Flow intermittence alters carbon processing in rivers through chemical diversification of leaf litter

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Scientific Significance Statement

Intermittent rivers (rivers that dry up at some point in space or time) exist worldwide and will expand due to climate change. The changing flow drives an extraordinary environmental heterogeneity in those systems, which makes their functioning difficult to predict. The decomposition and transport of leaf litter are driven by the alternation of dry and wet phases. In this article, we show that the environmental heterogeneity during the dry phase of intermittent rivers can result in a chemical diversification of leaf litter, which ultimately can accelerate its decomposition in downstream sections of the river network during the flowing phase. Our study highlights the complex biogeochemistry of those systems, whose understanding is critical to achieve a better model-based integration of intermittent rivers into the global carbon cycle.

Abstract

The dry phase of intermittent rivers promotes the accumulation of leaf litter on various terrestrial and aquatic habitats. This environmental heterogeneity causes a chemical diversification of leaf litter by a range of physical and biological degradation processes acting across the various habitats. After flow resumption, the chemically diversified leaves are mixed and subject to continued decomposition downstream. We hypothesized that the chemical diversification of leaf litter during the dry phase would affect leaf litter decomposition under re-established lotic conditions. Our laboratory treatments mimicking dry-phase habitats caused a strong chemical diversification of leaf litter, which—upon combination in mixed litter bags—accelerated its decomposition in a perennial river reach. We suggest that intermittent rivers may act as hotspots of organic matter diversification, with potential implications for organic matter processing at the river-network scale.

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The fundamental role of hydrology in regulating carbon (C) cycling in freshwater ecosystems (Raymond et al. 2016) becomes particularly evident in intermittent rivers (Datry et al. 2018). There, the alternation of dry and wet phases drives a pulsed processing of organic matter in cycles of accumulation, transport, and decomposition (Larned et al. 2010; Datry et al. 2018). During the dry phase, riparian leaf litter accumulates without much simultaneous decomposition on riverbeds (Sanpera-Calbat et al. 2016; Datry et al. 2018). In contrast, the wet phase supports the active processing of organic matter (Corti et al. 2011; Abril et al. 2016). In-between, surface flow is resumed and mobilizes and transports material downstream (Corti and Datry 2012). This model has been challenged because the exposure of leaf litter to various environmental conditions during the dry phase already triggers specific degradation processes (herewith called “preconditioning”) (del Campo et al. 2019) and cause chemical, physical, and biological changes, which ultimately affect leaf decomposition after flow resumption (Dieter et al. 2013; Mora-Gómez et al. 2019). For instance, the exposure to intense solar radiation on dry riverbeds can increase litter biodegradability by the photodegradation of lignin (Austin et al. 2016). In contrast, humid or aquatic conditions (wet sediments or pools) support microbial degradation of labile C and increase leaf litter recalcitrance depending on nutrient availability and temperature (Abril et al. 2016; Abelho and Descals 2019; del Campo et al. 2021a). Leaf biodegradability can also decrease in stagnant pools due to the leaching of nutrients or the accumulation of phenols (Dieter et al. 2013). An even greater variety of terrestrial and aquatic habitats (e.g., wet and shaded sediments, pools connected to hyporheic habitats, etc.) can emerge during the fragmentation of surface flow—both at local scale within a reach, as well as across tributaries of a drying river network (Stanley et al. 1997; Datry et al. 2014). As accumulation and preconditioning of leaf litter happen dynamically across this mosaic of aquatic-terrestrial habitats, the various degradation processes can cause a diversification of riparian leaf litter (Fig. 1). At network scale, the re-establishment of water flow and the reconnection of dry tributaries can then lead to mixing of the various preconditioned leaf litter during potentially far-reaching downstream transport (del Campo et al. 2021b). Finally, upon retention, decomposition proceeds in reassembled, diversified litter packs under lotic conditions.

Leaf litter decomposition is mediated by environmental conditions, the decomposer community and litter traits (Boyero et al. 2016). Under aquatic conditions, litter traits can become the main driver of decomposition due to the continuous supply of water and nutrients (García-Palacios et al. 2018; Zhang et al. 2019). The mixing of various litter species can have nonadditive effects on decomposition (Gessner et al. 2010), meaning that the decomposition rate of mixtures is either below or above those expected from individual species’ rates (Gartner and Cardon 2004). Negative effects of litter diversity are associated with inhibition of decomposer activity by secondary metabolites like polyphenols (Chomel et al. 2016). Positive effects are attributed to fungi-driven nutrient transfer (Tonin et al. 2017) or nutritional complementarity among leaves with contrasting chemical qualities (López-Rojo et al. 2020). Owing to the increased chance of obtaining essential compounds, the functional diversity of leaf mixtures per se may accelerate decomposition (Lecerf et al. 2011; Stoler et al. 2016). Even so, the effect of litter diversity can be mediated by the decomposer community (López-Rojo et al. 2020), with more complex communities processing litter mixtures more efficiently due to synergistic interactions among consumers (Liu et al. 2020).

Our understanding of chemical (bio)diversity effects on decomposition is still incomplete. Beyond plant diversity, natural mechanisms can promote chemical diversity in organic matter. For example, the combination of land use heterogeneity, in-stream processing and hydrological mixing triggers chemical diversity of dissolved organic matter along river networks (Casas-Ruiz et al. 2020; Peter et al. 2020). We suggest hydrological dynamics of intermittent tributaries could create a powerful mechanism of chemical diversification of leaf litter at local and river network scale with unknown consequences for decomposition dynamics. Intermittent rivers represent over half of the global river network length and this fraction will likely increase due to climate and global change (Messager et al. 2021); therefore, accounting for dry-phase-associated diversity effects could be critical to achieve a mechanistic understanding and realistic modeling of C fluxes at regional and global scale (Marcé et al. 2019).

Here, we test the hypothesis that environmental heterogeneity occurring during the dry phase of intermittent rivers can promote a chemical diversification of leaf litter and thereby affect its decomposition in downstream rivers (Fig. 1). To this aim, we first simulated the preconditioning of a single leaf litter species (Alnus glutinosa) under various environmental conditions. Then, we measured the decomposition of leaf litter mixtures assembled with an increasing number of preconditioning situations in (i) a lab-based bioassay, and (ii) fine- and coarse-mesh bags exposed in a perennial river. We predict that the increase of chemical diversity in mixtures of preconditioned leaves accelerates decomposition in aquatic conditions. Furthermore, we expect litter diversity to have the strongest influence on decomposition in coarse- than in fine-mesh bags due to weaker nutritional complementarity effects on microbial decomposers alone, but synergistic interactions between microbial decomposers and detritivores.

Materials and methods

Leaf litter preconditioning and chemical characterization

We collected fresh leaves of A. glutinosa (alder) directly from trees along the Löcknitz river (Brandenburg, Germany), a forested third-order lowland river in the Elbe catchment. The use of fresh litter was dictated by the timing of a postdoc fellowship and the absence of senescent leaves in summer.
Leaves were air-dried for 2 weeks and then exposed to seven preconditioning treatments mimicking these habitats (Table 1): Anoxic pools (T1), sunlight (T2), warm, nutrient-rich pools (T3), cold, nutrient-poor pools (T4), moist shaded sediments (T5), alternation between dry (T2) and wet (T3) habitats (T6), and fresh abscission during drought (T7).

Following preconditioning, subsets of leaves from all treatments were freeze-dried, ground using a ball mill and analyzed for C- and N-content (Elementar vario EL C/N elemental analyzer, Germany), other nutrients such as P, Ca, Mg, and K by ICP-OES (Thermo Scientific, iCAP 6500, USA), and macromolecular organic C moieties by Fourier-transform infrared spectroscopy (FTIR) (Duboc et al. 2012; Liu et al. 2016; Appendix 1).

Aquatic decomposition experiment

We prepared fine- and coarse-mesh bags (0.5 and 8 mm, respectively, 15 × 15 cm) containing leaves of single treatments (7 treatments × 4 replicates) and mixtures of leaves of increasing treatment richness in all possible combinations.
Table 1. Summary of the preconditioning treatments used in the study to mimic the terrestrial-aquatic habitat mosaic of intermittent rivers during the dry phase.

| Treatments   | Riverbed habitat during the dry phase                                      | Laboratory simulation                                                                                   | Physicochemical conditions                      |
|--------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|-----------------------------------------------|
| T1 Anoxic pool | Anoxic, stagnant pool                                                      | Container filled with mineral bottled water and 8 mg of Na₂SO₃ per mg dissolved oxygen to create anoxic conditions, kept at room temperature and in darkness. | T = 24.6°C  
DO = 0.15 mg L⁻¹  
pH = 5.5  
Cond = 1650 μS cm⁻¹ |
| T2*UV          | Dry riverbed exposed to intense solar irradiation                          | Irradiation for 12 h/d with a UV lamp (Cosmedico Arimed B6, Osram biolux 965, Germany; with 31% UVB of total UV). | Room temperature (-23°C)                        |
| T3 Warm pool   | Disconnected pool with warm and nutrient-rich water supporting algal growth | Aquarium filled with mineral bottled water and stones with biofilm from the Löcknitz river. The aquarium was continuously illuminated, oxygenated by air-bubbling and kept at room temperature and a nutrient solution (0.6 g L⁻¹ of NaNO₃ and 0.3 g L⁻¹ of KH₂PO₄) was added. | T = 25.1°C  
DO = 6.72 mg L⁻¹  
pH = 7.66  
Cond = 800 μS cm⁻¹ |
| T4 Cold pool   | Pool connected to hyporheic flow paths with cold and nutrient-poor water supporting limited algal growth | Same conditions as T3, except that the aquarium was kept at constant lower temperature and no nutrients were added. | T = 15.3°C  
DO = 9.45 mg L⁻¹  
pH = 7.94  
Cond = 925 μS cm⁻¹ |
| T5 Moist sediment | Shaded and humid riverbed sediment                                          | Container with soil from the Löcknitz river floodplain moistened with 500 mL of tap water every 4 d. | Room temperature (-23°C)                        |
| T6 Wet/dry     | Habitats subjected to wet/dry cycles associated with rain events           | Alternating T2 and T3 every 7 d.                                                                     | Room temperature (-23°C)                        |
| T7 Untreated   | No drying-phase habitat. Treatment simulating the vertical input of leaf litter shortly before flow resumption | Initially collected leaves, air-dried and kept in darkness.                                             | Room temperature (-23°C)                        |

T: water temperature, DO: dissolved oxygen, Cond: water specific conductivity. *The duration of preconditioning treatments was 21 d except for T2 and T6, which extended for 60 d, since photodegradation alterations occur at a longer time scale than those caused by aquatic microbial decomposition.

of 2, 4, and 6 treatments. This design resulted in four richness levels comprising a total of 91 bags (28 single-treatments, 21 2-treatment combinations, 35 4-treatment combinations, 7 6-treatment combinations) for each mesh size. We filled each litterbag with 12 leaves, which were partitioned across the component treatments as evenly as possible in mixtures. To determine exact contributions of each treatment on a dry mass (DM, 48 h, 105°C) basis required estimation of DM of wet material, which we achieved by flat-bed scanning leaves during bag assembly, measurement of treatment-specific leaf areas by image analysis (ImageJ, https://imagej.nih.gov/ij/), and conversion of area to DM using correction factors established from 20 leaves per treatment.

To measure aquatic decomposition, we incubated litterbags in the Löcknitz river (52°24′43.7″N, 13°49′33.6″E) for 23 d. Litterbags were fixed on the river in four 50 m-reaches with running water and homogeneous substrate and depth. During incubation, the water temperature oscillated between 13°C and 17°C, dissolved oxygen concentration was always above 6.5 mg L⁻¹, conductivity and pH averaged 560 μS cm⁻¹ and 7.5, respectively.

After retrieving the litterbags, leaves were washed in the laboratory with tap water above a 250 μm sieve to collect invertebrates, which were preserved in 70% ethanol. Individuals were counted, identified to family level and classified by guilds. The density of shredders was expressed as number of individuals per litter DM. From leaves in fine-mesh bags, we cut 12 discs with a cork borer (10 mm) to measure fungal biomass as ergosterol (Gessner 2005, Appendix 1). Litter mass loss was expressed as the percentage of lost DM from the initial DM. Initial DM was estimated with the scanning approach described above and final DM was measured by drying and weighing the remaining leaves.
Microbial respiration assay

Parallel to the decomposition experiment, we measured oxygen consumption rates by incubating 12 leaf discs from each treatment and mixture in 250 mL sealed bottles filled with mineral water (Volvic) at room temperature in a water bath. As microbial inoculum we used 10 mL of filtered (0.7 μμm, Whatman GF/F, Maidstone, UK) river water. Dissolved oxygen concentrations were measured 13 times over 24 d with a needle-based micro-optode (PM-PSt7 on a Microx 4, PreSens, Germany). Ten bottles were filled only with mineral water as a control. Oxygen consumption was computed as first order oxygen decay rate from log-linear regression.

Data analysis

We analyzed the effect of preconditioning on leaf litter decomposition using ANOVA models followed by Tukey post-hoc tests.

To analyze the effect of treatment richness of mixtures on leaf decomposition we used generalized additive models for location, scale and shape (GAMLSS) (Rigby and Stasinopoulos 2005). Models were built using the treatment richness (1, 2, 4, 6 treatments) as the explanatory variable and for the response variables: mass loss, fungal biomass, shredder density, and microbial respiration. GAMLSS allow to model effects on the average values (μμ) of the response as well as its variance (σσ). We also applied GAMLSS to test for the relationship between treatment richness and chemical diversity in mixtures. Further, we estimated expected values of all response variables for each mixture as the weighted averages of the observed values of component treatments. Synergistic mixing effects were identified based on paired Wilcoxon signed rank tests comparing observed and expected values of all mixtures (Gartner and Cardon 2004).

We combined information from FTIR peaks and elemental analysis of the preconditioning treatments to perform a principal component analyses (PCA) using z-standardized data. We estimated the chemical diversity of leaf litter mixtures as Rao’s quadratic entropy (RaoQ; Laliberté and Legendre 2010). For each mixture, RaoQ was computed as the mean pairwise Euclidean distance between component treatment centroids based on their scores on the first two PCA-axes (covering 84.9% of the overall dataset variance), weighted by the relative abundances of each treatment (Stoler et al. 2016). RaoQ equals 0 for litterbags containing single treatments. To estimate the chemical composition of leaf mixtures we used community-weighted means (Lavorel et al. 2008). This way we obtained average values of each chemical trait (FTIR peaks, nutrients) from their component treatment, weighted by the relative abundances of each treatment in the mixture. Weighted means of mixtures were combined with single treatment data to run a second PCA. Average scores of each single

Fig. 2. PCA describing changes in the chemical composition of leaf litter due to preconditioning under different treatments (A and B). (A) Variable loadings defining the PCA space. Nutrient ratios (in gray) are projected in the PCA space as supplementary variables. (B) Distribution of the preconditioning treatments across the PCA space. (C) GAMLSS identified a significant increase of the average (μμ, black line; df = 2; t-value = 3.57; p < 0.001) and a significant reduction of the variance (σσ, df = 2; t-value = −4.05; p < 0.001) of chemical diversity (RaoQ) with increasing richness or preconditioning treatments. Gray area shows 95% interval for model predictions. The colors in the pie charts used as symbols for mixtures indicate chemical composition as identified in (B), pie charts are plotted with small random variations along the categorical X axis to avoid overplotting.
treatment or mixture on the first two PCA axes served as a two-dimensional proxy of chemical composition.

Finally, to analyze the influence of chemical diversity and composition on decomposition we used general linear models that included RaoQ (chemical diversity), and PC1 and PC2 (summarizing chemical composition) as predictors. For each response variable, we built an initial model that included all main effects and first-order interactions between RaoQ and each PCA axis and then selected a top set of most parsimonious models with a multimodel inference approach (Grueber et al. 2011) using the R package MuMIm (Bartoń 2016). This top set included all models with delta AICc <2 from the most parsimonious model with the lowest AIC. By generating an average model from the top set using the natural average method (Burnham and Anderson 2002), we obtained weighted means for predictor coefficients and their errors (Grueber et al. 2011). All explanatory variables were z-standardized to obtain scaled, comparable average predictor coefficients. We evaluated the effect of chemical diversity and composition on decomposition by comparing the absolute magnitude and direction of the averaged predictor coefficients and checking whether 95% confidence intervals spanned zero. All data analysis was done in R 3.2.1 (R Core Team 2015). See del Campo et al. (2021c) to access all necessary data and R code to recreate the results of this manuscript.

**Results and discussion**

**The dry phase of intermittent rivers as promoter of leaf litter diversification**

The PCA based on the chemical traits of leaf litter clearly separated the various treatments (Fig. 2A,B), providing evidence for a strong chemical diversification of leaf litter by the heterogeneous preconditioning situations. PC1 (Fig. 2B) separated preconditioning treatments by differences in litter nutrient content and C-lability along a gradient from terrestrial to aquatic habitats. Leaves exposed to UVB (T2) were similar to untreated leaves (T1), indicating UVB exposure in the laboratory only weakly altered litter chemistry by photodegradation. From wet sediments (T3) to pools (T4, T6, and T7), the increase in water and nutrient availability increasingly benefited microbial decomposition and led to shifts along PC1 showing a loss of carbohydrates, increase of phenolic compounds, and microbial immobilization of nutrients (Abelho and Descals 2019; Mora-Gómez et al. 2019; del Campo et al. 2021a). Indeed, nutrient-rich warm pool habitats caused the highest accumulation of recalcitrant compounds (T6 and T7), suggesting leaf litter reached a more advanced decomposition stage in aquatic than in terrestrial habitats during preconditioning (Abril et al. 2016; Abelho and Descals 2019). PC2 separated stagnant pools (T5) from the other treatments by differences in litter cellulose content. In stagnant pools, the acidic and anoxic conditions
may drive a relative increase in cellulose due to the limitation of microbial activity and the leaching of more soluble C compounds (Canhoto et al. 2013; Dieter et al. 2013).

Mixing litter from various preconditioning treatments resulted in a clear increase of chemical diversity (Fig. 2C). These results point out that environmental heterogeneity during the dry phase, as realistically mimicked by our preconditioning treatments, indeed translates into higher chemical diversity. This is due to different decomposition agents and processes acting on leaf litter but also reflects different decomposition stages (see Wickings et al. 2012). Here, litter chemical differentiation goes hand in hand with differences in microbial colonization, which can affect the final decomposition pathway in downstream rivers through abundance but also functional profile of microbial communities (Abelho and Descals 2019; Mora-Gómez et al. 2019; del Campo et al. 2021a).

We recognize the limitations of our findings caused by mimicking natural preconditioning under laboratory conditions and using fresh green leaves. Green leaves have a higher nutrient content than senescent leaf litter, which can affect the decomposition process (Alves et al. 2021). Even so, we
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Flow intermittence alters carbon processing

Chemical diversity accelerates decomposition of leaf litter mixtures after flow resumption

Previous studies showed that river networks can promote the diversification of dissolved organic matter (Casas-Ruiz et al. 2020; Peter et al. 2020). Another recent study (Tanentzap et al. 2019) demonstrates that chemical diversity of dissolved organic matter can boost both biodiversity and ecosystem functioning by expanding available niche space for the consumer community. In our work, we prove for the first time that drying may also promote the diversification of particulate organic matter, which can ultimately affect ecosystem functioning downstream in the river network.

As we expected, the chemically diversified leaf litter in mixtures experienced accelerated decomposition under lotic conditions through synergistic effects on the activity of both microbial decomposers and detritivores, in a similar way as reported for mixtures of leaf litter species (Gessner et al. 2010; Lecerf et al. 2011). Increasing preconditioning treatment richness in mixtures significantly increased mass loss in coarse- and fine-mesh bags, fungal biomass and microbial respiration (Figs. 3A and 4), while this was not the case for expected values computed from single treatments for any response variable (data only shown for mass loss in Fig. 3B). Shredder density did not increase significantly along the gradient of treatment richness; but higher than expected shredder densities in leaf litter mixtures (Fig. 5F1) indicated a positive effect of litter diversity on detritivores. Indeed, all decomposition response variables showed significantly higher observed than expected values indicating a synergistic effect of leaf litter mixing (Gartner and Cardon 2004).

Increasing treatment richness in mixtures also caused a decrease in the variability in fungal biomass and mass loss in fine-mesh bags (Fig. 4A,C). This outcome of manipulating resource richness emerges by dampening of extreme contributions in more complex mixtures (Dang et al. 2005; Lecerf et al. 2007). A reduced variability in fungal-mediated decomposition with higher diversity of preconditioned leaf litter translates to decreased spatial variability and increased stability of this ecosystem process in downstream aquatic systems. Such a decrease in variance with treatment richness was not found for mass loss in coarse-mesh bags or shredder density (Figs. 2A and 4D). This result may point to strong influences of individual leaf litter types on the consumption of detritivores, which usually tend to preferentially consume leaf litter species richer in labile C compounds or nutrients when present in mixtures (Swan and Palmer 2006; López-Rojo et al. 2020).

Synergistic effects of leaf litter mixing on decomposition usually arise from facilitative interactions among litter components with contrasting chemical composition. With our experimental design, we cannot identify which precise mechanism drives the acceleration of decomposition by mixing; however, our results suggest chemical diversity as the main factor stimulating decomposition. Chemical diversity increased with treatment richness and was the main predictor in averaged models explaining the positive effect of mixing on mass loss in coarse-mesh bags, microbial respiration and fungal biomass (Fig. 5). These results agree with previous studies where chemical diversity strongly influenced decomposition of litter mixtures (Lecerf et al. 2011; Stoler et al. 2016). We suggest that chemical diversity in mixtures of preconditioned leaves enhances the activity of microbial communities by facilitating the acquisition of essential nutritional components for their growth and metabolism from multiple sources, such as nutrients, labile C compounds like carbohydrates, or long-lasting resources like cellulose (Gessner et al. 2010).

Besides chemical diversity, the chemical composition strongly influenced microbial decomposition of mixtures. It was the main predictor explaining mass loss in fine-mesh bags (positive effect of PC2) and microbial respiration (negative effect of PC1) in averaged models (Fig. 5, Table S1). The positive effect of PC2 on the mass loss in fine-mesh bags may indicate a higher microbial activity associated with high cellulose content in leaf litter (Talbot and Treseder 2012). On the other hand, the negative effect of PC1 on microbial respiration could be due to inhibition by recalcitrant compounds (Talbot and Treseder 2012; Chomel et al. 2016) and/or support through carbohydrates (Stoler et al. 2016).

![Fig. 5. Model-averaged coefficients (mean ± 95% CI) of predictors explaining fungal biomass (FB), leaf mass loss in coarse- (MLC) and fine-mesh bags (MLF), microbial respiration (MR), and shredder density (SD) of single treatments and mixtures. Chemical diversity (estimated through RaoQ) was the most important predictor for mass loss in coarse-mesh bags (z-value = 3.15, p < 0.05), fungal biomass (z-value = 2.73, p < 0.05) and shredder density (z-value = 1.76, p = 0.079), while chemical composition features (estimated through the average score of PC1 and PC2) were more important explaining mass loss in fine-mesh bags (PC2: Z-value = 4.15, p < 0.001) and microbial respiration (PC1: z-value = 7.95, p < 0.001).](image-url)
Intermittent rivers are the most predominant lotic ecosystem worldwide (Messager et al. 2021). Given their capacity to accumulate large amounts of organic matter during the dry phase (Datry et al. 2018), intermittent rivers often experience hot moments (sensu McClain et al. 2003) of microbial processing of C during rewetting events (Marcé et al. 2019; Shumilova et al. 2019). Our results demonstrate that, beyond the accumulation of organic matter, its chemical alteration and diversification during the dry phase may have river-network scale implications. Our results suggest that the pulse of organic matter caused by flow re-establishment and re-connection of dry tributaries to the network is actually chemically diversified, which—upon downstream transport—may alter organic matter fluxes at river-network scale. As mixing of variously preconditioned leaf litter accelerates its decomposition, the length of organic matter transport along the river network decreases. This spatial compression of organic matter processing along the river continuum in fact counteracts the classical view of intermittent rivers as pulsed bioreactors (Larned et al. 2010), where the organic-matter processing length is considered to increase due to the slower decomposition during the dry phase and the accelerated downstream transport during intensive rewetting events. Certainly, the experimental character of our study precludes a strong assessment of implications in real river networks. Future studies will have to achieve this under natural conditions, also considering the influence of other factors acting at larger spatial scales, such as land use, climate, or vegetation types. Here, we demonstrate that environmental heterogeneity can promote chemical diversity, which in turn may accelerate C processing in intermittent river networks. Our results reinforce the potential relevance of intermittent rivers in global C cycling and the necessity (and difficulties) of integrating them into larger scale modeling efforts.

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