Simulating rewetting events in intermittent rivers and ephemeral streams: A global analysis of leached nutrients and organic matter

Oleksandra Shumilova1,2,3 | Dominik Zak2,4,5 | Thibault Datry6

Daniel von Schiller7 | Roland Corti6 | Arnaud Foulquier8 | Biel Obrador9

Klement Tockner1,2,10 | Daniel C. Allan11 | Florian Altermatt12

María Isabel Arce1,13 | Shai Arnon14 | Damien Banas15 | Andy Banegas-Medina16

Erin Beller17 | Melanie L. Blanchette18 | Juan F. Blanco-Libreros19 | Joanna Blessing20

Iola Gonçalves Boëchat21 | Kate Boersma22 | Michael T. Bogan23 | Núria Bonada24

Nick R. Bond25 | Kate Bринtrup16 | Andreas Bruder26 | Ryan Burrows27

Tommaso Cancellario28 | Stephanie M. Carlson29 | Sophie Cauvy-Fraunié6

Núria Cid24 | Michael Danger30 | Bianca de Freitas Terra31

Anna Maria De Girolamo32 | Ruben del Campo33 | Fiona Dyer34

Arturo Elosegi7 | Emile Faye35 | Catherine Febría36,37 | Ricardo Figueroa16

Brian Four38 | Mark O. Gessner1,39 | Pierre Gnoussou40 | Rosa Gómez Cerezo33

Lluís Gomez-Gener41 | Manuel A.S. Graça42 | Simone Guareschi33 | Björn Gücker21

Jason L. Hwan29 | Skhumbuzo Kubheka43 | Simone Daniela Langhans44,45

Catherine Leigh27,46 | Chelsea J. Little12,47 | Stefan Lorenz48 | Jonathan Marshall20,27

Angus McIntosh36 | Clara Mendoza-Lera6 | Elisabeth Irmgard Meyer50 | Marko Miliša51

Musa C. Mlambo52 | Marcos Moleón53 | Peter Negus20 | Dev Niyogi54

Athina Papatheodoulou55 | Isabel Pardo56 | Petr Paril57 | Vladimir Pešić58

Pablo Rodriguez-Lozano29 | Robert J. Rolls59 | Maria Mar Sanchez-Montoya33

Ana Savić60 | Alisha Steward20,27 | Rachel Stubbington61

Ross Vander Vorste29 | Nathan Waltham63 | Annamaria Zoppini32

Christiane Zarfl64

1Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin, Germany
2Institute of Biology, Freie Universitaet Berlin (FU), Berlin, Germany
3Department of Civil, Environmental and Mechanical Engineering, Trento University, Trento, Italy
4Institute of Landscape Ecology and Site Evaluation, University of Rostock, Rostock, Germany

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.

© 2019 The Authors. Global Change Biology Published by John Wiley & Sons Ltd
INTRODUCTION

Human activities and climate change cause global-scale alterations in the flow regimes of rivers, which in turn are tightly linked to biogeochemical processes such as carbon processing (Arnell & Gosling, 2013; Bernhardt et al., 2018; Tonkin, Merritt, Olden, Reynolds, & Lytle, 2018). Currently, more than half of the global river network length is represented by intermittent rivers and ephemeral streams (IRES) – systems that cease to flow at some point in time and space (Acuña et al., 2014; Datry, Larned, & Tockner, 2014). Anthropogenic

Climate change and human pressures are changing the global distribution and the extent of intermittent rivers and ephemeral streams (IRES), which comprise half of the global river network area. IRES are characterized by periods of flow cessation, during which channel substrates accumulate and undergo physico-chemical changes (preconditioning), and periods of flow resumption, when these substrates are rewetted and release pulses of dissolved nutrients and organic matter (OM). However, there are no estimates of the amounts and quality of leached substances, nor is there information on the underlying environmental constraints operating at the global scale. We experimentally simulated, under standard laboratory conditions, rewetting of leaves, riverbed sediments, and epilithic biofilms collected during the dry phase across 205 IRES from five major climate zones. We determined the amounts and qualitative characteristics of the leached nutrients and OM, and estimated their areal fluxes from riverbeds. In addition, we evaluated the variance in leachate characteristics in relation to selected environmental variables and substrate characteristics. We found that sediments, due to their large quantities within riverbeds, contribute most to the overall flux of dissolved substances during rewetting events (56%–98%), and that flux rates distinctly differ among climate zones. Dissolved organic carbon, phenolics, and nitrate contributed most to the areal fluxes. The largest amounts of leached substances were found in the continental climate zone, coinciding with the lowest potential bioavailability of the leached OM. The opposite pattern was found in the arid zone. Environmental variables expected to be modified under climate change (i.e. potential evapotranspiration, aridity, dry period duration, land use) were correlated with the amount of leached substances, with the strongest relationship found for sediments. These results show that the role of IRES should be accounted for in global biogeochemical cycles, especially because prevalence of IRES will increase due to increasing severity of drying events.

KEYWORDS

biofilms, leaching, leaf litter, rewetting, sediments, temporary rivers
pressures alter the hydrological regime of perennial rivers toward intermittency, although the opposite can also happen at some locations. On the one hand, flow regulation, water diversion, groundwater extraction, and land-use alteration promote the prevalence of river flow intermittency both spatially and temporally (Datry, Bonada, & Boulton, 2017; Pekel, Cottam, Gorelick, & Belward, 2016). On the other hand, naturally intermittent rivers turn permanent due to effluents from wastewater treatment plants or artificially enhanced discharge required for livestock and irrigation (Chiu, Leigh, Mazor, Cid, & Resh, 2017).

From a biogeochemical perspective, IRES function as punctuated biogeochemical reactors (Larned, Datry, Arscott, & Tockner, 2010; von Schiller, Bernal, Dahm, & Martí, 2017). During the dry phase, a diversity of substrates (leaf litter, epilithic biofilms, wood, animal carcasses, sediments) accumulate on the dry riverbed (Datry et al., 2018). Absence of water reduces decomposition rates of substrates (for particulate organic matter, OM), while sunlight and intense desiccation alter their physico-chemical properties, a process known as preconditioning (Abril, Muñoz, & Menéndez, 2016; Bruder, Chauvet, & Gessner, 2011; del Campo & Gómez, 2016; Dieter et al., 2011; Taylor & Bärlocher, 1996). When surface water returns after drying events, accumulated organic and inorganic substrates are rewetted and can be transported downstream (Corti & Datry, 2012; Obermann, Froebrich, Perrin, & Tournoud, 2007; Rosado, Morais, & Tockner, 2015). Rewetting during the so-called "first flush events" also leads to massive pulsed releases of dissolved nutrients and dissolved organic matter (DOM; Arce, Sánchez-Montoya, & Gómez, 2015; Gessner, 1991; von Schiller et al., 2011). Importantly, concentrations of the released substrates may exceed baseflow values in perennial watercourses by several orders of magnitude and can thus substantially contribute to annual fluxes (Bernal, von Schiller, Sabater, & Martí, 2013; Corti & Datry, 2012; Skoulikidis & Amazidis, 2009). Released nutrients and DOM fuel primary producers and heterotrophic organisms, alter nutrient and carbon cycling, and thus influence stream ecosystem metabolism (Austin et al., 2004; Baldwin & Mitchell, 2000; Fellman, Petrone, & Grierson, 2013; Jacobson & Jacobson, 2013; Skoulikidis, Vardakas, Amazidis, & Michalopoulou, 2017). Furthermore, eutrophication and hypoxia can be a consequence of excess nutrient transport to downstream lakes, reservoirs, and coastal areas, where the mortality of fish and other aquatic organisms can increase (Bunn, Thoms, Hamilton, & Capon, 2006; Datry, Corti, Foulquier, Schiller, & Tockner, 2016; Hladyz, Watkins, Whitworth, & Baldwin, 2011; Whitworth, Baldwin, & Kerr, 2012).

Despite their widespread distribution and distinct role in biogeochemical cycling, IRES are notably missing in current analyses of global carbon budgets and other biogeochemical processes such as cycling of nutrients and DOM (Datry et al., 2018). Still, research on IRES is based primarily on studies spanning fine spatial extents (Leigh et al., 2016), which limits our understanding of their roles in ecosystem processes at the global scale (Datry et al., 2014; Skoulikidis, Sabater et al., 2017; von Schiller et al., 2017; but see Datry et al., 2018; Soria, Leigh, Datry, Bini, & Bonada, 2017). The contribution of IRES particularly to biogeochemical processes must be understood and quantified to correctly estimate carbon and nutrient fluxes. Studies indicating altered distribution of IRES in the future due to climate change (e.g. Milly, Dunne, & Vecchia, 2005) also emphasizes the need to adjust future river monitoring and conservation strategies.

The amounts and quality of dissolved compounds released from IRES upon rewetting, a process referred to as leaching (e.g. Gessner, 1991; Nykvist, 1963), depends primarily on the physico-chemical characteristics and amounts of substrates accumulated on riverbeds. Leachates from leaf litter, the most abundant form of coarse particulate organic matter (CPOM) accumulated in dry riverbeds (Datry et al., 2018), are rich in dissolved organic carbon (DOC; up to 39% of the leaf bulk carbon content) including soluble sugars, carbonic and amino acids, phenolic substances, proteins, and inorganic nutrients (e.g., phosphorus, nitrogen, potassium; Bärlocher, 2005; Gessner, 1991; Harris, Silvester, Rees, Pengelly, & Puskar, 2016; Nykvist, 1963). Likewise, leaching from rewetted sediments of IRES releases large amounts of inorganic nitrogen (e.g. Arce, Sánchez-Montoya, Vidal-Abarca, Suárez, & Gómez, 2014; Merbt, Proia, Prosser, Casamayor, & von Schiller, 2016; Ostojc, Rosado, Miliša, Morais, & Tockner, 2013; Tzaroki, Nikolaidis, Amazidis, & Skoulkis, 2007). Furthermore, riverbeds can be covered by biofilm mats (hereafter referred to as "biofilm"), composed of microorganisms (algae, bacteria, fungi) embedded in a matrix of extracellular polymeric substances (Sabater, Timoner, Borrego, & Acuña, 2016), whose remnants can often be seen even during the dry phase. Biofilm’s leachate may contain highly bioavailable organic carbon and nitrogen due to the accumulation of exudates and products of cell lysis (Romani et al., 2017; Schimel, Balser, & Wallenstein, 2007). Physico-chemical characteristics of substrates accumulated within IRES during the dry phase as well as the amounts of leached substances depend on environmental variables that act at both regional (climate influenced) and local scales (e.g. influenced by river geomorphology, land use, riparian canopy cover) (Aerts, 1997; Catalan, Obrador, Alomar, & Pretus, 2013; Datry et al., 2018; von Schiller et al., 2017).

The quantity and quality of dissolved substances leached from the channel beds of IRES during the rewetting process, and the environmental variables associated with variation in differences in leached amounts, has been little studied. However, such knowledge is essential for disentangling the role of IRES in biogeochemical processes under different scenarios of climate change. In the present study, we experimentally simulated pulsed rewetting events under controlled standardized laboratory conditions using substrates collected from 205 IRES located in 27 countries in five continents and covering five major climate zones. We aimed (a) to compare the amounts of nutrients and DOM, and the quality of DOM leached from leaf litter, biofilms, and bed sediments accumulated on dry IRES beds at the global scale as well as in different climate zones, (b) to explore and identify the environmental variables related to the variability in leached amounts, and (c) to estimate the potential are-specific fluxes (per m² of bed surface) of nutrients and OM leached during pulsed rewetting events. We focused on common nutrient and DOM species, which control essential ecosystem processes...
such as primary production and microbial respiration (Conley et al., 2009; Elser et al., 2007). Furthermore, we estimated the size categories and optical properties of released DOM as proxies of its quality.

Our first hypothesis was that in comparison with mineral substrates (sediments), leachates from organic substrates (biofilms and leaves) contain higher amounts of nutrients and DOM relative to the content of the respective element (carbon or nitrogen) in the substrate. In addition, substrates of organic origin also have a higher variability in the composition of leachates due to a higher species richness and compositional heterogeneity. Within our second hypothesis we expected that significant differences in the amounts of leached substances are observed among substrates sampled across different climate zones, with the highest amounts of nutrients and OM leached in the continental climate zone compared to others due to high litter quality (Boyero et al., 2017). In combination with the highest mass of litter observed (Datry et al., 2018) we expect this to result in the highest nutrient and OM fluxes from a representative area of dry river bed in the continental zone. Finally, we hypothesized that quantitative and qualitative composition of leachates will depend on substrate characteristics, which in turn are expected to correlate with environmental variables sampled at the study sites.

2 | MATERIALS AND METHODS

2.1 | Sampling sites, substrate collection, and environmental variables

A total of 205 IRES, located in 27 countries and spanning five major Köppen–Geiger climate classes, were sampled during dry phases, following the standardized protocol of the 1,000 Intermittent Rivers Project (Datry et al., 2016, http://1000_intermittent_rivers_project.irstea.fr, Figure 1). Five major climate zones were assigned to sites based on their location: arid (merging Köppen–Geiger classes BSh, BSk, BWh and BWk, n = 29), continental (Dfb, Dfc, n = 13), temperate (Cfa, Cfb, Csa, Csb, Cwa, n = 142), tropical (As, Aw, n = 19), and polar (ET, n = 1). Differences in sample size resulted from the occurrence of IRES and accessibility of sampling sites by researchers involved in the sampling campaign. A larger sample size increases the variability of the results while increasing the precision of the mean/median values, that is, reducing the variability of the sample mean/median. This needs to be considered in data evaluation and interpretation. For each river, one reach was selected and sampled for leaf litter (further referred as leaves), epilithic biofilms (biofilms), and sediments (details on material collection are provided in Supporting Information). After collection, field samples were further processed in the laboratory. Leaves and biofilms were oven-dried (60°C, 12 hr) to achieve constant mass, reduce variability from fluctuations in water content (Boulton & Boon, 1991), and ensure cellular death of the leaf tissue. Oven-drying mainly affects volatile and oxidizable compounds, which were not in the focus of our study. However, oven-drying may increase the amount of leached substances from leaves and biofilms (e.g. Gessner & Schwoerbel, 1989). Bed sediments were sieved (2 mm) and air-dried for 1 week. The dry material was placed in transparent plastic bags, shipped to laboratories responsible for further analyses (see Acknowledgements), and stored in a dry and dark room until processing and analysis.

Nine environmental variables were selected to analyze their association with leachate characteristics (Table 1). The variables were selected based on a conceptual understanding of the leaching process. As proxies of a regional-scale influence, we used the aridity index and potential evapotranspiration (PET) extracted from the Global Aridity and PET database (for details see Datry et al., 2018). River width, riparian cover (% visually estimated as the proportion of river reach covered by vegetation), dry period duration (estimated either with water loggers or repeated observations, precision: 2 weeks), altitude, and land cover (%) of pasture, forest, and
urban areas within the catchment were selected as proxies of local influence. These local-scale parameters (apart from land cover) were recorded in situ by participants of the 1,000 Intermittent Rivers Project. Land cover was derived using GIS maps. For details on the environmental variables sampled and substrate characteristics, see Table S1.

### Table 1: Overview of the variables included in the partial least squares (PLS) regression models and transformations applied to meet assumptions of analysis

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Measurement units</th>
<th>Transformation</th>
<th>Variable in the PLS model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Environmental variables</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PET</td>
<td>Mean potential evapotranspiration for 1950–2000</td>
<td>mm/month</td>
<td>log(x)</td>
<td>X</td>
</tr>
<tr>
<td>Aridity</td>
<td>Mean annual aridity index for years 1950–2000</td>
<td>–</td>
<td>log(x)</td>
<td>X</td>
</tr>
<tr>
<td>Altitude</td>
<td>Altitude of the sampled reach m above sea level</td>
<td>log(x)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Riparian cover</td>
<td>Percentage of the sampled reach covered by vegetation</td>
<td>log(x + 1)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Width of the sampled reach</td>
<td>Active channel width m</td>
<td>log(x)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Dry period</td>
<td>Duration of the drying period days</td>
<td>log(x)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Pasture cover</td>
<td>Percentage of pasture area within the river catchment %</td>
<td>log(x + 1)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Forest cover</td>
<td>Percentage of forested area within the river catchment %</td>
<td>log(x + 1)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Urban cover</td>
<td>Percentage of urban area within the river catchment %</td>
<td>log(x + 1)</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td><strong>Chemical substrates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% C</td>
<td>Carbon content %</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td>% N</td>
<td>Nitrogen content %</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td>C:N</td>
<td>Molar C:N ratio –</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td><strong>Specific sediment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silt</td>
<td>Silt fraction %</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>Sand fraction %</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>Clay fraction %</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td>Mean size</td>
<td>Mean particle size mm</td>
<td>log(x)</td>
<td>X, Y</td>
<td></td>
</tr>
<tr>
<td><strong>Quantitative chemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon mg/g dry mass</td>
<td>log(x)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>DON</td>
<td>Dissolved organic nitrogen mg/g dry mass</td>
<td>log(x)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>SRP</td>
<td>Soluble reactive phosphorous mg/g dry mass</td>
<td>log(x)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>N-NH₄⁺⁺</td>
<td>Ammonium mg/g dry mass</td>
<td>log(x)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>N-NO₃⁻</td>
<td>Nitrate mg/g dry mass</td>
<td>log(x)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td><strong>Qualitative chemical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SUVA₂₅₄</td>
<td>Specific ultraviolet absorbance mg C/L</td>
<td>–</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>FI</td>
<td>Fluorescence index –</td>
<td>log(x + 1)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>HIX</td>
<td>Humification index –</td>
<td>log(x + 1)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>β:α</td>
<td>Ratio of autochthonous to allochtonous dissolved organic matter –</td>
<td>log(x + 1)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>DOC:DON</td>
<td>Ratio of DOC to DON concentration –</td>
<td>–</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>Phenolics:DOC</td>
<td>Ratio of phenolics to DOC concentration –</td>
<td>log(x + 1)</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>LMWS</td>
<td>Low molecular weight substances %</td>
<td>–</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>BP</td>
<td>Biopolymers %</td>
<td>–</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>HS</td>
<td>Humic substances %</td>
<td>–</td>
<td>Y</td>
<td></td>
</tr>
</tbody>
</table>
2.2 | Leaching experiments

Rewetting was simulated in the laboratory by exposing dried sub-
strates to leaching solutions as a proxy for their exposure in situ to
river water during first flush events. Leaves were cut into approxi-
mately 0.5 cm × 0.5 cm pieces and homogenized in glass beakers
using a spoon. If the sample contained conifer-needles (approxi-
mately 30% of samples), these were cut into fragments of approxi-
mately 4 ± 0.5 cm length. From each sample, 0.5 ± 0.01 g were
weighed, put into 250 ml dark glass bottles and filled with 200 ml
of a 200 mg/L NaCl leaching solution to mimic ionic strength of the
stream water and thus to avoid extreme osmotic stress on micro-
organisms’ cells upon rewetting (e.g. McNamara & Leff, 2004). For
biofilms, sub-samples homogenized as previously described were
weighed to 1 ± 0.01 g, and placed in dark glass bottles filled with
100 ml of the leaching solution. Sediment samples (20–60 g) were
homogenized in the same way, weighed to 10 ± 0.1 g, transferred
into 250 ml dark glass bottles, and filled with 100 ml of the leaching
solution. The selected mass of each substrate in relation to the vol-
ume of leaching solution aimed on maximizing the leaching yield by
avoiding high concentrations of dissolved substances that could lead
to saturation so that substances cannot dissolve further.

Preliminary investigations of the effect of temperature and time
on leaching (tested at temperatures of 4 and 20°C and leaching du-
rations of 4 and 24 hr, corresponding to temperatures and durations
most commonly applied in leaching studies due to the rapid nature
of the leaching process, data not shown), indicated selection of a
constant temperature of 20°C and leaching duration of 4 hr. The
selected duration reflects the time when most of the dissolved sub-
stances are leached and minimizes microbial modification of leach-
ates upon rewetting. Bottles containing substrates and the leaching
solution were capped and placed on shaking tables (100 rpm) in a
climate chamber in darkness. Two subsamples (technical replicates)
of each substrate type from each sampling site were leached whenever
enough material was available (70% of the samples). Otherwise a
single technical replicate was used.

After 4 hr, the leachate from the bottle was filtered through
8.0 µm cellulose acetate and 0.45 µm cellulose nitrate membrane filters
(both Sartorius, AG Göttingen, Germany) which were prerinsed
with 1 L of de-ionized water per filter, using a vacuum pump. Filtered
leachates were collected in 200 ml glass flasks prerinsed with 50 ml
of the filtered leachate. If sufficient substrate was available, two
subsamples were leached to cover possible heterogeneity of sub-
strate composition, but combined later in one glass flask to have
one representative composite sample for further analysis. Leachates
were then transferred into HCl prewashed 25 ml plastic bottles prior
to further chemical analyses (see details in Supporting Information).

2.3 | Physical and chemical characterization of
substrates and leachates

Organic carbon (C) and total nitrogen (N) content of substrates (%C
and %N, respectively) were determined using elemental analyzers
(for details see Supporting Information). Sediment texture descrip-
tors (fractions [%] of sand, silt, clay, and their mean and median par-
ticle size) were determined with a laser-light diffraction instrument
(see Supporting Information).

Using standard analytical methods (for details see Supporting
Information) we analyzed the following substances in leachates:
DOC, soluble reactive phosphorus (SRP), ammonium (N-NH₄⁺), ni-
trate (N-NO₃⁻), and phenolics.

The concentration of nutrients and OM in leachates was used to
calculate leached amounts per gram of dry substrate (total leached
amounts) and per gram of the respective element, C or N, in the sub-
strate (relative leached amounts). Areal fluxes upon rewetting were
calculated from total leached amounts and mass of substrate accu-
mulated in the field.

2.4 | Characterization of DOM quality

To determine concentrations of dissolved organic nitrogen (DON)
and the composition of DOM based on size categories, we used size-
exclusion chromatography with organic carbon and organic nitrogen
detection (LC-OCD-OND analyzer, DOC-Labor Huber, Karlsruhe,
Germany) (details are provided in Supporting Information). A sub-
set of leaves, biofilms, and sediments sampled from 77 rivers was
selected randomly to cover all climate zones. We selected limited
samples due to the time-consuming nature of this analysis (2.5 hr per
sample). Leachates produced from these substrates (as described
previously) were selected for further analysis, in cases where con-
centrations of DOC in leachates did not exceed the measuring limits
of the chromatograph (the final set included leachates from 52 leaf,
11 biofilm, and 77 sediment samples). We classified DOM into three
major sub-categories: (a) biopolymers (BP), (b) humic or humic-like
substances (HS) including building blocks (HS-like material of lower
molecular weight), and (c) low molecular-weight substances (LMWS).
The concentration of each category was normalized to the total DOC
concentration, and is thus given as the fraction (%) of the total DOC.

To obtain indices of DOM quality (for details see Fellman, Hood,
& Spencer, 2010; Hansen et al., 2016), we simultaneously determined
absorbance spectra of DOM and fluorescence excitation-emission
matrices (EEM) using a spectrofluorometer (Horiba Jobin Yvon
Aqualog; Horiba Scientific Ltd, Kyoto, Japan). Specific UV absor-
bance values were calculated at a wavelength of 254 nm (SUVA254),
which are correlated with aromatic carbon content (Weisshaar et al.,
2003), by dividing decadal absorbance by DOC concentration (mg
C/L) and cuvette length (m). The fluorescence index (Fl), humifi-
cation index (HIX), and freshness index (β/α) were calculated from
fluorescence EEM for all DOM samples (for details see Supporting
Information). The Fl indicates whether DOM is derived from terres-
trial sources (e.g. plant or soil, Fl value ~1.4) or microbial sources (e.g.
extracellular release, leachates from bacterial and algal cells lysis,
Fl value ~1.9) (McKnight et al., 2001). The HIX indicates the extent
of DOM humification (degradation) (Ohno, 2002; Zsolnay, Baigar,
Jimenez, Steinweg, & Saccomandi, 1999), with HIX <0.9 indicating
DOM derived from relatively recent (plant and algae) inputs (Hansen

SHUMILOVA ET  AL .
### Table 2: Total and relative leaching rates of nutrients and organic matter species from leaves and bed sediments of IRES (median). For abbreviations, see Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Leaching rate</th>
<th>Leaves</th>
<th>Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Arid</td>
<td>Continental</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>86.28</td>
<td>108.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.38</td>
<td>18.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.60</td>
<td>2.01</td>
</tr>
<tr>
<td>DOC</td>
<td>mg/g dry mass</td>
<td>Total</td>
<td>30.98</td>
<td>47.40</td>
</tr>
<tr>
<td></td>
<td>mg/g C</td>
<td>Relative</td>
<td>86.28</td>
<td>108.86</td>
</tr>
<tr>
<td>N-NH₄⁺</td>
<td>mg/g dry mass</td>
<td>Total</td>
<td>0.06</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>mg/g N</td>
<td>Relative</td>
<td>7.80</td>
<td>11.70</td>
</tr>
<tr>
<td>N-NO₃⁻</td>
<td>mg/g dry mass</td>
<td>Total</td>
<td>0.004</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>mg/g N</td>
<td>Relative</td>
<td>0.43</td>
<td>0.32</td>
</tr>
<tr>
<td>DON</td>
<td>mg/g dry mass</td>
<td>Total</td>
<td>0.32</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>mg/g N</td>
<td>Relative</td>
<td>22.03</td>
<td>17.80</td>
</tr>
<tr>
<td>SRP</td>
<td>mg/g dry mass</td>
<td>Total</td>
<td>0.11</td>
<td>0.24</td>
</tr>
<tr>
<td>Phenolics</td>
<td>mg of GAE/g of substrate</td>
<td>Total</td>
<td>9.08</td>
<td>20.18</td>
</tr>
<tr>
<td></td>
<td>mg of GAE/g of C</td>
<td>Relative</td>
<td>0.23</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Note. GAE: gallic acid equivalent.

2.6 Statistical analyses

### Calculation of the total areal flux of nutrients and OM

Total areal flux of nutrients and OM per square meter of the mass of leaves and sediments was calculated based on information (e.g., Pak & Frossard, 2015) and contribution of nutrient and OM leached from all substrates on the dry riverbed.

Overall, the total areal flux is the sum of nutrients and OM leached from all substrates found within the dry riverbed. To execute a global comparison of total fluxes, samples from 157 reaches were selected for which complete set of nutrients and OM were available. Reaches for which only one sampling location in this category, biofilm were excluded from the comparison. The majority of samples were excluded from the cross-climate comparison due to multiple exceptions among the four main climate zones (e.g., Pak & Frossard, 2015). The polar difference quartile of data distribution minus quartile one was taken in the temperate zone (35 out of 41 samples). Variability was calculated based on interquartile range of sampled IRES.
<table>
<thead>
<tr>
<th>Predictors</th>
<th>Sediments</th>
<th>Leaves</th>
<th>Biofilms</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>1.445</td>
<td>0.111</td>
<td>0.557</td>
</tr>
<tr>
<td>Aridity</td>
<td>0.371</td>
<td>1.444</td>
<td>0.388</td>
</tr>
<tr>
<td>Dry period</td>
<td>0.495</td>
<td>0.580</td>
<td>1.767</td>
</tr>
<tr>
<td>River width</td>
<td>0.867</td>
<td>0.920</td>
<td>1.095</td>
</tr>
<tr>
<td>Riparian cover</td>
<td>0.955</td>
<td>1.243</td>
<td>0.805</td>
</tr>
<tr>
<td>% pasture</td>
<td>0.153</td>
<td>0.506</td>
<td>0.727</td>
</tr>
<tr>
<td>% forest</td>
<td>0.445</td>
<td>0.264</td>
<td>1.030</td>
</tr>
<tr>
<td>% urban</td>
<td>0.389</td>
<td>0.073</td>
<td>0.929</td>
</tr>
<tr>
<td>Altitude</td>
<td>0.784</td>
<td>0.731</td>
<td>0.547</td>
</tr>
<tr>
<td>%C</td>
<td>1.768</td>
<td>1.390</td>
<td>0.889</td>
</tr>
<tr>
<td>%N</td>
<td>2.062</td>
<td>1.657</td>
<td>1.345</td>
</tr>
<tr>
<td>C:N</td>
<td>0.336</td>
<td>0.897</td>
<td>0.509</td>
</tr>
<tr>
<td>% sand</td>
<td>0.897</td>
<td>1.368</td>
<td>1.100</td>
</tr>
<tr>
<td>% silt</td>
<td>0.960</td>
<td>0.744</td>
<td>1.139</td>
</tr>
<tr>
<td>% clay</td>
<td>0.920</td>
<td>1.055</td>
<td>1.145</td>
</tr>
<tr>
<td>Mean size</td>
<td>0.902</td>
<td>1.136</td>
<td>1.067</td>
</tr>
<tr>
<td>Var explained %</td>
<td>25.1</td>
<td>37.8</td>
<td>58.6</td>
</tr>
</tbody>
</table>

**Table 3**: Ranking of environmental variables and substrates characteristics that explain variance in quantitative composition (A) and qualitative characteristics (B) of leachates at global and regional scales according to their value of VIP (variable influence on projection) in the PLS analysis. VIP > 1 indicate highly influential predictors (dark grey), 1 > VIP > 0.8 indicate moderately influential variables (medium grey), VIP < 0.8 – variables of low influence (light grey).
expressed in percentages. This measure of variability accounts for differences in data distributions of nutrients and DOM amounts leached from different substrates and facilitates comparison.

In order to identify the environmental variables and substrate characteristics driving the quantitative (amounts of nutrients and OM) and qualitative (DOM quality) characteristics of the leachates partial least squares (PLS) regression models were applied (Wold, Šjöstrom, & Eriksson, 2001). This approach allows exploration of the relationship between collinear data in matrices $X$ (independent variable) and $Y$ (dependent variable). An overview of the components to be included in the models is given in Table 1. Performance of the model is expressed by $R^2_Y$ (explained variance). The influence of every $X$ variable on the $Y$ variable across the extracted PLS components (latent vectors that explain as much as possible of the co-variance between $X$ and $Y$) is summarized by the variable influence on projection (VIP) score (Table 3). The VIP scores of every model term ($X$-variables) are cumulative across components and weighted according to the amount of $Y$-variance explained in each component (Eriksson, Johansson, Kettaneh-Wold, & Wold, 2006). $X$-variables with VIP > 1 are most influential on the $Y$-variable, while variables with 1 > VIP > 0.8 are moderately influential. Values negatively correlated with the $Y$-variable were multiplied by a coefficient of negative one to facilitate interpretation. Data were transformed prior to analyses to meet the assumptions of normal distribution and homoscedasticity (Table 1).

In order to partition the variance in quantitative and qualitative characteristics of nutrients and DOM explained by different groups of variables (environmental variables, substrate characteristics, and the effect of environmental variables through their effect on measured substrate characteristics), we used the approach suggested in Borcard, Legendre, and Drapeau (1992) (Figure 2). The following PLS-regression models were run to distinguish fractions of explained variance in the quantitative/qualitative characteristics of the leachates:

- Fraction $[a + b]$ – explained by substrate characteristics;
- Fraction $[b + c]$ – explained by environmental variables;
- Fraction $[a + b + c]$ – explained by environmental variables and measured substrate characteristics.

From each PLS-regression model, the explained variance $R^2_Y$ was calculated and used to calculate the fraction of variance explained by each set of predictors separately (Borcard et al., 1992). For the PLS regression analysis, we selected the complete set of variables for which the required data (all predictors and response variables, Table 1) were available. We ran partitioning of variance for the set of samples on the global scale and individually for each climate zone. For biofilms, the analysis was done for samples of the temperate zone only because of the limited number of samples from other climate zones.

All statistical analyses were performed in R 3.2.2 (R Core Team, 2017), except for the PLS analysis which was conducted using XLSTAT software (XLSTAT, 2017, Addinsoft, Germany).
3 | RESULTS

3.1 | Leached amounts of nutrients and DOM species

3.1.1 | Total and relative leaching rates

The total leached amounts (mg/g dry mass) of nutrients (except N-NO₃⁻) and DOM were highest for leaves, followed by biofilms, and sediments (Figure 3; Table S2). The leached amounts of N-NO₃⁻ were highest for biofilms (Kruskal–Wallis test, \( \chi^2 = 15.8 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test for multiple comparison, \( p < 0.0001 \)), and no significant difference was found between leaves and sediments (Dunn’s test, \( p = 0.3 \)). Leached amounts of DON from leaves and biofilms were not significantly different (Kruskal–Wallis test, \( \chi^2 = 105.7 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p = 0.2 \)).

The total leached amounts of nutrients and DOM from leaves and biofilms decreased in a similar sequence: DOC > phenolics > DON > SRP > N-NH₄⁺ > N-NO₃⁻ (based on median values). The total leached amounts from sediments decreased in the following order: DOC > phenolics > N-NO₃⁻ > N-NH₄⁺ = DON > SRP (Table S2).

The relative leached amounts of DOC and phenolics (mg/g C) and DON (mg/g N) were highest for leaves, followed by biofilms and sediments (Figure 3; Table S2). However, there were no significant differences for the amounts of DON between leaves and biofilm leachates (Kruskal–Wallis test, \( \chi^2 = 51.6 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p = 0.8 \)), nor for phenolics between biofilms and sediments (Kruskal–Wallis test, \( \chi^2 = 204.4 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p = 0.2 \)). Relative leached amounts of N-NH₄⁺ were highest for biofilms, followed by leaves and bed sediments, with a significant difference between leaves and sediments (Kruskal–Wallis test, \( \chi^2 = 265.4 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p < 0.001 \)). For N-NO₃⁻, relative leached amounts decreased significantly from sediments to biofilms and leaves (Kruskal–Wallis test, \( \chi^2 = 204.4 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p < 0.001 \); Figure 3; Table S2).

For all substrates, we observed large variations in the total and relative leached amounts of nutrients and DOM (Figure 3, Table S2). The highest variability in total and relative leached amounts of DOC, N-NO₃⁻, and SRP was observed for biofilms, which was up to 10 times higher than for sediments and leaves. Sediments had the highest variability in the total leached amounts of DON and relative leached amounts of N-NH₄⁺ and phenolics. For leaves, the highest variability was found in the relative leached amounts of DON.

3.2 | Qualitative DOM characterization

Values of SUVA₂₅₄, a proxy for aromatic carbon content, decreased from sediments and leaves to biofilms, with no significant difference between sediments and leaves (Kruskal–Wallis test, \( \chi^2 = 55.8 \), \( df = 2 \), \( p < 0.0001 \); Dunn’s test, \( p = 0.4 \) (Figure 4; Table S3).
leaves, but there was no significant difference between biofilms and sediments (Kruskal–Wallis test, $\chi^2 = 197.4, df = 2, p < 0.0001$; Dunn’s test, $p = 0.4$). The degree of DOM humification based on HIX values was highest for sediments followed by biofilms and leaves, with statistically significant differences among all substrates (Kruskal–Wallis test, $\chi^2 = 96.94, df = 2, p < 0.0001$; Dunn’s tests <0.0001). Values of FI indicated the presence of OM derived from terrestrial sources in all leachates, with no significant differences among substrates (Kruskal–Wallis test, $\chi^2 = 6.3, df = 2, p = 0.043$).

In all leachates, HS was the dominant fraction of DOM followed by BP and LMWS (Figure 5; Table S3). The highest proportion of HS in DOM was in sediment leachates, while between leachates of leaves and biofilms the percentage of HS did not significantly differ (Kruskal–Wallis test, $\chi^2 = 29.9, df = 2, p < 0.0001$; Dunn’s test, $p = 0.9$). The highest percentage of LMWS was present in leaf leachates with the median twice as high as in sediments and biofilms. The highest percentage of BP was found in leachates from biofilms with the median values two and six times higher than in sediments and leaves, respectively. For LMWS and BP, the difference between biofilms and sediments was not statistically significant (Dunn’s test following a Kruskal–Wallis test, $p = 0.7$ and $p = 0.06$ respectively).

### 3.3 Differences in amounts of leached substances and DOM quality across climate zones

Cross-climate differences in amounts of leached substances and qualitative characteristics of DOM depended on the type of substrate (Table 2; Table S4). For leaves, a significant difference in the total leached amounts was observed only for N-$\text{NH}_4^+$ between continental and arid zones, as well as between continental and temperate zones (Dunn post-hoc tests following a Kruskal–Wallis test, $p < 0.0001$, Table S4). All variables measured in leaves showed highest concentration in the continental zone, except for N-$\text{NO}_3^-$ (highest in the tropical zone) and DON (highest in the arid zone). For sediments, significant differences in leached amounts were found for all variables except phenolics (Kruskal–Wallis test, $\chi^2 = 5.43, df = 3, p = 0.143$). In all cases, the highest total leached amounts were found in samples from the continental zone and the lowest in leachates from the arid zone (Table 2; Table S4). Leached amounts of nutrients and DOM from leaves and sediments from the temperate zone, the most commonly sampled zone in the study, followed leached amounts found in the tropical zone, however, with no significant difference (Table 2; Table S4). The relative leached amounts did not differ significantly among climate zones for leaves or sediments (Table S4).

Aromatic carbon content (a proxy used to access cross-climate differences in bioavailability) leached from leaves was not significantly different among climate zones (Kruskal–Wallis test, $\chi^2 = 3.82, df = 3, p = 0.28$). For sediments, a statistically significant difference was found between samples from the arid and the continental zone (Dunn’s test, $p = 0.003$; Table S4), with leachates from the arid zone having lower aromaticity.
3.4 | Effects of environmental variables and substrate characteristics

3.4.1 | Effects on the amounts of leached nutrients and DOM

On a global scale, 25% of the variance in the amounts of nutrients and DOM leached from sediments could be explained by selected variables (fraction \([a + b + c]\)), which was more than twice that for leaves (11%) (Figure 6a,b). For sediments, around 23% of the variance could be explained by the effect of substrate characteristics (fraction \([a + b]\)), around 15% by the effect of environmental variables (fraction \([b + c]\)), and 13% by the effect of environmental variables on substrate characteristics (fraction \([b]\)) (Figure 6a). For leaves, the substrate characteristics and the environmental variables explained approximately an equal percentage of variance, 8% and 6% respectively, which was much lower than that explained for sediments. Environmental variables and substrate characteristics accounted for 3% of variance in the quantitative composition of leaf leachates. For both substrates, the most influential variables (VIP >1) were C fraction, N fraction, PET, and in the case of leaves, C:N and pasture cover within the river catchment (Table 3).

3.5 | Effects on qualitative characteristics of DOM

For sediments and leaves, the percentage of variance that was explained for qualitative characteristics of DOM on the global-scale was much lower (around 7% for each of the substrates) than that for the amounts of leached substances (Figure 6b). The contribution of environmental variables, substrate characteristics, and effect of environmental variables on substrate characteristics to the total variance was approximately equal (Figure 6). Influential variables with VIP >1 were altitude and C fraction (for both substrates), PET and texture (for sediments), and river width and urban cover (for leaves).
For sediments, as in the case of amounts of leached substances, the variance across sampling sites was explained best in the tropical (58%) and continental (53%) zones, and was driven mainly by the environmental variables and their effect on substrate characteristics. Variables with VIP >1 in both zones were sediment texture (fraction of silt and clay) and, additionally PET, aridity, and urban cover in samples from the tropical zone, and pasture and forest cover, riparian cover, aridity, and dry period duration in samples from the continental zone (Table 3). For sediments in the arid zone, the explained variance was around 28% and the share of groups of variables that explained the observed variance was different. In particular, almost all variance explained by environmental variables was due to the effect of environmental variables on substrates (VIP >1 for texture, %C, %N, and forest cover). This was the opposite for leaf leachates, where the variance was explained mainly by the effect of environmental variables alone (PET, aridity, and dry period duration).

In samples from the temperate zone, variance of leachate quality was best explained for biofilms (27%) followed by leaves (13%) and sediments (6%) (Table 3). The same was found for the amounts of leached substances, where the explained variance for biofilms was due to the effect of environmental variables (PET and fraction of different land use types), and for leaves due to the effect of substrate characteristics (%C, %N). For sediments, the share of variance explained by the effect of substrate characteristics and the effect of environmental variables was approximately equal (VIP >1 for sediment texture classes, river width, altitude).

### 3.6 Estimated areal fluxes of nutrients and OM across IRES riverbeds

Area-specific fluxes differed by two to four orders-of-magnitude among the sampled riverbeds, depending on the nutrient and OM species (Figure 51, Table 4). Fluxes of DOC and SRP differed by two orders-of-magnitude and ranged for DOC from 3 to 163 g/m² riverbed surface (median: 15.2) and for SRP from 0.015 to 2.63 g/m² (median: 0.12). Fluxes of N-NH₄⁺ and phenolics spanned three orders-of-magnitude (N-NH₄⁺: 0.009–6.67 g/m², median: 0.27; phenolics: 0.012–35 g/m², median: 1.39). N-NO₃⁻ fluxes spanned the largest range, from 0.008 to 18.88 g/m² (median: 0.59 g/m²). Overall, the released fluxes decreased in the following order: DOC > phenolics > N-NO₃⁻ > N-NH₄⁺ > SRP.

Major contributions to the areal fluxes from riverbeds were made by sediments: 98 ± 7% (mean ± SD) for N-NO₃⁻, 97 ± 6% for N-NH₄⁺, 86 ± 19% for SRP, 85 ± 20% for DOC, and 56 ± 33% for phenolics. Leaves provided the second highest contribution to the total areal flux. In contrast to sediments and leaves, the relative contribution of biofilms to area-specific flux rates was very low for all substances (in average: <0.1%), but slightly higher for N-NO₃⁻ (1.5 ± 7%) (values above 100% or lower than 0% reflect deviation and not the real data).

The highest fluxes were estimated from riverbeds in the continental zone (Table 4), whose areal flux of N-NH₄⁺ and phenolics was three times higher than that of the arid zone, four times higher for N-NO₃⁻, and five times higher for SRP and DOC. For all nutrients and OM species, except phenolics (Kruskal–Wallis test, $\chi^2 = 4.68$, $df = 3$, $p = 0.2$), the differences between continental and arid zones were statistically significant (Dunn’s test, $p < 0.001$ for all pairwise comparisons). Compared to the continental zone, a lower flux was found for DOC in temperate and tropical zones (Kruskal–Wallis test, $\chi^2 = 24.8$, $df = 3$, $p = 0.003$; Dunn’s tests $p = 0.001$ and $p = 0.005$ respectively) and SRP (Kruskal–Wallis test, $\chi^2 = 20.02$, $df = 3$, $p < 0.001$; Dunn’s tests $p = 0.001$ and $p = 0.004$ respectively). The flux of N-NH₄⁺ was lower in the temperate zone than in the continental zone (Kruskal–Wallis test, $\chi^2 = 16.5$, $df = 3$, $p < 0.001$; Dunn’s test $p = 0.006$).

### 4 DISCUSSION

#### 4.1 Rewetting events in IRES in the context of global biogeochemical cycles

Our globally comparable assessment of nutrient and DOM leaching in rewetted IRES shows that the quantity and quality of leached nutrients and DOM are substrate- and climate-specific, with the highest amounts leached in continental climate and with sediments contributing most to the total areal flux from dry river beds. These data provide a basis on which to develop models of biogeochemical cycling in river networks including IRES.

According to our first hypothesis, we found a high variability in the amount of leached substances and the quality of leachates from organic, but also from inorganic substrates, mainly as a consequence of inherent substrate properties and their modification during the drying period. Leaching from organic materials (leaves and biofilms) was relatively enriched in P vs N in contrast to sediments. Due to their higher mass within the riverbeds, sediments were the main contributors to the areal fluxes. Sediments leached high amounts of N-NO₃⁻, the accumulation of which in dry riverbeds is promoted by aerobic conditions (Amalfitano et al., 2008; Arce et al., 2014; Borken & Matzner, 2009; Merbt et al., 2016). Considering quality of leached DOM, we found that depending on the proportion of each substrate within the riverbed, different ecosystem processes can be affected. For example, leachates from biofilms with a high proportion of biopolymers may play a key role as sources of bioavailable DOM in IRES and are more likely to be retained within the riverbed upon rewetting (Romani, Vazquez, & Butturini, 2006; von Schiller et al., 2015). A high proportion of LMWS leached from leaves suggests that such leachates can trigger ecosystem processes in downstream surface waters and groundwaters, as molecules of this size fraction can easily be transported through the hyporheic zone with limited immobilization (Romani et al., 2006). DOM leached from sediments was mainly of microbial origin, suggesting its high potential bioavailability (Marxsen, Zoppini, & Wilczek, 2010; Schimel et al., 2007). Overall, we suggest that rewetting of sediments is key for understanding biogeochemical cycles in fluvial networks with IRES, and that leaves and biofilms can introduce regional variabilities in the global scale patterns depending on the accumulated amount of these substrates.
in the channel during the dry phase. Indeed, accumulation of plant litter on the dry riverbed ranges from 0 to 963 g/m² depending on aridity, river width, catchment area, riparian cover, and drying duration (Datry et al., 2018 and Table S1). In our study, accumulations of biofilms were very common in the temperate zone and ranged from 0.3 to 327 g/m² (Table S1).

We also found differences in the amounts of leached substances among climate zones, in accordance with our second hypothesis, but only for sediments. Initially, we expected cross-climate differences to be more pronounced for leaves due to climatic effects on vegetation composition and leaf litter quality (e.g. Aerts, 1997; Boyero et al., 2017), rather than for sediments whose composition is controlled mainly by geology and geomorphology. The absence of significant differences among climate zones for leaves could be explained by the considerable variability we observed among leaf material collected within climate zones, both in terms of species composition and drying history. Although we did not assess the site-specific composition of riparian vegetation, previous studies indicated that up to 40% of variation in leaf traits at a given site can be explained by small-scale spatial and temporal environmental heterogeneity in environmental factors such as hydrology and disturbance regime (Cornwell et al., 2008).

High concentrations leached in the continental climate zone suggest that nutrient loads to freshwaters will increase with the projected increase in the extent of IRES in such regions. In the arid zone where terrestrial primary production is severely constrained by water availability (Austin et al., 2004), rewetting events are expected to stimulate stream ecosystem productivity not only due to water availability, but also because the potential bioavailability of leachates is particularly high in this climate zone. However, despite a high potential bioavailability of DOM, leachates from the arid zone were characterized by low amounts of nutrients, probably resulting from leaf traits that reflect adaptation to dry conditions (Cornwell et al., 2008).

Comparison of fluxes from 1 m² of IRES within the 4 hr duration of the experiment with the annual flux from 1 m² of watersheds (Table S5) showed that rewetting events in IRES represent a significant pulse of dissolved substances in ecosystems, including some estimates exceeding known annual fluxes from watersheds with perennial rivers (although differences in the size of watersheds and stream area of IRES should be accounted). While there can be some confounding factors between laboratory conditions and those that occur in a natural setting (i.e. intensity and duration of rewetting events, ambient temperature, increased leaching caused by oven-drying (Gessner & Schwoerbel, 1989), presence of terrestrial plants in dry riverbeds (Gómez, Arce, Sánchez, & del Mar Sánchez-Montoya, 2012)), the results of our experiment across various climate regions indicate that rewetting of IRES produces a pulsed release of dissolved substances. Decomposition of substrates accumulated in IRES, and thus carbon turnover, are affected by drying-rewetting

![FIGURE 6](image_url)
cycles (Fierer & Schimel, 2002). Given the predicted increase in the duration of droughts, the exacerbation of extreme low-flow conditions, and the intensity of storm events (De Girolamo, Bouraoui, Buffagni, Pappagallo, & Lo Porto, 2017; Huntington, 2006; IPCC, 2014), the results of this study emphasize the need to integrate IRES in global carbon cycles and budgets, from which they are currently excluded (Raymond et al., 2013; although see Datry et al., 2018).

4.2 | Environmental variables correlated with release of nutrients and OM

Environmental variables that are prone to be affected by climate change (namely PET, aridity, dry period duration, land-use) correlated with amounts and quality of leachates, particularly for sediments. For leaves, these correlations were less pronounced, suggesting that leaching may be affected by substrate characteristics other than those examined here. Characteristics such as toughness and content of secondary metabolites in substrates could have affected leaching through the effect on their mass loss during the dry phase and simulated rewetting, and on activity of microbial community in leachates (e.g. Pérez-Harguindeguy et al., 2000; Ristock et al., 2017). Latitude, although not considered in the study, may also be responsible for the unexplained variance given that litter quality generally increases with latitude (Boyero et al., 2017).

The amounts of leached substances from both leaves and sediments were correlated with PET. This variable is expected to be intensified in the future (Milly & Dunne, 2016) and will most likely lead to fluctuations in moisture conditions in dry riverbeds. Low moisture level reduces litter decomposition and C consumption, thereby promoting the release of DOM upon rewetting (Abril et al., 2016; Aerts, 1997; Bruder et al., 2011; Gessner, 1991) and hence increasing the probability of negative consequences for stream ecosystems such as blackwater events leading to hypoxia (Hladyz et al., 2011).

Differences among climate zones in terms of correlations of environmental variables with amounts of leached substances indicate that climate change can have different effects on IRES in different geographical regions. For example, in the arid zone, where IRES are usually characterized by open canopy (Steward, Schiller, Tockner, Marshall, & Bunn, 2012), aridity and percentage of riparian vegetation best explained the variance in sediment leachates. Inputs of riparian vegetation litter onto the dry riverbeds and its subsequent decomposition, can represent an additional input of nutrients to sediments in the arid zone areas (Abril et al., 2016), where soils generally contain less carbon and nitrogen compared to the continental zone (Table S1 and Delgado-Baquerizo et al., 2013). Changes in land-use (particularly, in the percentage of pasture cover at the global scale as well as within individual climate zones except continental) were correlated with the amount of leached substances from leaves, potentially through modifying the composition of plant material accumulated in beds of IRES. This suggests that modification of land use in the catchments with IRES can also affect their contribution to nutrient load due to changes in the composition of CPOM accumulating in dry riverbeds.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arid (N = 23)</th>
<th>Continental (N = 12)</th>
<th>Tropical (N = 15)</th>
<th>Temperate (N = 105)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>Median: 9.40</td>
<td>Median: 11.00 ± 6.07</td>
<td>Median: 15.90</td>
<td>Median: 162.67 ± 29.82</td>
</tr>
<tr>
<td></td>
<td>Min: 2.96</td>
<td>Min: 2.56 ± 0.33</td>
<td>Min: 6.27</td>
<td>Min: 0.25 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Max: 26.71</td>
<td>Max: 20.66 ± 0.01</td>
<td>Max: 30.00</td>
<td>Max: 1.65 ± 0.01</td>
</tr>
<tr>
<td>N-PO4</td>
<td>Median: 0.22</td>
<td>Median: 0.29 ± 0.33</td>
<td>Median: 0.56 ± 0.02</td>
<td>Median: 0.62 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Min: 0.01</td>
<td>Min: 0.01</td>
<td>Min: 0.01</td>
<td>Min: 0.01</td>
</tr>
<tr>
<td></td>
<td>Max: 0.25</td>
<td>Max: 1.65 ± 0.02</td>
<td>Max: 1.56 ± 0.27</td>
<td>Max: 1.65 ± 0.02</td>
</tr>
<tr>
<td>SRP</td>
<td>Median: 0.07</td>
<td>Median: 0.12 ± 0.01</td>
<td>Median: 0.65 ± 0.78</td>
<td>Median: 0.10</td>
</tr>
<tr>
<td></td>
<td>Min: 0.01</td>
<td>Min: 0.01</td>
<td>Min: 0.03</td>
<td>Min: 0.01</td>
</tr>
<tr>
<td></td>
<td>Max: 0.15</td>
<td>Max: 1.65 ± 0.01</td>
<td>Max: 3.64</td>
<td>Max: 0.50</td>
</tr>
<tr>
<td>Phenolics</td>
<td>Median: 1.10</td>
<td>Median: 1.57 ± 2.08</td>
<td>Median: 0.65 ± 0.78</td>
<td>Median: 0.20 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Min: 0.01</td>
<td>Min: 0.01</td>
<td>Min: 0.03</td>
<td>Min: 0.01</td>
</tr>
<tr>
<td></td>
<td>Max: 1.45</td>
<td>Max: 1.45 ± 0.20</td>
<td>Max: 3.64</td>
<td>Max: 0.50</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arid (N = 12)</th>
<th>Continental (N = 25)</th>
<th>Tropical (N = 15)</th>
<th>Temperate (N = 105)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>Median: 43.80</td>
<td>Median: 44.79 ± 21.15</td>
<td>Median: 74.09</td>
<td>Median: 15.90 ± 7.53</td>
</tr>
<tr>
<td></td>
<td>Min: 15.04</td>
<td>Min: 15.04</td>
<td>Min: 3.71</td>
<td>Min: 4.02</td>
</tr>
<tr>
<td></td>
<td>Max: 82.58</td>
<td>Max: 82.58</td>
<td>Max: 30.01</td>
<td>Max: 19.53 ± 2.76</td>
</tr>
<tr>
<td>N-PO4</td>
<td>Median: 0.68</td>
<td>Median: 0.68 ± 0.23</td>
<td>Median: 0.42 ± 0.28</td>
<td>Median: 0.33 ± 0.33</td>
</tr>
<tr>
<td></td>
<td>Min: 0.61</td>
<td>Min: 0.61</td>
<td>Min: 0.04</td>
<td>Min: 0.03</td>
</tr>
<tr>
<td></td>
<td>Max: 1.65</td>
<td>Max: 1.65 ± 0.34</td>
<td>Max: 1.16</td>
<td>Max: 1.16 ± 0.04</td>
</tr>
<tr>
<td>SRP</td>
<td>Median: 0.16</td>
<td>Median: 0.15 ± 0.03</td>
<td>Median: 0.19 ± 0.15</td>
<td>Median: 0.10 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Min: 0.10</td>
<td>Min: 0.15</td>
<td>Min: 0.03</td>
<td>Min: 0.03</td>
</tr>
<tr>
<td></td>
<td>Max: 0.43</td>
<td>Max: 0.43 ± 0.07</td>
<td>Max: 0.55</td>
<td>Max: 0.08</td>
</tr>
</tbody>
</table>
Although dry period duration is an important factor affecting the amounts and quality of litter accumulations in IRES (del Campo & Gómez, 2016; von Schiller et al., 2017), we found its influence on the variance in leachates only in continental and tropical zones. This indicates that during the dry phase materials with different drying history (as affected by different climates) and potential to leach nutrients and OM can accumulate in IRES. This also suggests that dry period duration cannot invariably be used as a master proxy to assess potential impacts of nutrient loading from IRES upon rewetting. Under field conditions, other factors such as severity and timing of a rewetting event as well as presence/absence of plant material growing in dry channels can affect nutrient fluxes from riverbeds, and the fate of nutrients in ecosystems, as well as potential ecosystem impacts (e.g. eutrophication, mass mortality of aquatic organisms) in downstream receiving waters and groundwater (Baldwin & Mitchell, 2000; Bernal et al., 2013; Cavanaugh, Richardson, Strauss, & Bartsch, 2006; Hladyz et al., 2011; Ocampo, Oldham, Sivapalan, & Turner, 2006). Substrate moisture content and variability in associated microbial communities can potentially be responsible for the unexplained part of the variance in the leachates, due to their effect on decomposition rates of accumulated CPOM, nutrient processing in sediments, release of DOM upon rewetting, and its modification by microbial communities (Abril et al., 2016; Arce et al., 2015; Dieter, Frindte, Krüger, & Wurzbacher, 2013; McIntyre, Adams, Ford, & Grierson, 2009; Meisner, Leizeaga, Rousk, & Bååth, 2017).

### 4.3 Implications for freshwater ecosystems and future research

We identified IRES to function as pulsed biogeochemical reactors (sensu Larned et al., 2010) at a global scale even though the experiments were conducted under laboratory conditions and magnitudes of leached substances may differ in the natural environment. Our data serve also as a basis for further upscaling and modeling of the processes observed in the laboratory to address ecological implications of rewetting events at catchment scales. Potential implications for the functioning of rivers could be determined by the effect of leached substances on the degree of nutrient limitation of microorganisms downstream, and therefore community composition (Demi, Benstead, Rosemond, & Maerz, 2018) as well as on the fate of refractory substances and intensification of their decomposition through the so-called “priming effect” (Guenet, Danger, Abbadie, & Lacroix, 2010). The results of our study support the recent call for developing effective strategies for the management of IRES to avoid negative consequences for downstream ecosystems caused by excessive nutrient and OM load.

### ACKNOWLEDGEMENTS

This work was carried out within the SMART Joint Doctorate Programme "Science for the MAnagement of Rivers and their Tidal systems" funded by the Erasmus Mundus Joint Doctorate Programme of the European Union (http://www.riverscience.it). O.S. was also supported by a grant for a short-term scientific mission to the University of the Basque Country, Spain, within the COST Action CA15113 (SMIRES, Science and Management of Intermittent Rivers and Ephemeral Streams, www.smires.eu). O.S. is thankful for a partial support from IGB equal opportunity fund for young female scientists and DFG (SU 405/10-1). F.A. was supported by the Swiss National Science Foundation grants no PP00P3_179089 and PP00P3_150698 and the URPP Global Change and Biodiversity, University of Zurich. S.D.L. has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 748625. R.F. acknowledges support of the CONICYT/FONDAP/15130015 Chile. The experiments and the chemical analyses of leachates were conducted at the Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB) in Berlin, Germany. Organic C and total N content of substrates were determined at the Laboratory of Alpine Ecology (LECA), Grenoble, France (leaves and biofilm), and the Catalan Institute for Water Research in Girona, Spain (sediments). Analyses of sediment texture were done at the University of Barcelona, Spain. We are thankful to Thomas Rossoll, Claudia Schmalsch, Sarah Krocker, Elisabeth Schütte, and Jan Oestmann at IGB’s Department of Chemical Analytics and Biogeochemistry for support with laboratory analyses; to Gabriel Singer for statistical advice; to Jeremy Fonvielle for support with the absorbance-fluorescence analysis; and to Thomas Mehner and participants of IGB’s Scientific Writing course for valuable comments on an earlier version of the manuscript. We are thankful to Christopher Robinson, Eduardo Martin, Sarig Gafny, Marek Polášek, Michal Straka for collecting part of the samples used in the study.

### ORCID

**Oleksandra Shumilova** [https://orcid.org/0000-0002-6270-7242](https://orcid.org/0000-0002-6270-7242)

**Dominik Zak** [https://orcid.org/0000-0002-1229-5294](https://orcid.org/0000-0002-1229-5294)

**Thibault Datry** [https://orcid.org/0000-0003-1390-6736](https://orcid.org/0000-0003-1390-6736)

**Daniel von Schiller** [https://orcid.org/0000-0002-9493-3244](https://orcid.org/0000-0002-9493-3244)

**Roland Corti** [https://orcid.org/0000-0001-9548-1772](https://orcid.org/0000-0001-9548-1772)

**Arnaud Foulquier** [https://orcid.org/0000-0002-8308-5841](https://orcid.org/0000-0002-8308-5841)

**Biel Obrador** [https://orcid.org/0000-0003-4050-0491](https://orcid.org/0000-0003-4050-0491)

**Klement Tockner** [https://orcid.org/0000-0002-0038-8151](https://orcid.org/0000-0002-0038-8151)

**Daniel C. Allan** [https://orcid.org/0000-0002-0451-0564](https://orcid.org/0000-0002-0451-0564)

**Florian Altermatt** [https://orcid.org/0000-0002-4831-6958](https://orcid.org/0000-0002-4831-6958)

**Maria Isabel Arce** [https://orcid.org/0000-0001-7407-3884](https://orcid.org/0000-0001-7407-3884)

**Shai Arnon** [https://orcid.org/0000-0002-7109-8979](https://orcid.org/0000-0002-7109-8979)

**Juan F. Blanco-Libreros** [https://orcid.org/0000-0003-0507-2401](https://orcid.org/0000-0003-0507-2401)

**Joanna Blessing** [https://orcid.org/0000-0001-7679-1222](https://orcid.org/0000-0001-7679-1222)

**Iola Gonçalves Boëchat** [https://orcid.org/0000-0002-9651-6364](https://orcid.org/0000-0002-9651-6364)

**Kate Boersma** [https://orcid.org/0000-0002-0707-3283](https://orcid.org/0000-0002-0707-3283)

**Núria Bonada** [https://orcid.org/0000-0002-2983-3335](https://orcid.org/0000-0002-2983-3335)

**Nick R. Bond** [https://orcid.org/0000-0003-4294-6008](https://orcid.org/0000-0003-4294-6008)

**Andreas Bruder** [https://orcid.org/0000-0002-4591-491X](https://orcid.org/0000-0002-4591-491X)


REFERENCES

intergovernmental panel on climate change (pp. 1–32). Cambridge, UK: Cambridge University Press.


Additional supporting information may be found online in the Supporting Information section at the end of the article.