. Freixa, E. Vazquez, A. Guarch, S. Amalfitano, S. Fazi, A. M. Romani, and A. Butturini. 2017. Quality and reactivity of dissolved organic matter in a Mediterranean river across hydrological and spatial gradients. *Sci. Total Environ.* **599–600**: 1802–1812. doi:[10.1016/J.SCITOTENV.2017.05.113](https://doi.org/10.1016/J.SCITOTENV.2017.05.113)
- Elser, J. J., M. Kyle, W. Makino, T. Yoshida, and J. Urabe. 2003. Ecological stoichiometry in the microbial food web: A test of the light: nutrient hypothesis. *Aquat. Microb. Ecol.* **31**: 49–65. doi:[10.3354/ame031049](https://doi.org/10.3354/ame031049)
- Fasching, C., A. J. Ulseth, J. Schelker, G. Steniczka, and T. J. Battin. 2016. Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone. *Limnol. Oceanogr.* **61**: 558–571. doi:[10.1002/lno.10232](https://doi.org/10.1002/lno.10232)
- Fellows, C. S., M. H. Valett, and C. N. Dahm. 2001. Whole stream metabolism in two montane streams: Contribution of the hyporheic zone. *Limnol. Oceanogr.* **46**: 523–531. doi:[10.4319/lo.2001.46.3.0523](https://doi.org/10.4319/lo.2001.46.3.0523)
- Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner. 2001. Export of organic carbon from peat soils. *Nature* **412**: 785–785. doi:[10.1038/35090628](https://doi.org/10.1038/35090628)
- Goletz, C., M. Wagner, A. Gröbel, W. Schmidt, N. Korf, and P. Werner. 2011. Standardization of fluorescence excitation–emission–matrices in aquatic milieu. *Talanta* **85**: 650–656. doi:[10.1016/j.talanta.2011.04.045](https://doi.org/10.1016/j.talanta.2011.04.045)
- Guarch-Ribot, A., and A. Butturini. 2016. Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis. *Sci. Total Environ.* **571**: 1358–1369. doi:[10.1016/j.scitotenv.2016.07.060](https://doi.org/10.1016/j.scitotenv.2016.07.060)
- Guenet, B., and others. 2014. Fast mineralization of land-born C in inland waters: First experimental evidences of aquatic priming effect. *Hydrobiologia* **721**: 35–44. doi:[10.1007/s10750-013-1635-1](https://doi.org/10.1007/s10750-013-1635-1)
- Haggerty, R., M. Ribot, G. A. Singer, E. Martí, A. Argerich, G. Agell, and T. J. Battin. 2014. Ecosystem respiration increases with biofilm growth and bed forms: Flume measurements with resazurin. *J. Geophys. Res. Biogeosci.* **119**: 2220–2230. doi:[10.1002/2013JG002498](https://doi.org/10.1002/2013JG002498)
- Hall, R. O., C. B. Yackulic, T. A. Kennedy, M. D. Yard, E. J. Rosi-Marshall, N. Voichick, and K. E. Behn. 2015. Turbidity, light, temperature, and hydropeaking control primary productivity in the Colorado River, Grand Canyon. *Limnol. Oceanogr.* **60**: 512–526. doi:[10.1002/lno.10031](https://doi.org/10.1002/lno.10031)
- Hannah, D. M., L. E. Brown, A. M. Milner, A. M. Gurnell, G. R. McGregor, G. E. Petts, B. P. G. Smith, and D. L. Snook. 2007. Integrating climate–hydrology–ecology for alpine river systems. *Aquat. Conserv.* **17**: 636–656. doi:[10.1002/aqc.800](https://doi.org/10.1002/aqc.800)
- Helms, J. R., A. Stubbins, J. D. Ritchie, E. C. Minor, D. J. Kieber, and K. Mopper. 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photo-bleaching of chromophoric dissolved organic matter. *Limnol. Oceanogr.* **53**: 955–969. doi:[10.4319/lo.2008.53.3.0955](https://doi.org/10.4319/lo.2008.53.3.0955)
- Helsel, D. R., and R. M. Hirsch. 2002. *Statistical methods in water resources*, US Geological survey Reston, VA.
- Hill, W. R., B. J. Roberts, S. N. Francoeur, and S. E. Fanta. 2011. Resource synergy in stream periphyton communities. *J. Ecol.* **99**: 454–463. doi:[10.1111/j.1365-2745.2010.01785.x](https://doi.org/10.1111/j.1365-2745.2010.01785.x)
- Hoellein, T. J., D. A. Bruesewitz, and D. C. Richardson. 2013. Revisiting Odum (1956): A synthesis of aquatic ecosystem metabolism. *Limnol. Oceanogr.* **58**: 2089–2100. doi:[10.4319/lo.2013.58.6.2089](https://doi.org/10.4319/lo.2013.58.6.2089)
- Hotchkiss, E. R., R. O. Hall, M. A. Baker, E. J. Rosi-Marshall, and J. L. Tank. 2014. Modeling priming effects on microbial consumption of dissolved organic carbon in rivers. *J. Geophys. Res. Biogeosci.* **119**: 982–995. doi:[10.1002/2013JG002599](https://doi.org/10.1002/2013JG002599)
- Huguet, A., L. Vacher, S. Relexans, S. Saubusse, J. M. Froidefond, and E. Parlanti. 2009. Properties of fluorescent dissolved organic matter in the Gironde Estuary. *Org. Geochem.* **40**: 706–719. doi:[10.1016/j.orggeochem.2009.03.002](https://doi.org/10.1016/j.orggeochem.2009.03.002)
- Jones, J. B., S. G. Fisher, and N. B. Grimm. 1996. A long-term perspective of dissolved organic carbon transport in Sycamore Creek, Arizona, USA. *Hydrobiologia* **317**: 183–188. doi:[10.1007/BF00036468](https://doi.org/10.1007/BF00036468)
- Kane, E. S., L. R. Mazzoleni, C. J. Kratz, J. A. Hribljan, C. P. Johnson, T. G. Pypker, and R. Chimner. 2014. Peat pore-water dissolved organic carbon concentration and lability increase with warming: A field temperature manipulation experiment in a poor-fen. *Biogeochemistry* **119**: 161–178. doi:[10.1007/s10533-014-9955-4](https://doi.org/10.1007/s10533-014-9955-4)
- Kaplan, L. A., and T. L. Bott. 1982. Diel fluctuations of DOC generated by algae in a piedmont stream. *Limnol. Oceanogr.* **27**: 1091–1100. doi:[10.4319/lo.1982.27.6.1091](https://doi.org/10.4319/lo.1982.27.6.1091)
- Kim, S., L. A. Kaplan, and P. G. Hatcher. 2006. Biodegradable dissolved organic matter in a temperate and a tropical stream determined from ultra-high resolution mass spectrometry. *Limnol. Oceanogr.* **51**: 1054–1063. doi:[10.4319/lo.2006.51.2.1054](https://doi.org/10.4319/lo.2006.51.2.1054)
- Lakowicz, J. R. 2006. *Principles of fluorescence spectroscopy*, 3rd ed. Springer.
- Lapierre, J.-F., and P. A. del Giorgio. 2014. Partial coupling and differential regulation of biologically and photochemically labile dissolved organic carbon across boreal aquatic networks. *Biogeosciences* **11**: 5969–5985. doi:[10.5194/bg-11-5969-2014](https://doi.org/10.5194/bg-11-5969-2014)

- Larned, S. T., V. I. Nikora, and B. J. F. Biggs. 2004. Mass-transfer-limited nitrogen and phosphorus uptake by stream periphyton: A conceptual model and experimental evidence. *Limnol. Oceanogr.* **49**: 1992–2000.
- Larned, S. T., T. Datry, D. B. Arscott, and K. Tockner. 2010. Emerging concepts in temporary-river ecology. *Freshw. Biol.* **55**: 717–738. doi:[10.1111/j.1365-2427.2009.02322.x](https://doi.org/10.1111/j.1365-2427.2009.02322.x)
- Leichtfried, M. 1996. Organic matter in bed-sediments of the River Danube and a small unpolluted stream, the Oberer Seebach. *River Syst.* **10**: 87–98. doi:[10.1127/lr/10/1996/87](https://doi.org/10.1127/lr/10/1996/87)
- Lyon, D. R., and S. E. Ziegler. 2009. Carbon cycling within epilithic biofilm communities across a nutrient gradient of headwater streams. *Limnol. Oceanogr.* **54**: 439–449. doi:[10.4319/lo.2009.54.2.0439](https://doi.org/10.4319/lo.2009.54.2.0439)
- Maiolini, B., and M. Bruno. 2008. The river continuum concept revisited: Lessons from the Alps, p. 67–76. *In* R. Psenner, and R. Lackner [eds.], *The Water Balance of the Alps, Alpine Space - Man & Environment*. Innsbruck Univ. Press
- MATLAB. 2016. version 7.10.0 (R2016a), The MathWorks Inc.
- McDonough, O. T., J. D. Hosen, and M. A. Palmer. 2011. Temporary streams: The hydrology, geography, and ecology of non-perennially flowing waters, p. 259–289. *In* S. E. Elliot, and L. E. Martin [eds.], *River ecosystems: Dynamics, management and conservation*. Nova Science Publishers.
- McKnight, D. M., E. W. Boyer, P. K. Westerhoff, P. T. Doran, T. Kulbe, and D. T. Andersen. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnol. Oceanogr.* **46**: 38–48. doi:[10.4319/lo.2001.46.1.0038](https://doi.org/10.4319/lo.2001.46.1.0038)
- Meybeck, M., P. Green, and C. Vörösmarty. 2001. A new typology for mountains and other relief classes: An application to global continental water resources and population distribution. *Mt. Res. Dev.* **21**: 34–45. doi:[10.1659/0276-4741](https://doi.org/10.1659/0276-4741)
- Mulholland, P. J. 1997. Organic matter dynamics in the West Fork of Walker Branch, Tennessee, USA. *J. North Am. Benthol. Soc.* **16**: 61–67. doi:[10.2307/1468235](https://doi.org/10.2307/1468235)
- Mulholland, P. J., and others. 2001. Inter-biome comparison of factors controlling stream metabolism. *Freshw. Biol.* **46**: 1503–1517. doi:[10.1046/j.1365-2427.2001.00773.x](https://doi.org/10.1046/j.1365-2427.2001.00773.x)
- Müllner, A. N., and M. Schagerl. 2003. Abundance and vertical distribution of the phytobenthic community within a pool and riffle sequence of an alpine gravel stream. *Int. Rev. Hydrobiol.* **88**: 243–254. doi:[10.1002/iroh.200390022](https://doi.org/10.1002/iroh.200390022)
- Murphy, K. R., C. A. Stedmon, D. Graeber, and R. Bro. 2013. Fluorescence spectroscopy and multi-way techniques. *PARAFAC. Anal. Methods* **5**: 6557. doi:[10.1039/c3ay41160e](https://doi.org/10.1039/c3ay41160e)
- Murphy, M. L. 1998. Primary production, p. 144–168. *In* R. E. Bilby and R. J. Naiman [eds.], *River ecology and management: Lessons from the Pacific coastal ecoregion*. Springer-Verlag.
- Odum, H. T. 1956. Primary production in flowing waters. *Limnol. Oceanogr.* **1**: 102–117. doi:[10.4319/lo.1956.1.2.0102](https://doi.org/10.4319/lo.1956.1.2.0102)
- Ohno, T. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environ. Sci. Technol.* **36**: 742–746. doi:[10.1021/es0155276](https://doi.org/10.1021/es0155276)
- Peter, H., G. A. Singer, C. Preiler, P. Chiffard, G. Steniczka, and T. J. Battin. 2014. Scales and drivers of temporal pCO₂ dynamics in an Alpine stream. *J. Geophys. Res. Biogeosci.* **119**: 1078–1091. doi:[10.1002/2013JG002552](https://doi.org/10.1002/2013JG002552)
- Proia, L., and others. 2016. Microbial carbon processing along a river discontinuum. *Freshw. Sci.* **35**. doi:[10.1086/689181](https://doi.org/10.1086/689181), [1133](https://doi.org/10.1086/689181), [1147](https://doi.org/10.1086/689181)
- R Team Development Core. 2008. R: A language and environment for statistical computing.
- Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. *Ecology* **97**: 5–16. doi:[10.1890/14-1684.1](https://doi.org/10.1890/14-1684.1)
- Reichert, P., U. Uehlinger, and V. Acuña. 2009. Estimating stream metabolism from oxygen concentrations: Effect of spatial heterogeneity. *J. Geophys. Res. Biogeosci.* **114**: G03016. doi:[10.1029/2008JG000917](https://doi.org/10.1029/2008JG000917)
- Roberts, B. J., P. J. Mulholland, and W. R. Hill. 2007. Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream. *Ecosystems* **10**: 588–606. doi:[10.1007/s10021-007-9059-2](https://doi.org/10.1007/s10021-007-9059-2)
- Robinson, C. T., D. Tonolla, B. Imhof, R. Vukelic, and U. Uehlinger. 2016. Flow intermittency, physico-chemistry and function of headwater streams in an Alpine glacial catchment. *Aquat. Sci.* **78**: 327–341. doi:[10.1007/s00027-015-0434-3](https://doi.org/10.1007/s00027-015-0434-3)
- Sabater, S., A. Elosegi, V. Acuña, A. Basaguren, I. Muñoz, and J. Pozo. 2008. Effect of climate on the trophic structure of temperate forested streams. A comparison of Mediterranean and Atlantic streams. *Sci. Total Environ.* **390**: 475–484. doi:[10.1016/j.scitotenv.2007.10.030](https://doi.org/10.1016/j.scitotenv.2007.10.030)
- Sand-Jensen, K., N. L. Pedersen, and M. Sondergaard. 2007. Bacterial metabolism in small temperate streams under contemporary and future climates. *Freshw. Biol.* **52**: 2340–2353. doi:[10.1111/j.1365-2427.2007.01852.x](https://doi.org/10.1111/j.1365-2427.2007.01852.x)
- Saraceno, J. F., B. A. Pellerin, B. D. Downing, E. Boss, P. Am Bachand, and B. A. Bergamaschi. 2009. High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes. *J. Geophys. Res. Biogeosci.* **114**: G00F09. doi:[10.1029/2009JG000989](https://doi.org/10.1029/2009JG000989)
- Schelker, J., T. Grabs, K. Bishop, and H. Laudon. 2013. Drivers of increased organic carbon concentrations in stream water following forest disturbance: Separating effects of changes in flow pathways and soil warming. *J. Geophys. Res. Biogeosci.* **118**: 1814–1827. doi:[10.1002/2013JG002309](https://doi.org/10.1002/2013JG002309)
- Schelker, J., G. A. Singer, A. J. Ulseth, S. Hengsberger, and T. J. Battin. 2016. CO₂ evasion from a steep, high gradient stream network: Importance of seasonal and diurnal variation in aquatic pCO₂ and gas transfer. *Limnol. Oceanogr.* **61**: 1826–1838. doi:[10.1002/lno.10339](https://doi.org/10.1002/lno.10339)

- Singer, G., K. Besemer, P. Schmitt-Kopplin, I. Hödl, and T. J. Battin. 2010. Physical heterogeneity increases biofilm resource use and its molecular diversity in stream mesocosms. *PLoS One* **5**: e9988. doi:[10.1371/journal.pone.0009988](https://doi.org/10.1371/journal.pone.0009988)
- Sivirichi, G. M., S. S. Kaushal, P. M. Mayer, C. Welty, K. T. Belt, T. A. Newcomer, K. D. Newcomb, and M. M. Grese. 2011. Longitudinal variability in streamwater chemistry and carbon and nitrogen fluxes in restored and degraded urban stream networks. *J. Environ. Monit.* **13**: 288–303. doi:[10.1039/COEM00055H](https://doi.org/10.1039/COEM00055H)
- Skoulikidis, N. T., L. Vardakas, Y. Amaxidis, and P. Michalopoulos. 2017. Biogeochemical processes controlling aquatic quality during drying and rewetting events in a Mediterranean non-perennial river reach. *Sci. Total Environ.* **575**: 378–389. doi:[10.1016/j.scitotenv.2016.10.015](https://doi.org/10.1016/j.scitotenv.2016.10.015)
- Sterner, R. W., J. J. Elser, E. J. Fee, S. J. Guildford, and T. H. Chrzanowski. 1997. The light:nutrient ratio in lakes: The balance of energy and materials affects ecosystem structure and process. *Am. Nat.* **150**: 663–684. doi:[10.1086/286088](https://doi.org/10.1086/286088)
- Suberkropp, K. F. 1998. Microorganisms and organic matter decomposition, p. 144–168. *In* R. E. Bilby and R. J. Naiman [eds.], *River ecology and management: Lessons from the Pacific coastal ecoregion*. Springer-Verlag.
- Uehlinger, U., and M. W. Naegeli. 1998. Ecosystem metabolism, disturbance, and stability in a prealpine gravel bed river. *J. North Am. Benthol. Soc.* **17**: 165–178. doi:[10.2307/1467960](https://doi.org/10.2307/1467960)
- Ulseth, A. J., E. Bertuzzo, G. A. Singer, J. Schelker, and T. J. Battin. 2017. Climate-induced changes in spring snowmelt impact ecosystem metabolism and carbon fluxes in an alpine stream network. *Ecosystems* **23**: 1–18. doi:[10.1007/s10021-017-0155-7](https://doi.org/10.1007/s10021-017-0155-7)
- Vázquez, E., S. Amalfitano, S. Fazi, and A. Butturini. 2011. Dissolved organic matter composition in a fragmented Mediterranean fluvial system under severe drought conditions. *Biogeochemistry* **102**: 59–72. doi:[10.1007/s10533-010-9421-x](https://doi.org/10.1007/s10533-010-9421-x)
- Velasco, J., A. Millan, M. R. Vidal-Abarca, M. L. Suarez, C. Guerrero, and M. Ortega. 2003. Macrophytic, epipelic and epilithic primary production in a semiarid Mediterranean stream. *Freshw. Biol.* **48**: 1408–1420. doi:[10.1046/j.1365-2427.2003.01099.x](https://doi.org/10.1046/j.1365-2427.2003.01099.x)
- Villanueva, V. D., J. Font, T. Schwartz, and A. M. Romaní. 2011. Biofilm formation at warming temperature: Acceleration of microbial colonization and microbial interactive effects. *Biofouling* **27**: 59–71. doi:[10.1080/08927014.2010.538841](https://doi.org/10.1080/08927014.2010.538841)
- Von Schiller, D., D. Graeber, M. Ribot, X. Timoner, V. Acuña, E. Martí, S. Sabater, and K. Tockner. 2015. Hydrological transitions drive dissolved organic matter quantity and composition in a temporary Mediterranean stream. *Biogeochemistry* **123**: 429–446. doi:[10.1007/s10533-015-0077-4](https://doi.org/10.1007/s10533-015-0077-4)
- Wagner, K., M. M. Bengtsson, R. H. Findlay, T. J. Battin, and A. J. Ulseth. 2017. High light intensity mediates a shift from allochthonous to autochthonous carbon use in phototrophic stream biofilms. *J. Geophys. Res. Biogeosci.* **122**: 1806–1820. doi:[10.1002/2016JG003727](https://doi.org/10.1002/2016JG003727)
- Ward, J. V., and J. A. Stanford. 1982. Thermal responses in the evolutionary ecology of aquatic insects. *Annu. Rev. Entomol.* **27**: 97–117. doi:[10.1146/annurev.en.27.010182.000525](https://doi.org/10.1146/annurev.en.27.010182.000525)
- Webster, J. R., and J. L. Meyer. 1997. Organic matter budgets for streams: A synthesis. *J. North Am. Benthol. Soc.* **16**: 141–161. doi:[10.2307/1468247](https://doi.org/10.2307/1468247)
- Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**: 4702–4708. doi:[10.1021/es030360x](https://doi.org/10.1021/es030360x)
- Wiegner, T. N., R. L. Tubal, and R. A. MacKenzie. 2009. Bioavailability and export of dissolved organic matter from a tropical river during base- and stormflow conditions. *Limnol. Oceanogr.* **54**: 1233–1242. doi:[10.4319/lo.2009.54.4.1233](https://doi.org/10.4319/lo.2009.54.4.1233)
- Wolfaardt, G. M., J. R. Lawrence, R. D. Roberts, and D. E. Caldwell. 1994. The role of interactions, sessile growth, and nutrient amendments on the degradative efficiency of a microbial consortium. *Can. J. Microbiol.* **40**: 331–340. doi:[10.1139/m94-055](https://doi.org/10.1139/m94-055)
- Yamashita, Y., L. J. Scinto, N. Maie, and R. Jaffé. 2010. Dissolved organic matter characteristics across a subtropical wetland's landscape: Application of optical properties in the assessment of environmental dynamics. *Ecosystems* **13**: 1006–1019. doi:[10.1007/s10021-010-9370-1](https://doi.org/10.1007/s10021-010-9370-1)
- Yamashita, Y., B. D. Kloeppel, J. Knoepp, G. L. Zausen, and R. Jaffé. 2011. Effects of watershed history on dissolved organic matter characteristics in headwater streams. *Ecosystems* **14**: 1110–1122. doi:[10.1007/s10021-011-9469-z](https://doi.org/10.1007/s10021-011-9469-z)
- Yvon-Durocher, G., and others. 2012. Reconciling the temperature dependence of respiration across timescales and ecosystem types. *Nature* **487**: 472–476. doi:[10.1038/nature11205](https://doi.org/10.1038/nature11205)

Acknowledgments

We thank Stefan Kloimüller, Gertraud Steniczka, Nicolas Escoffier, and Kyle Boodoo for their help with the set-up of the experiment and the laboratory analysis, and Anna Lupon for advice with the NEP calculations. We also thank two anonymous reviewers for their helpful comments. This project is funded by the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no. 607150 (FP7-PEOPLE-2013-ITN – INTERFACES - Ecohydrological interfaces as critical hotspots for transformations of ecosystem exchange fluxes and biogeochemical cycling) and was partly supported by the project GLOBAQUA (603629-ENV-6.2.1) and by funding from the Austrian Academy of Sciences (ÖAW) as part of the project "Influence of climate extremes on carbon dynamics across the boundaries of aquatic ecosystems (EXCARB)".

Conflict of Interest

None declared.

Submitted 26 October 2017

Revised 28 January 2018

Accepted 26 June 2018

Associate editor: Emily Bernhardt