Global Change Biology

Global Change Biology (2017), doi: 10.1111/gcb.13609

Global synthesis of the temperature sensitivity of leaf litter breakdown in streams and rivers

JENNIFER J. FOLLSTAD SHAH[1,2], JOHN S. KOMINOSKI[3], MARCELO ARDÓN[4], WALTER K. DODDS[5], MARK O. GESSNER[6,7], NATALIE A. GRIFFITHS[8], CHARLES P. HAWKINS[2], SHERRI L. JOHNSON[9], ANTOINE LECERF[10], CARRI J. LEROY[11], DAVID W. P. MANNING[12], AMY D. ROSEMOND[13], ROBERT L. SINSABAUGH[14], CHRISTOPHER M. SWAN[15], JACKSON R. WEBSTER[16] and LYDIA H. ZEGLIN[5]

[1]*Environmental and Sustainability Studies/Department of Geography, University of Utah, Salt Lake City, UT 84112, USA,* [2]*Department of Watershed Sciences, Utah State University, Logan, UT 84322, USA,* [3]*Department of Biological Sciences, Florida International University, Miami, FL 33199, USA,* [4]*Department of Forestry and Environmental Resources, North Carolina State University, Raleigh, NC 27695, USA,* [5]*Division of Biology, Kansas State University, Manhattan, KS 66506, USA,* [6]*Department of Experimental Limnology, Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB), 16775 Stechlin, Germany,* [7]*Department of Ecology, Berlin Institute of Technology (TU Berlin), Ernst-Reuter-Platz 1, 10587 Berlin, Germany,* [8]*Climate Change Science Institute and Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA,* [9]*Pacific Northwest Research Station, US Forest Service, Corvallis, OR 97331, USA,* [10]*Université de Toulouse, UPS, INP, CNRS, EcoLab (Laboratoire d'Écologie Fonctionnelle et Environnement), 31062 Toulouse, France,* [11]*Environmental Studies Program, The Evergreen State College, Olympia, WA 98505, USA,* [12]*School of Environment and Natural Resources, Ohio State University, Columbus, OH 43210, USA,* [13]*Odum School of Ecology, University of Georgia, Athens, GA 30602, USA,* [14]*Department of Biology, University of New Mexico, Albuquerque, NM 87131, USA,* [15]*Department of Geography and Environmental Systems, University of Maryland-Baltimore County, Baltimore, MD 21250, USA,* [16]*Department of Biological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA*

Abstract

Streams and rivers are important conduits of terrestrially derived carbon (C) to atmospheric and marine reservoirs. Leaf litter breakdown rates are expected to increase as water temperatures rise in response to climate change. The magnitude of increase in breakdown rates is uncertain, given differences in litter quality and microbial and detritivore community responses to temperature, factors that can influence the apparent temperature sensitivity of breakdown and the relative proportion of C lost to the atmosphere vs. stored or transported downstream. Here, we synthesized 1025 records of litter breakdown in streams and rivers to quantify its temperature sensitivity, as measured by the activation energy (E_a, in eV). Temperature sensitivity of litter breakdown varied among twelve plant genera for which E_a could be calculated. Higher values of E_a were correlated with lower-quality litter, but these correlations were influenced by a single, N-fixing genus (*Alnus*). E_a values converged when genera were classified into three breakdown rate categories, potentially due to continual water availability in streams and rivers modulating the influence of leaf chemistry on breakdown. Across all data representing 85 plant genera, the E_a was 0.34 ± 0.04 eV, or approximately half the value (0.65 eV) predicted by metabolic theory. Our results indicate that average breakdown rates may increase by 5–21% with a 1–4 °C rise in water temperature, rather than a 10–45% increase expected, according to metabolic theory. Differential warming of tropical and temperate biomes could result in a similar proportional increase in breakdown rates, despite variation in E_a values for these regions (0.75 ± 0.13 eV and 0.27 ± 0.05 eV, respectively). The relative proportions of gaseous C loss and organic matter transport downstream should not change with rising temperature given that E_a values for breakdown mediated by microbes alone and microbes plus detritivores were similar at the global scale.

Keywords: activation energy, breakdown, carbon cycling, climate change, detritivore, leaf chemistry, metabolic theory, microbe, organic matter, temperature sensitivity

Received 21 October 2016 and accepted 26 November 2016

Introduction

Understanding the temperature sensitivity of ecosystem processes that govern carbon (C) cycling is imperative as global temperatures rise (Yvon-Durocher *et al.*, 2012; Welter *et al.*, 2015; Demars *et al.*, 2016). Inland freshwaters are an important contributor to the global C cycle, although they cover only about 3% of the Earth's land surface (Battin *et al.*, 2009; Raymond *et al.*, 2013). Elevated temperature affects the C balance

Correspondence: Jennifer J. Follstad Shah, tel. +1 801 585 5730, e-mail: jennifer.shah@envst.utah.edu

of aquatic ecosystems, with the strength of effects depending on the temperature sensitivity of key metabolic processes (Yvon-Durocher *et al.*, 2010; Demars *et al.*, 2011) and the responses of biological communities to warming (Boyero *et al.*, 2011b).

Most freshwater ecosystems are net heterotrophic, so temperature increases are likely to enhance net C losses. The breakdown of leaf litter (hereafter 'litter') and other particulate organic matter produces a large fraction of the particulate, dissolved, and gaseous forms of C that are exported from streams and rivers (Gessner *et al.*, 1999) through downstream transport and efflux to the atmosphere (Dodds & Cole, 2007; Battin *et al.*, 2009). Litter breakdown is an integrative ecosystem process that involves multiple organisms, fuels aquatic food webs, and links biogeochemical cycles (Wallace *et al.*, 1997; Gessner *et al.*, 1999). The process involves leaching of dissolved constituents, degradation by microbes, feeding by detritivores, and physical fragmentation, all of which are mediated, in part, by leaf chemistry and physical structure (Webster & Benfield, 1986; Gessner *et al.*, 1999).

Mean annual water temperature for some streams and rivers is rising on the order of 0.01–0.1 °C yr^{-1} from changes in climate and land use (Kaushal *et al.*, 2010). Rates of litter breakdown are predicted to increase exponentially with temperature (Boyero *et al.*, 2011b) because elevated temperature stimulates metabolism by accelerating biochemical reactions (Brown *et al.*, 2004) and leaf litter is used as a substrate to support the metabolic processes of microbes and detritivores (Gessner *et al.*, 1999). However, the magnitude of change in breakdown rates is unclear because drivers other than the direct temperature effect on metabolism can influence the temperature sensitivity of the process.

The temperature sensitivity of chemical reactions is quantified by the activation energy, E_a (Arrhenius, 1915). As the scale increases from single reactions to ecosystem processes involving multiple organisms, the activation energy represents an apparent (i.e., empirical), rather than an inherent, temperature sensitivity. According to metabolic theory, metabolic rate controls processes at all levels of ecological organization by setting rates of resource uptake from the environment and resource allocation to maintenance, growth, and reproduction of organisms (Brown *et al.*, 2004). Thus, an E_a of ~0.65 eV is expected, according to metabolic theory, if rates of litter breakdown reflect the temperature sensitivity of microbial and detritivore metabolism (Allen *et al.*, 2005). Conversely, a lower E_a, or reduced temperature sensitivity, is expected if rates of litter breakdown are limited by the activity of microbial 'ecoenzymes' (enzymes expressed by microbes or released to the environment via cell lysis; Sinsabaugh *et al.*, 2009), which on average have E_a values of ~0.31–0.56 eV (Sinsabaugh & Follstad Shah, 2012; Wang *et al.*, 2012). Lower E_a values also may arise if other factors interact with temperature in ways that augment rates at low temperature relative to rates expected based on temperature alone (Boyero *et al.*, 2011b).

Examples of extrinsic and intrinsic factors that can influence the apparent temperature sensitivity of litter breakdown include variation in detritivore density (Boyero *et al.*, 2011b; Griffiths & Tiegs, 2016), thermal adaptation of organisms (Bradford, 2013; Strickland *et al.*, 2015), and litter quality (Cornwell *et al.*, 2008; Makkonen *et al.*, 2012). Empirical data from 22 sites located between 0° and 48° north and south suggest that the relative contribution of detritivores to litter breakdown increases with latitude, which may have the effect of diminishing or negating the apparent temperature sensitivity of litter breakdown (Boyero *et al.*, 2011b). Many relatively large-bodied detritivores that consume leaf litter (e.g., various taxa of the orders Plecoptera and Trichoptera) evolved in cool waters 200 million years ago and are still restricted to cool habitats (Ward & Stanford, 1982). Hence, densities of litter-consuming detritivores are generally greater at higher latitudes relative to the tropics (Boyero *et al.*, 2011a). Greater densities could persist at higher latitudes relative to the tropics as water temperatures rise, but dominance within macroinvertebrate communities may shift to smaller-bodied taxa (Friberg *et al.*, 2009). Elevated temperature also can alter the catabolic processes by which litter is processed through changes in microbial community composition, production of ecoenzymes, and microbial metabolism (Dang *et al.*, 2009; Ferreira & Chauvet, 2011b; Bradford, 2013). Litter chemistry is an important control on breakdown rate in streams and rivers (Boyero *et al.*, 2016; García-Palacios *et al.*, 2016). Labile litter (i.e., litter low in complex C compounds and high in nutrient concentrations) loses mass more rapidly than recalcitrant litter (Gessner & Chauvet, 1994; Ardón *et al.*, 2009; Martínez *et al.*, 2013). However, studies in terrestrial ecosystems have shown that the breakdown of low-quality, recalcitrant litter is more sensitive to temperature compared with high-quality, labile litter (Hobbie, 1996; Fierer *et al.*, 2005). Thus, it is critical to understand the consequences of climate change on litter breakdown not only through temperature but also through the influences of other key drivers that interact with temperature.

Here, we used data from 169 published studies (Supplemental Information) corresponding to 1025 individual cases (Fig. 1; Appendix S1) across 85 plant genera at globally distributed reference sites to quantify the apparent temperature sensitivity of litter breakdown in streams and rivers. We also examined the effects of extrinsic (detritivore density, location) and intrinsic

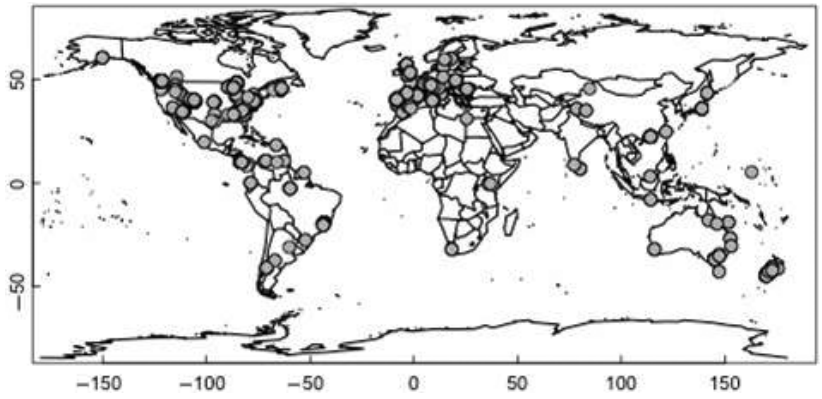

Fig. 1 Global distribution of litter breakdown records in streams and rivers (n = 1025).

(litter quality) drivers on the apparent temperature sensitivity of litter breakdown. Our analyses were guided by four predictions: (1) The global apparent temperature sensitivity of litter breakdown in streams and rivers is close to the inherent activation energy of 0.65 eV, according to metabolic theory; (2) litter breakdown mediated by microbes plus detritivores has a lower activation energy than breakdown mediated by microbes alone (Boyero *et al*., 2011b); (3) temperature sensitivity for different biomes may vary if microbes or detritivores maintain high activities despite low water temperature in temperate biomes; and (4) temperature sensitivity varies among plant genera, with low-quality litter having greater activation energy than high-quality litter.

Materials and methods

Database compilation and calculations

Data on litter breakdown published through 2011 were compiled by conducting a systematic literature search using the *ISI Web of Science* database and the keywords '(leaf OR litter) AND (breakdown OR decomposition OR processing) AND (stream OR river)'. Search results were compared to references cited in published reviews of litter breakdown (Webster & Benfield, 1986; Young *et al*., 2008; Tank *et al*., 2010). Papers not found in the literature search were added to the initial list of potential data sources. Data were extracted from 300 of these papers meeting the following criteria: (1) Breakdown of litter (no wood, other plant litter, or proxies such as cotton strips) was measured in a freshwater stream or river (no experimental flumes or mesocosms; no brackish waters); (2) either a breakdown rate coefficient or mass loss over a known period of time was reported; and (3) water temperature was recorded during the experiment. Papers that did not meet these three criteria were excluded.

To limit the confounding influence of experimental design and human impacts on streams in the analyses, we retained data from single species (i.e., no litter mixtures) studies conducted at reference sites with no experimental manipulation located between latitudes of 0° and 60° on both the northern and southern hemisphere (169 studies, 1025 cases). We omitted sites located above 60° to ensure a similar distribution in latitudinal range for data derived from both fine and coarse mesh bag methods (fine mesh ≤1 mm vs. coarse mesh >1 mm or no mesh; the latter allows access by a more complete assemblage of consumers). Designation as a reference site was based upon authors' study site descriptions (i.e., low impact by agricultural, industrial, or urban land uses) and thresholds of <1.0 mg L^{-1} NO_3–N and <0.1 mg L^{-1} soluble reactive phosphorus (SRP). These nutrient concentration thresholds were applied because many sites designated as reference sites in Europe had elevated nitrate and/or SRP concentrations. Data were extracted from the main text of papers, tables, and/or digitized graphs. Authors were contacted if it was clear that desired data had been collected but values were not reported in the paper.

Information extracted from each paper included stream name, latitude, longitude, altitude, water temperature, litter genus and species names, litter breakdown methodology (bundles of leaves secured with nylon string; leaves placed in mesh bags or tubes with ends covered in mesh), leaf-bag mesh size, initial leaf dry mass (DM) or ash-free dry mass (AFDM), study duration, breakdown rate coefficient or percent mass loss, detritivore density at each sampling date, and initial litter chemistry (% C, N, P, lignin, and cellulose).

Breakdown coefficients were recorded directly as reported or, when missing, calculated from litter mass loss data by linear regression analysis of log-transformed data. Daily breakdown rate (k_D, day^{-1}) is expressed as the breakdown coefficient, or decay constant, in the simple exponential decay model:

$$m_t \propto e^{-k_D t}, \quad (1)$$

where m_t is the proportion of litter mass remaining at time t (days) (Boulton & Boon, 1991).

We used temperature-adjusted breakdown coefficients to assess the effects of physical and biological controls on breakdown rate in isolation from temperature. We calculated temperature-adjusted breakdown coefficients (per degree day; k_{DD}) by replacing time with cumulative daily mean

temperature in Eqn 1 (Woodward *et al.*, 2012). We approximated k_{DD} by dividing the breakdown coefficient by the mean water temperature during the study when thermal sum was not reported.

Reference to k_D and k_{DD} denotes breakdown coefficients per day and per degree day, respectively, across litter confinement methods (i.e., fine mesh bag vs. coarse mesh bag or nylon string; nylon string is henceforth grouped with coarse mesh). Differences in leaf-bag mesh size were used to distinguish between breakdown caused by microbes alone (fine mesh) versus by microbes and detritivores together (coarse mesh). Coefficients with the subscript '*f*' indicate breakdown in fine mesh bags and with the subscript '*c*' indicate breakdown in coarse mesh bags.

Information on site characteristics also was included in the database. Mean water temperature was estimated as the mean of reported minimum and maximum values when continuous records or mean values were unavailable. Latitude and longitude of study sites were obtained from Google Earth when coordinates were omitted from data sources. Altitude was estimated from GPS Visualizer (http://www.gpsvisualizer.com/elevation) if missing from data sources and verified using Google Earth.

Detritivore data collected at or near the time at which litter mass was 50% of the initial mass (T_{50} in days; calculated as ln $0.5/k_D$) were selected to ensure meaningful comparisons of the influence of detritivores across studies varying widely in duration and sampling frequency. Because few studies reported detritivore density precisely at T_{50}, the criterion for selection was relaxed according to the following rules: (1) The sampling day was within ±20% of T_{50}; (2) data from the sampling day preceding T_{50} were used where two sampling days were about equidistant from T_{50}; and (3) data from the first sampling day were used where T_{50} was very short or from the last sampling day when T_{50} was very long.

Data analysis

Apparent temperature sensitivity of litter breakdown. The Arrhenius equation describes the temperature sensitivity of reaction rates, *r* (Arrhenius, 1915):

$$\ln r = \ln r_0 - E_a \times (1/k_B T - 1/k_B T_0), \quad (2)$$

where r_0 is a normalization constant, E_a is the apparent activation energy (eV; 1 eV = 1.6×10^{-19} joule or 96 kJ mol^{-1}), k_B is the Boltzmann constant (8.62×10^{-5} eV K^{-1}), T is temperature in Kelvin (K), and T_0 is a standard water temperature. This normalization centers the temperature data on the standard temperature (Allen *et al.*, 2005; Yvon-Durocher *et al.*, 2012), such that values of 0 on the *x*-axis represent rates at the standard temperature. We used a standard temperature of 10 °C (283.15 K) because it was close to the median water temperature (10.5 °C) in our database. In this case, *r* represents the breakdown coefficient (k_{Df} or k_{Dc}). Equation 2 shows that the value of E_a may be obtained from the slope of the relationship between inverse absolute temperature (i.e., $1/k_B T - 1/k_B T_0$) and ln *r*. The higher the value of E_a, the more sensitive a process is to temperature.

We assessed the temperature sensitivity of litter breakdown using linear mixed-effect (LME) models. Mixed-effects models are appropriate statistical tools for carrying out syntheses of data collected from multiple locations across broad spatial scales using nonuniform methods (Zuur *et al.*, 2009). The inclusion of both fixed and random factors in LME models allows for the assessment of independent variables while accounting for hierarchical structure or related groupings (Zuur *et al.*, 2009). Generalized least squares (GLS) models were used in the absence of groupings.

To test whether litter breakdown has an activation energy (E_a) close to 0.65 eV (prediction 1), we built a set of LME models with litter breakdown rate, k_D (day^{-1}), as the response variable, inverse normalized temperature, $1/k_B T - 1/k_B T_0$ (eV), as a covariate, and mesh size category (fine vs. coarse) as a random (intercept) factor. This random intercept model assumes that detritivore exclusion influences breakdown rate but not its temperature sensitivity. We fit another model with a random intercept (mesh size category) and slope (inverse normalized temperature) to test the validity of this assumption (prediction 2).

Temperature variation across the dataset was largely determined by latitude and altitude (see Supporting Information). To test whether these spatial factors influenced litter breakdown rates independent of temperature, we fitted a second set of LME models with temperature-adjusted breakdown rate (ln k_{DD}, degree day^{-1}; n = 1017) as the response variable, latitude and altitude as fixed effects, and mesh size category as a random (intercept) factor.

Detritivore density can lower the apparent activation energy (E_a) of litter breakdown if density positively covaries with temperature along latitudinal gradients (Boyero *et al.*, 2011b; prediction 2). We thus built GLS models to assess the effects of detritivore density at ~T_{50}, latitude, altitude, and interactions of these terms on breakdown rate per degree day (ln k_{DD}), as another approach to testing our second prediction. These models were based on subsets of the studies in our database for which these data were available (n = 61). The simplest model was obtained by sequentially omitting the least important explanatory variables as described in *Model building and statistical inference*.

To test whether apparent temperature sensitivity varies by biome (prediction 3), we separated latitude into two categories (tropics: 0°–30°, temperate: 31°–60°) and built another set of LME models in which latitudinal category was specified as the random intercept term and inverse normalized temperature was the random slope term.

We built a set of LME models with litter breakdown in coarse mesh bags, k_{Dc} (day^{-1}), as the response variable, inverse normalized temperature as a covariate, with and without slope as a random factor, and plant genus as a random (intercept) factor to test whether the temperature sensitivity of breakdown varies among plant genera (prediction 4). We used 12 (of 85) plant genera with eight or more values of k_{Dc} for these analyses, which represented the minimal sample size needed to estimate E_a with a significance level of $P \leq 0.10$. We carried out several analyses that included indicators of litter quality. First, we regressed averaged values of initial litter

chemistry against genus-specific values of E_a. We obtained average values of initial litter chemistry from our dataset (30% of records), which we augmented with data from published literature not used in our synthesis (see Appendix S2 in Supporting Information). Individual GLS models were constructed for each litter chemistry parameter because some data were missing for two genera (*Melicytus* and *Phragmites*). These models also allowed us to quantify relationships when influential data points were excluded from each analysis.

In a second approach, we classified litter from all 85 plant genera as having 'fast' (k_D >0.0100 day^{-1}), 'medium' (k_D = 0.0050–0.0100 day^{-1}), or 'slow' (k_D < 0.0050 day^{-1}) breakdown rate based on median values of k_D in our dataset and the categories established by Petersen & Cummins (1974). We used these categories as a proxy for litter quality because litter species classified as having fast breakdown are usually of higher quality than litter species classified as breaking down at medium or slow rates (Schindler & Gessner, 2009) and we could apply this categorization to all plant genera in our dataset. We then used LME models to quantify the E_a (random slope term) of litter breakdown (k_{Dc}; response variable) by breakdown rate category (random intercept term). We also used a Kruskal–Wallis test to determine whether temperature sensitivity differed among breakdown rate categories for the 12 genera with genus-specific E_a values.

Model building and statistical inference. Statistical analyses were conducted in R v.3.0.1 (R Core Team 2013). GLS and LME models were computed using the 'NLME' package (Pinheiro *et al*., 2014). LME models were built sequentially, starting with the inclusion of all fixed effects (Zuur *et al*., 2009). Significance of random effects (i.e., intercept and slope) was assessed using likelihood ratio tests, each comparing models with and without the term to test for significance. We sequentially omitted explanatory variables and compared each model with more complex models using Akaike's information criterion (AIC) scores and likelihood ratio (L) tests until the most parsimonious model composed of significant factors (P < 0.05) was found. Model comparisons were based on the restricted estimated maximum likelihood (REML) when fitting random effects and maximum likelihood (ML) when fitting fixed effects. Once the simplest fixed effects model was found, it was refitted in REML to provide the best estimates of standard errors and random effects.

Model assumptions of linearity, normality, and homoscedasticity were checked by plotting normalized residuals based on the REML fit against fitted values and explanatory variables (for LME models) and by plotting histograms of the residuals. These assumptions were met for breakdown coefficients (k_D, day^{-1}; k_{DD}, degree day^{-1}) and detritivore densities at ~T_{50} (no. of individuals g^{-1} litter DM or AFDM) after a natural log transformation (or ln [n + 1] in case of detritivore density at ~T_{50}). We used density data reported in units per g litter DM and AFDM to increase sample size used in analyses. Model parameters are reported along with their standard errors (SE). For E_a, 95% confidence intervals (CI) also are reported to show the precision of the estimate and distance from temperature invariance (i.e., 0 eV).

Results

Temperature sensitivity of litter breakdown mediated by microbes and microbes plus detritivores

The apparent activation energy (E_a) of litter breakdown in fine (k_{Df}) and coarse (k_{Dc}) mesh bags was 0.37 ± 0.09 eV (95% CI: 0.19–0.56 eV; Fig. 2a) and 0.33 ± 0.04 eV (95% CI: 0.25–0.40 eV; Fig. 2b). These E_a values were statistically similar (P = 0.91; Model M2 in Table S1), with a pooled E_a value of 0.34 ± 0.04 eV (95% CI: 0.27–0.40 eV, P < 0.0001, n = 1025). However, breakdown rate was faster for litter enclosed in coarse mesh than in fine mesh bags (P = 0.003; Table S1), with coefficients of 0.0130 day^{-1} for coarse mesh and 0.0096 day^{-1} for fine mesh at 10 °C, based on model normalization constants.

Effect of detritivores and geographic location on temperature sensitivity

Latitude, but not altitude, was a predictor of temperature-adjusted breakdown rate (k_{DD}, degree day^{-1}) of litter in both fine and coarse mesh bags (Model M6 in Table S2). Both k_{DDf} and k_{DDc} increased with latitude and had a similar slope, but temperature-adjusted rates were greater for litter in coarse mesh bags than in fine mesh bags (P = 0.003; Fig. 2c and d, Table S2). Temperature-adjusted breakdown rates increased by 0.0166 ± 0.0029 degree day^{-1} per degree latitude regardless of mesh size and were 2.7 times higher at 60° latitude relative to the equator.

Absolute latitude, detritivore density at ~T_{50}, and the interaction between these two factors were predictors of ln k_{DDc} in the subset of data including information about detritivores (Fig. 3a and b; Model M2 in Table S3). In general, k_{DDc} increased with higher latitude (Fig. 3a) and greater detritivore density (Fig. 3b). Although detritivore density at ~T_{50} was unrelated to latitude (n = 61, P > 0.05; Fig. 3c), the significant interaction between these variables suggests that greater detritivore density promoted faster breakdown rate at a given latitude.

The positive relationship we observed between latitude and temperature-adjusted litter breakdown indicates that rates are faster at higher vs. lower latitude once the effect of temperature is removed. This pattern contributed to a lower value of E_a at temperate latitudes (0.27 ± 0.05 eV, 95% CI: 0.18–0.37 eV) relative to the tropics (0.75 ± 0.13 eV, 95% CI: 0.50–1.01 eV, P = 0.03; Fig. 4, Model M3 in Analysis 1 of Table S4).

Effects of plant genus and litter quality on temperature sensitivity

We found mixed support for our prediction that differences in E_a would be related to litter quality (prediction

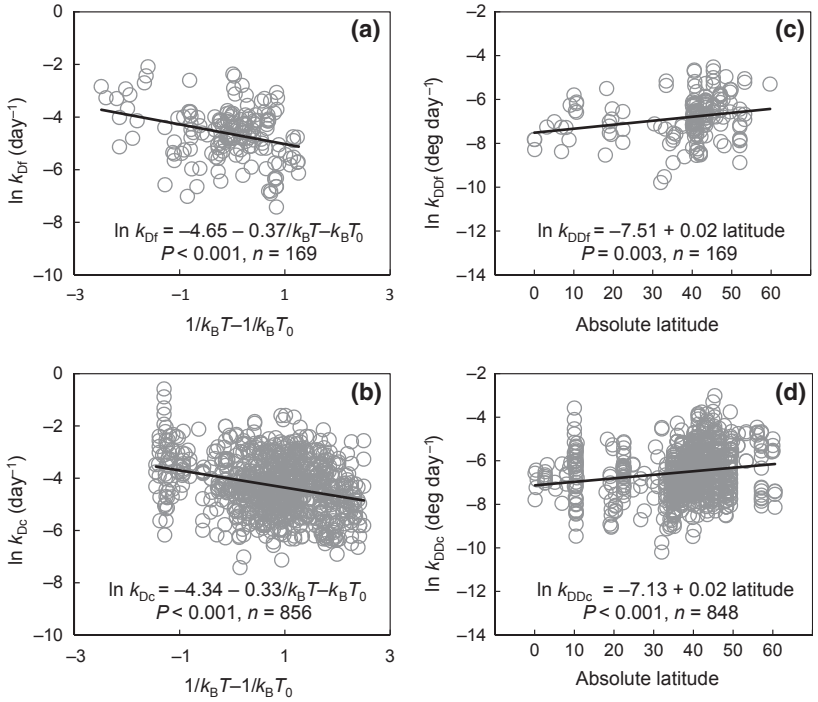

Fig. 2 The apparent activation energy (E_a, eV; 1 eV = 1.6 × 10^{-19} joule or 96 kJ mol^{-1}) of litter breakdown (k_D, day^{-1}; a, b) and the rate of increase in temperature-adjusted breakdown (k_{DD}, degree day^{-1}; C,D) per degree latitude are consistent across fine (a, c) and coarse (b, d) mesh bags. The *x*-axes in a and b are inverse absolute water temperature (*T*) in Kelvin (K) multiplied by the Boltzmann constant (k_B, 8.62 × 10^{-5} eV K^{-1}) and normalized by a standard stream temperature (T_0), 283.15 K or 10 °C. Slopes in a and b approximate the inverse of E_a. Absolute latitude in c and d refers to degrees north or south from the equator.

4). E_a values significantly varied among the 12 genera for which we could estimate temperature sensitivity (P = 0.0001; Model M3 in Table S5), ranging from 0.16 to 0.88 eV (Table 1). *Alnus* had high N concentration (2.6%) relative to other plant genera (0.6–1.7%; Table S6). *Alnus* also had low C:N (19), lignin:N (5), and lignin:P (73) ratios relative to other plant genera (C:N: 23–141, lignin:N: 13–33, lignin:P: 54–668; Table S6). These characteristics led E_a among genera to be negatively correlated with the initial litter %N and positively correlated with C:N, lignin:N, and lignin:P ratios (Fig. 5). However, these patterns were not evident when *Alnus* was excluded from the analyses (Fig. 5). E_a was not correlated with other litter chemistry parameters among genera (Fig. S1). Among all 85 plant genera, E_a values for 'fast', 'medium', or 'slow' breakdown rate categories were similar (P = 0.62), with a common slope of 0.23 ± 0.03 eV (95% CI: 0.18–0.29 eV, P < 0.0001, n = 1025; Model M2 in Table S7, Fig. 6a). Differences in E_a values were not significant when the 12 genera for which we could estimate E_a were combined into 'fast' (0.61 ± 0.16 eV, n = 6), 'medium' (0.84 ± 0.23 eV, n = 3), or 'slow' (0.84 ± 0.23 eV, n = 3) breakdown rate categories (Kruskal–Wallis test: χ^2 = 2.28, d.f. = 2, P = 0.32; Fig. 6b, Table 1). However, among these 12 genera, breakdown rates at 10 °C for genera in the 'fast' category were twice as fast as rates for genera in the 'medium' category and seven times faster than rates for genera in the 'slow' category (Table 1).

Discussion

The overall apparent temperature sensitivity (E_a) we calculated across 1025 estimates of litter breakdown rates (0.34 ± 0.04 eV) was considerably lower than the expected value based on metabolic theory (0.65 eV; Brown *et al.*, 2004; Allen *et al.*, 2005). The wide variation we detected around this value reflects the multiplicity of drivers controlling litter breakdown in addition to differences in experimental methodologies among studies. Here, we discuss how some of these extrinsic (microbial ecoenzyme expression, detritivore density, thermal adaptation by consumers) and intrinsic (litter supply regime, litter quality) controls also potentially influence the temperature sensitivity we observed at the global scale.

The overall E_a of litter breakdown was similar to the average E_a of microbial ecoenzyme activity associated with the acquisition of N and P and the degradation of

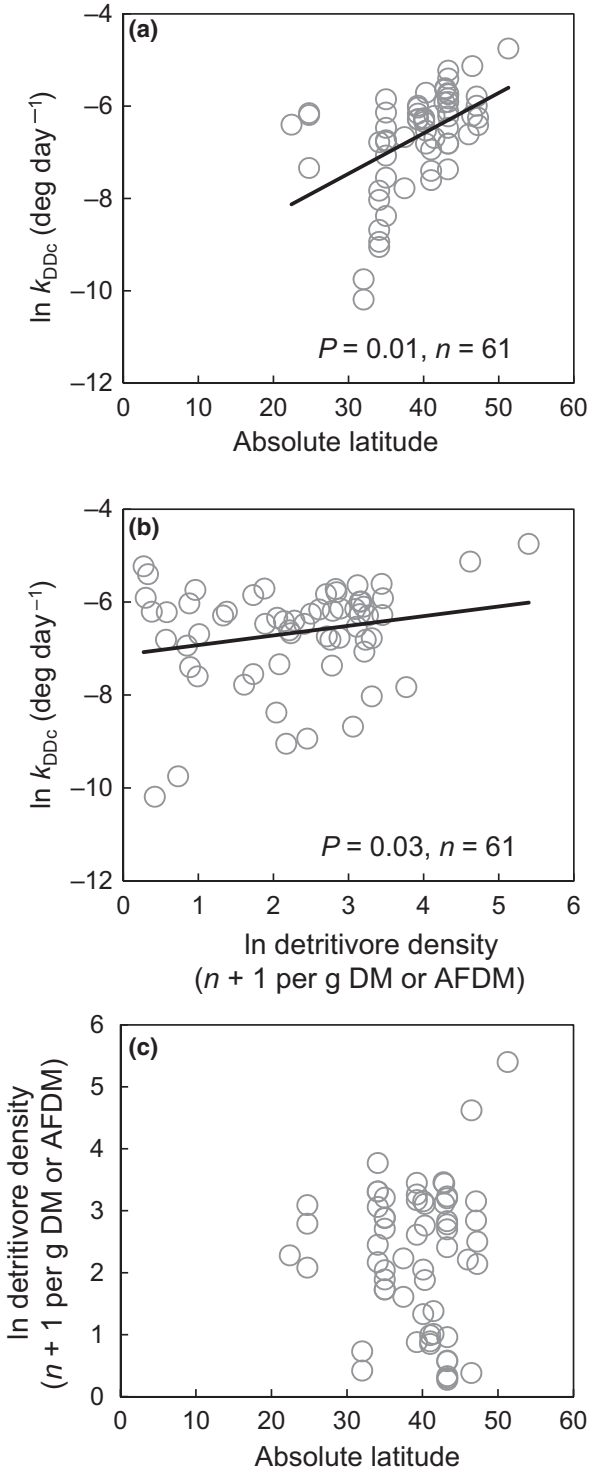

Fig. 3 Relationships between litter breakdown, absolute latitude, and detritivore density at ~T_{50} (time until litter mass is half the original mass). Litter breakdown per degree day in coarse mesh bags (k_{DDc}) was positively correlated with (a) absolute latitude and (b) detritivore density at ~T_{50} (ln k_{DDc} = −14.62 + 1.80 ln detritivore density + 0.19 absolute latitude − 0.04 ln detritivore density * absolute latitude). Detritivore density at T_{50} and absolute latitude were unrelated (c).

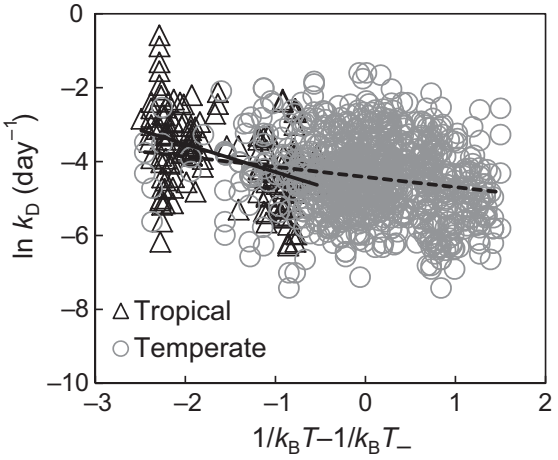

Fig. 4 Apparent activation energy (E_a) lessens with latitude. Litter breakdown (k_D, day^{-1}) within tropical latitudes (solid slope) had an E_a (ln k_D = −5.03 to $0.75/k_BT - k_BT_0$, $P < 0.001$, n = 152) greater than the E_a of temperate latitudes (dashed slope; ln k_D = −4.41 to $0.27/k_BT - k_BT_0$, $P < 0.001$, n = 873). Data from fine and coarse mesh bags were combined in this analysis because E_a was similar across mesh size (Fig. 2).

cellulose and lignin (0.31–0.49 eV; Sinsabaugh & Follstad Shah, 2012; Wang *et al*., 2012). This implies that the E_a of litter breakdown in streams and rivers may reflect rate-limiting steps associated with the enzymatic degradation of macromolecular leaf constituents more than the assimilation and mineralization of its constituents. This interpretation is consistent with the observation that aquatic hyphomycetes, the main microbial decomposers of leaf litter in streams (Gessner *et al*., 2007; Krauss *et al*., 2011), are particularly efficient at producing pectinases that degrade the middle lamella of leaf tissue, a process that results in rapid leaf fragmentation (Suberkropp & Klug, 1980; Chamier & Dixon, 1982).

The common value for the activation energy of k_{Df} and k_{Dc} we observed at the global scale indicates that the temperature sensitivity of litter breakdown is similar whether mediated by microbes alone or by microbes and detritivores. This result is contrary to our second prediction, which was based on the results of Boyero *et al*. (2011b) who found that the E_a of *Alnus* litter breakdown mediated by microbes alone was 0.46 ± 0.21 eV, while breakdown mediated by microbes plus detritivores was invariant with respect to temperature (i.e., 0 eV). The authors attributed this result to greater detritivore-mediated breakdown via higher densities in temperate biomes, thus compensating for slowed microbial activity as temperature decreases from the tropics toward higher latitudes. A similar relationship between detritivore density and latitude did not emerge in our much larger, although less

Table 1 Apparent activation energy (E_a, eV) of litter breakdown in coarse mesh bags (k_{Dc}, day^{-1}) varied among 12 plant genera. Genera are listed in order of lowest to highest E_a given by the best-fit linear mixed-effect model (LME). Breakdown rate category was determined using the framework of Petersen & Cummins (1974) and k_D values at 10 °C (i.e., intercept) given by the LME. Temperature range refers to the mean temperature values reported by studies of each genus

Genus	Temperature range (°C)	Breakdown category	k_{Dc} at 10 °C (day^{-1})	E_a (eV)	n
Alnus	0.0–26.8	Fast	0.0231	0.16	224
Quercus	1.5–27.5	Medium	0.0087	0.32	105
Acer	0.7–26.8	Fast	0.0146	0.53	68
Melicytus	5.0–19.6	Fast	0.0240	0.58	10
Cornus	3.1–26.8	Fast	0.0257	0.65	12
Liriodendron	2.0–14.7	Fast	0.0103	0.66	23
Liquidambar	9.2–27.0	Medium	0.0080	0.68	22
Phragmites	10.3–26.5	Medium	0.0079	0.77	23
Pinus	0.0–12.7	Slow	0.0049	0.78	13
Rhododendron	8.7–17.9	Slow	0.0038	0.83	21
Fagus	1.0–27.5	Medium	0.0069	0.87	14
Carya	2.5–12.4	Fast	0.0106	0.88	14

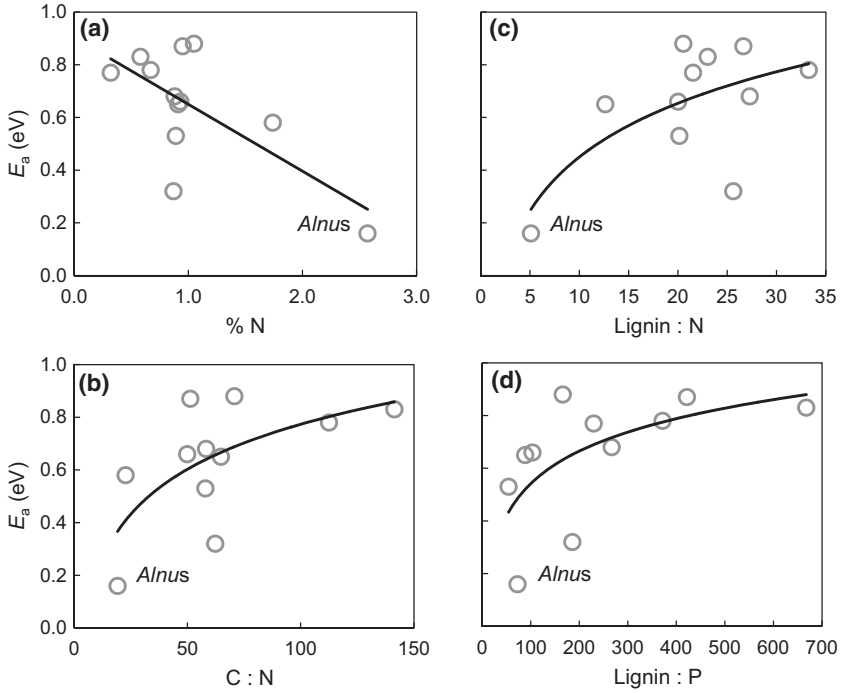

Fig. 5 Relationships between select litter traits and apparent activation energy (E_a). Models: (a) $E_a = -0.25 \times$ %N + 0.90, $r^2 = 0.46$, $P = 0.02$, $n = 12$; (b) $E_a = 0.25 \times$ C:N – 0.36, $r^2 = 0.40$, $P = 0.04$, $n = 11$; (c) $E_a = 0.29 \times$ ln (lignin:N) – 0.23, $r^2 = 0.43$, $P = 0.03$, $n = 11$; (d) $E_a = 0.18 \times$ ln (lignin:P) – 0.28, $r^2 = 0.37$, $P = 0.05$, $n = 11$. E_a is unrelated to %N ($P = 0.34$, $n = 11$; a) and ratios of C:N ($P = 0.29$, $n = 10$; b), lignin:N ($P = 0.77$, $n = 10$; (c), and lignin:P ($P = 0.12$, $n = 10$; d) when *Alnus* is omitted from the analyses. The data point for *Alnus* is identified in each figure.

standardized dataset, in accordance with the similar E_a values we observed for litter breakdown in fine and coarse mesh bags. However, it is clear that detritivores enhance breakdown, as has been found in a global synthesis of terrestrial litter breakdown studies (García-Palacios *et al.*, 2013).

In temperate biomes, evolutionary adaptation by both microbes and detritivores to pulses of allochthonous C during cool seasons allows litter breakdown to proceed more rapidly than expected based on temperature alone, as shown by positive relationships between latitude and k_{DD} and a lower value of E_a at higher vs.

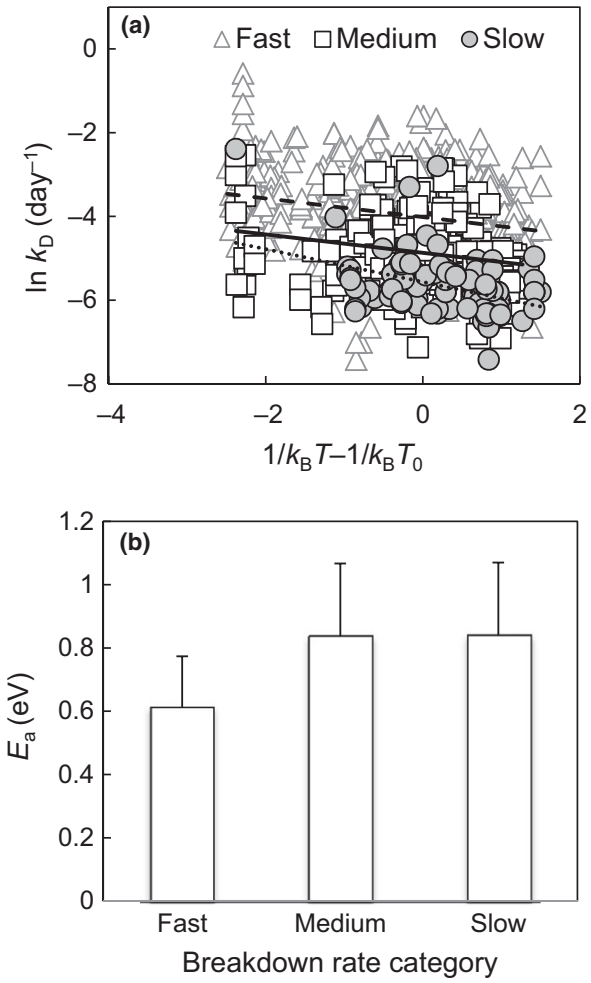

Fig. 6 Temperature sensitivity is not significantly different among breakdown rate categories comprised of (a) all 85 plant genera in the global dataset (fast: dashed slope, medium: solid slope, slow: dotted slope) and (b) the 12 genera listed in Table 1. Data from fine and coarse mesh bags were combined in the global dataset analysis (a) because E_a was similar across mesh size (Fig. 2).

lower latitudes. Detritus falls into streams draining catchments at mid- to upper latitudes mainly in the autumn and early winter when low ambient temperatures prevail and stream flows, especially during storms, can remove deposited litter from the streambed. Selection pressure on aquatic organisms that capitalize on pulsed litter inputs at low temperatures could have led to physiological adaptations (e.g., properties of enzymes, maximum growth rate; Wallenstein *et al*., 2011; Bradford, 2013), community compositions (Dang *et al*., 2009; Friberg *et al*., 2009; Handa *et al*., 2014; Strickland *et al*., 2015), and trophic interactions (Rall *et al*., 2010) that facilitate high activity at low temperature and rapid litter exploitation, with a potential trade-off consisting of reduced assimilation or growth efficiencies (López-Urrutia & Morán, 2007; Manzoni *et al*., 2010; Rall *et al*., 2010; but see Bradford, 2013; Cross *et al*., 2015). More constant litter inputs to tropical streams and rivers relative to temperate biomes may explain why the temperature sensitivity of litter breakdown in the tropics was similar to the expected value based on metabolic theory, which assumes steady-state resource supply (Brown *et al*., 2004; Yvon-Durocher *et al*., 2012). Variation in E_a between tropical and temperate latitudes due to differences in the timing and magnitude of resource inputs provides a plausible alternative explanation for the lower than predicted value of E_a at the global scale.

Values of E_a varied among plant genera, highlighting the importance of species identity. We found provisional evidence of increasing temperature sensitivity with decreasing litter quality (prediction 4). We expected litter high in structural or secondary compounds (e.g., *Rhododendron, Pinus*) to have higher E_a, based on the rationale that the enzymatic reactions required by microbes to metabolize complex, low-quality macromolecules have higher apparent activation energies than enzymatic reactions that metabolize chemically simpler leaf constituents (Bosatta & Ågren, 1999; Conant *et al*., 2008; Wagai *et al*., 2013). Accordingly, a range of 0.45–0.56 eV has been found for the degradation of lignocellulose and phenolic compounds, whereas the range for the hydrolysis of polysaccharides and the mineralization of N and P was only 0.31–0.40 eV (Sinsabaugh & Follstad Shah, 2012; Wang *et al*., 2012). A higher E_a for lower-quality litter also was expected given that detritivore consumption of structurally complex litter is promoted by microbial conditioning (Suberkropp, 1992; Wright & Covich, 2005). Terrestrial studies of leaf litter and soil organic matter breakdown often find a stronger response to elevated temperature by recalcitrant organic matter relative to labile organic matter (Fierer *et al*., 2005; Conant *et al*., 2011). In addition, higher temperature sensitivity of benthic community respiration has been observed in streams with lower-quality C substrates (Jankowski *et al*., 2014). Our results are provisional, given that greater E_a with decreasing litter quality was dependent on the inclusion of *Alnus*, a N-fixing genus, in the analyses. Absence of other N-fixing genera and low representation of tropical genera, which are typically more recalcitrant relative to temperate genera, suggest further experimentation is needed. Future experiments should include concurrent measures of breakdown and litter quality, given that litter chemistry can vary substantially from mean values within and among genera, depending on local conditions.

Although we find some evidence of an inverse relationship between litter quality and temperature

sensitivity at the scale of individual genera, differences in E_a were not apparent when genera were classified into coarsely defined breakdown rate categories. Small sample size and variation in median values of breakdown rate coefficients may have masked potential differences among the 12 genera for which we could estimate E_a, but this explanation does not apply across all 85 genera. Alternatively, the seemingly disparate results at the scales of genus and breakdown rate category may be reconciled by considering characteristics unique to streams and rivers. Continual availability of water and constant flow of dissolved nutrients across leaves in streams and rivers contribute to potentially rapid (i.e., over several days) biological degradation of recalcitrant forms of terrestrially derived organic matter (e.g., lignin) and phenolic compounds (Ward *et al*., 2013). Unlike terrestrial systems, higher temperature in perennial streams and rivers does not result in moisture becoming a limiting factor (Gessner *et al*., 2010), allowing temperature to assume greater importance in affecting litter breakdown than litter quality when temperature is elevated (Ferreira & Chauvet, 2011a). These attributes of streams and rivers remove or mitigate key constraints operating on land, thereby promoting a convergence of E_a values across coarsely defined litter types.

Projections of leaf litter breakdown response to rising temperature

Equivalence in the temperature sensitivity of litter breakdown driven by microbes alone and microbes and detritivores combined suggests that it is possible to make an initial, broad-scale forecast of breakdown rate response to altered stream temperatures. Given an overall average E_a of 0.34 eV and a standard water temperature of 10 °C, litter breakdown rates would be expected to increase by 5–21% with a 1–4 °C increase in mean water temperature (IPCC 2013), rather than a 10–45% increase if E_a was 0.65 eV in accordance with metabolic theory. Stream temperature is expected to rise less in the tropics than at mid- to upper latitudes (IPCC 2013). However, we estimate that a roughly 10% increase in litter breakdown rate requires only a 1 °C rise in the tropics but a 4 °C rise in temperate biomes, based on the E_a values and normalization constants (i.e., intercepts) we observed for tropical and temperate latitudes. Thus, differential regional warming could result in a similar proportional increase in breakdown rates despite regional variation in E_a.

Litter breakdown dominated by microbial activity converts a sizeable fraction of organic matter to CO_2, while detritivores generate large amounts of fine particulate organic C due to low assimilation efficiencies (Ward *et al*., 1994; Baldy *et al*., 2007). Similarity in the temperature sensitivity of litter breakdown mediated by microbes alone and microbes plus detritivores suggests that the fractions of gaseous C loss and particulate C transport attributed to litter breakdown will not significantly change over broad scales as temperatures rise.

Acknowledgements

We thank many authors who graciously provided requested information that was not included in published literature and three anonymous reviewers who provided suggestions that improved the clarity of the manuscript. The US Long Term Ecological Research (LTER) Network provided financial support for this project, through an award (DEB#0936498) from the National Science Foundation (NSF). JSK was supported by NSF EF#1064998. MA was supported by NSF DBI#1216512. NAG was supported by the Department of Energy's Office of Science, Biological and Environmental Research. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the US DOE under contract DE-AC05-00OR22725.

Statement of authorship

JJFS, JSK, and MA obtained funding for collaborators to participate in research workshops, JJFS, JSK, MA, WKD, MOG, NAG, SLJ, AL, CJL, DWPM, ADR, CMS, JRW, and LHZ compiled data and conducted preliminary analyses, JJFS, AL, and RLS developed the statistical approach, JJFS conducted final analyses, JJFS and JSK created tables and figures, JJFS wrote the first draft of the manuscript, and all authors contributed substantially to manuscript revisions.

References

Allen AP, Gillooly JF, Brown JH (2005) Linking the global carbon cycle to individual metabolism. *Functional Ecology*, **19**, 202–213.

Ardón M, Pringle CM, Eggert SL (2009) Does leaf chemistry differentially affect breakdown in tropical vs. temperate streams? Importance of standardized analytical techniques to measure leaf chemistry. *Journal of the North American Benthological Society*, **28**, 440–453.

Arrhenius S (1915) *Quantitative Laws in Biological Chemistry*. Bell, London, UK.

Baldy V, Gobert V, Guerold F, Chauvet E, Lambrigot D, Charcosset JY (2007) Leaf litter breakdown budgets in streams of various trophic status: effects of dissolved inorganic nutrients on microorganisms and invertebrates. *Freshwater Biology*, **52**, 1322–1335.

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ (2009) The boundless carbon cycle. *Nature Geoscience*, **2**, 598–600.

Bosatta E, Ågren GI (1999) Soil organic matter quality interpreted thermodynamically. *Soil Biology and Biochemistry*, **31**, 1889–1891.

Boulton AJ, Boon PI (1991) A review of methodology used to measure leaf litter decomposition in lotic environments – time to turn over an old leaf. *Australian Journal of Marine and Freshwater Research*, **42**, 1–43.

Boyero L, Pearson RG, Dundgeon D *et al*. (2011a) Global distribution of a key trophic guild contrasts with common latitudinal diversity patterns. *Ecology*, **92**, 1839–1848.

Boyero L, Pearson RG, Gessner MO *et al*. (2011b) A global experiment suggests climate warming will not accelerate litter decomposition in streams but might reduce carbon sequestration. *Ecology Letters*, **14**, 289–294.

Boyero L, Pearson RG, Hui C *et al*. (2016) Biotic and abiotic variables influencing plant litter breakdown in streams: a global study. *Proceedings of the Royal Society B*, **283**, 20152664.

Bradford MA (2013) Thermal adaptation of decomposer communities in warming soils. *Frontiers in Microbiology*, **4**, 1–16, Article 333.

Brown J, Gillooly J, Allen A, Savage V, West G (2004) Toward a metabolic theory of ecology. *Ecology*, **85**, 1771–1789.

Chamier AC, Dixon PA (1982) Pectinases in leaf degradation by aquatic hyphomycetes the enzymes and leaf maceration. *Journal of General Microbiology*, **128**, 2469–2484.

Conant RT, Drijber RA, Haddix ML *et al.* (2008) Sensitivity of organic matter decomposition to warming varies with its quality. *Global Change Biology*, **14**, 868–877.

Conant RT, Ryan MG, Ågren GI *et al.* (2011) Temperature and soil organic matter decomposition rates – synthesis of current knowledge and a way forward. *Global Change Biology*, **17**, 3392–3404.

Cornwell WK, Cornelissen JHC, Amatangelo K *et al.* (2008) Plant species traits are the predominant control on litter decomposition rates within biomes worldwide. *Ecology Letters*, **11**, 1065–1071.

Cross WF, Hood JM, Benstead JP, Huryn AD, Nelson D (2015) Interactions between temperature and nutrients across levels of ecological organization. *Global Change Biology*, **21**, 1025–1040.

Dang CK, Schindler M, Chauvet E, Gessner MO (2009) Temperature oscillation coupled with fungal community shifts can modulate warming effects on litter decomposition. *Ecology*, **90**, 122–131.

Demars BOL, Manson JR, Ólaffson JS *et al.* (2011) Temperature and the metabolic balance of streams. *Freshwater Biology*, **56**, 1106–1121.

Demars BOL, Gíslason GM, Ólaffson JS *et al.* (2016) Impact of warming on CO_2 emissions from streams countered by aquatic photosynthesis. *Nature Geoscience*, **9**, 758–761.

Dodds WK, Cole JJ (2007) Expanding the concept of trophic state in aquatic ecosystems: It's not just the autotrophs. *Aquatic Science*, **69**, 427–439.

Ferreira V, Chauvet E (2011a) Future increase in temperature more than decrease in litter quality can affect microbial litter decomposition in streams. *Oecologia*, **167**, 279–291.

Ferreira V, Chauvet E (2011b) Synergistic effects of water temperature and dissolved nutrients on litter decomposition and associated fungi. *Global Change Biology*, **17**, 551–564.

Fierer N, Craine JM, McLauchlan K, Schimel JP (2005) Litter quality and the temperature sensitivity of decomposition. *Ecology*, **86**, 320–326.

Friberg N, Dybkjaer JB, Ólafsson JS, Gíslason GM, Larsen SE, Lauridsen TL (2009) Relationships between structure and function in streams contrasting in temperature. *Freshwater Biology*, **54**, 2051–2068.

García-Palacios P, Maestre FT, Kattge J, Wall D (2013) Climate and litter quality differently modulate the effects of soil fauna on litter decomposition across biomes. *Ecology Letters*, **16**, 1045–1053.

García-Palacios P, McKie BG, Handa IT, Frainer A, Hättenschwiler S (2016) The importance of litter traits and decomposers for litter decomposition: a comparison of aquatic and terrestrial ecosystems within and across biomes. *Functional Ecology*, **30**, 819–829.

Gessner MO, Chauvet E (1994) Importance of stream microfungi in controlling breakdown rates of leaf-litter. *Ecology*, **75**, 1807–1817.

Gessner MO, Chauvet E, Dobson M (1999) A perspective on leaf litter breakdown in streams. *Oikos*, **85**, 377–378.

Gessner MO, Gulis V, Kuehn KA, Chauvet E, Suberkropp K (2007) Fungal decomposers of plant litter in aquatic ecosystems. In: *The Mycota, Vol. 4: Environmental and Microbial Relationships*, 2nd edn (eds Kubicek CP, Druzhinina IS). pp. 301–324. Springer, Berlin.

Gessner MO, Swan CM, Dang CK, McKie BG, Bardgett RD, Wall DH, Hättenschwiler S (2010) Diversity meets decomposition. *Trends in Ecology and Evolution*, **25**, 372–380.

Griffiths NG, Tiegs SD (2016) Organic-matter decomposition along a temperature gradient in a forested headwater stream. *Freshwater Science*, **35**, 518–533.

Handa IT, Aerts R, Berendse F *et al.* (2014) Consequences of biodiversity loss for litter decomposition across biomes. *Nature*, **509**, 218–221.

Hobbie SE (1996) Temperature and plant species control over litter decomposition in Alaskan tundra. *Ecological Monographs*, **66**, 503–522.

IPCC (2013) Climate change 2013: the physical science basis. In: *Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* (eds Stocker TF, Qin D, Plattner GK, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM). Cambridge University Press, Cambridge.

Jankowski K, Schindler DE, Lisi PJ (2014) Temperature sensitivity of community respiration rate associated with watershed geomorphic features. *Ecology*, **95**, 2707–2714.

Kaushal SS, Likens GE, Jaworski NA *et al.* (2010) Rising stream and river temperatures in the United States. *Frontiers in Ecology and the Environment*, **8**, 461–466.

Krauss GJ, Solé M, Krauss G, Schlosser D, Wesenberg D, Bärlocher F (2011) Fungi in freshwaters: ecology, physiology and biochemical potential. *FEMS Microbiology Review*, **35**, 620–651.

López-Urrutia A, Morán XAG (2007) Resource limitation of bacterial production distorts the temperature dependence of oceanic carbon cycling. *Ecology*, **88**, 817–822.

Makkonen M, Berg MP, Handa IT *et al.* (2012) Highly consistent effects of plant litter identity and functional traits on decomposition across a latitudinal gradient. *Ecology Letters*, **15**, 1033–1041.

Manzoni S, Trofymow JA, Jackson RB, Porporato A (2010) Stoichiometric controls on carbon, nitrogen, and phosphorus dynamics in decomposing litter. *Ecological Monographs*, **80**, 89–106.

Martínez A, Larrañaga A, Pérez J, Basaguren A, Pozo J (2013) Leaf-litter quality effects on stream ecosystem functioning: a comparison among five species. *Fundamental and Applied Limnology*, **183**, 239–248.

Petersen RC, Cummins KW (1974) Leaf processing in a woodland stream. *Freshwater Biology*, **4**, 343–368.

Pinheiro J, Bates D, DebRoy S, Sarkar D, R Core Team (2014) nlme: Linear and Nonlinear Mixed Effects Models. R package version 3.1–117. Available at: http://cran.r-project.org/web/packages/nlme/index.html (accessed 10 January 2014).

R Core Team (2013) *R: A language and environment for statistical computing*. R Foundation for Statistical Computing, Vienna, Austria. Available at: http://www.R-project.org/ (accessed 11 November 2017).

Rall BC, Vucic-Pestic O, Ehnes RB, Emmerson M, Brose U (2010) Temperature, predator-prey interaction strength and population stability. *Global Change Biology*, **16**, 2145–2157.

Raymond PA, Hartmann J, Lauerwald R *et al.* (2013) Global carbon dioxide emissions from inland waters. *Nature*, **503**, 355–359.

Schindler MH, Gessner MO (2009) Functional leaf traits and biodiversity effects on litter decomposition in a stream. *Ecology*, **90**, 1641–1649.

Sinsabaugh RL, Follstad Shah JJ (2012) Ecoenzymatic stoichiometry and ecological theory. *Annual Review of Ecology Evolution and Systematics*, **43**, 313–343.

Sinsabaugh RL, Hill BH, Follstad Shah JJ (2009) Ecoenzymatic stoichiometry of microbial organic nutrient acquisition in soil and sediment. *Nature*, **462**, 795–798.

Strickland MS, Keiser AD, Bradford MA (2015) Climate history shapes contemporary leaf litter decomposition. *Biogeochemistry*, **122**, 165–174.

Suberkropp K (1992) Interactions with invertebrates. In: *Ecological Studies, Vol. 4: The Ecology of Aquatic Hyphomycetes* (ed. Bärlocher F), pp. 118–134. Springer, Berlin.

Suberkropp K, Klug MJ (1980) The maceration of deciduous leaf litter by aquatic hyphomycetes. *Canadian Journal of Botany*, **58**, 1025–1031.

Tank JL, Rosi-Marshall EJ, Griffiths NA, Entrekin SA, Stephen ML (2010) A review of allochthonous organic matter dynamics and metabolism in streams. *Journal of the North American Benthological Society*, **29**, 118–146.

Wagai R, Kishimoto-Mo AW, Yonemura S, Shirato Y, Hiradate S, Yagasaki Y (2013) Linking temperature sensitivity of soil organic matter decomposition to its molecular structure, accessibility, and microbial physiology. *Global Change Biology*, **19**, 1114–1125.

Wallace JB, Eggert SL, Meyer JL, Webster JR (1997) Multiple trophic levels of a forest stream linked to terrestrial litter inputs. *Science*, **277**, 102–104.

Wallenstein MD, Allison SD, Ernakovich J, Steinweg JM, Sinsabaugh RL (2011) Controls on the temperature sensitivity of soil enzymes: a key driver of in-situ enzyme activity rates. In: *Soil Enzymology* (eds Shukla G, Varma A), pp. 245–258. Springer Verlag, Berlin.

Wang GS, Post WM, Mayes MA, Frerichs JT, Sindhu J (2012) Parameter estimation for models of ligninolytic and cellulolytic enzyme kinetics. *Soil Biology and Biochemistry*, **48**, 28–38.

Ward JV, Stanford JA (1982) Thermal responses in the evolutionary ecology of aquatic insects. *Annual Review of Entomology*, **27**, 97–117.

Ward GM, Ward AK, Dahm CN, Aumen NG (1994) Origin and formation of organic and inorganic particles in aquatic systems. In: *The Biology of Particles in Aquatic Systems* (ed Wotton RS), pp. 45–73. Lewis Publishers, Ann Arbor, MI.

Ward ND, Keil RG, Medeiros PM *et al.* (2013) Degradation of terrestrially derived macromolecules in the Amazon River. *Nature Geoscience*, **6**, 530–533.

Webster JR, Benfield EF (1986) Vascular plant breakdown in freshwater ecosystems. *Annual Review of Ecology Evolution and Systematics*, **17**, 567–594.

Welter JR, Benstead JP, Cross WF, Hood JM, Huryn AD, Johnson PW, Williamson TJ (2015) Does N_2-fixation amplify the temperature dependence of ecosystem metabolism? *Ecology*, **96**, 603–610.

Woodward G, Gessner MO, Giller PS *et al.* (2012) Continental-scale effects of nutrient pollution on stream ecosystem functioning. *Science*, **336**, 1438–1440.

Wright MS, Covich AP (2005) Relative importance of bacteria and fungi in a tropical headwater stream: leaf decomposition and invertebrate feeding preference. *Microbial Ecology*, **49**, 536–546.

Young RG, Matthaei CD, Townsend CR (2008) Organic matter breakdown and ecosystem metabolism: functional indicators for assessing river ecosystem health. *Journal of the North American Benthological Society*, **27**, 605–625.

Yvon-Durocher G, Jones JI, Trimmer M, Woodward G, Montoya JM (2010) Warming alters the metabolic balance of ecosystems. *Philosophical Transactions of the Royal Society B*, **365**, 2117–2126.

Yvon-Durocher G, Caffrey JM, Cescatti A *et al.* (2012) Reconciling the temperature dependence of respiration across timescales and ecosystem types. *Nature*, **487**, 472–476.

Zuur A, Ieno EN, Walker N, Saveliev AA, Smith GM (2009) Mixed effects modeling for nested data. *Mixed Effects Models and Extensions in Ecology with R*, pp. 101–142. Springer, Berlin.

Supporting Information

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

Appendix S1. Data and data sources.
Appendix S2. Database characteristics and supporting data analyses.
Table S1. Results of linear mixed effect modeling predicting global breakdown rate coefficients, ln k_D (per day, d^{-1}), by method code.
Table S2. Results of linear mixed effect modeling predicting global temperature-adjusted breakdown rate coefficients, ln k_{DD} (per degree day, dd^{-1}), by method code.
Table S3. Results of generalized least squares modeling predicting breakdown rate coefficients per degree day in coarse mesh bags (ln $k_{DDc,}$ dd^{-1}), using subsets of data with information on detritivore and total macroinvertebrate densities at T_{50} (#/g DM or AFDM).
Table S4. Results of linear mixed effect modeling predicting breakdown rate coefficients among and within mesh sizes (fine or coarse), ln k_D, k_{Df}, or k_{Dc} (all per day, d^{-1}), by biome (tropical vs. temperate).
Table S5. Results of linear mixed effect modeling predicting breakdown rate coefficients in coarse mesh bags, ln k_{Dc} (per day, d^{-1}), by plant genus (n = 12 genera).
Table S6. Apparent activation energy (E_a, eV) of leaf litter breakdown and mean leaf chemistry for twelve riparian plant genera.
Table S7. Results of linear mixed effect modeling predicting breakdown rate coefficients, ln k_D (per day, d^{-1}), by breakdown rate category (85 plant genera).
Figure S1. Apparent activation energy (E_a, eV; 1 eV = 1.6×10^{-19} joule or 96 kJ mol^{-1}) of genus-specific leaf litter breakdown is related to neither initial leaf litter content (%) of C, P, lignin, and cellulose nor ratios of C:P and N:P.