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Shifting stoichiometry: Long-term trends in stream-dissolved organic matter reveal altered C:N ratios due to history of atmospheric acid deposition

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Abstract

Dissolved organic carbon (DOC) and nitrogen (DON) are important energy and nutrient sources for aquatic ecosystems. In many northern temperate, freshwater systems DOC has increased in the past 50 years. Less is known about how changes in DOC may vary across latitudes, and whether changes in DON track those of DOC. Here, we present long-term DOC and DON data from 74 streams distributed across seven sites in biomes ranging from the tropics to northern boreal forests with varying histories of atmospheric acid deposition. For each stream, we examined the temporal trends of DOC and DON concentrations and DOC:DON molar ratios. While some sites displayed consistent positive or

negative trends in stream DOC and DON concentrations, changes in direction or magnitude were inconsistent at regional or local scales. DON trends did not always track those of DOC, though DOC:DON ratios increased over time for ~30% of streams. Our results indicate that the dissolved organic matter (DOM) pool is experiencing fundamental changes due to the recovery from atmospheric acid deposition. Changes in DOC:DON stoichiometry point to a shifting energy-nutrient balance in many aquatic ecosystems. Sustained changes in the character of DOM can have major implications for stream metabolism, biogeochemical processes, food webs, and drinking water quality (including disinfection by-products). Understanding regional and global variation in DOC and DON concentrations is important for developing realistic models and watershed management protocols to effectively target mitigation efforts aimed at bringing DOM flux and nutrient enrichment under control.

KEYWORDS
atmospheric acid deposition, C:N stoichiometry, dissolved organic carbon, dissolved organic matter, dissolved organic nitrogen, long-term trends, streams

1 | INTRODUCTION

Dissolved organic matter (DOM) provides an essential energy and nutrient source to aquatic ecosystems (Webster & Meyer, 1997). DOM varies in availability to biota along the hydrologic continuum (McArthur et al., 1985) and its composition and properties are closely linked to the surrounding landscape (Jaffé et al., 2008; Mattsson et al., 2005; Wymore et al., 2021c; Yates et al., 2019). The DOM pool is a complex mixture of organic compounds mostly composed of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) to a minor extent (Pagano et al., 2014). Numerous studies have confirmed that increases in DOC concentrations in north temperate freshwater ecosystems have occurred over time. For example, DOC concentrations have increased between 50% and 91% in streams and lakes of northern and central Europe, the United Kingdom, and eastern North America since the 1980s (Couture et al., 2012; de Wit et al., 2016; Driscoll et al., 2003; Evans et al., 2005; Gavin et al., 2018; Hall et al., 2021; Lawrence et al., 2011; Monteith et al., 2007; Worrall et al., 2004). Increased DOC concentration is often attributed to the recovery from acid deposition after the implementation of the Clean Air Act in the United States and similar legislation in Europe (Driscoll et al., 2003). The leading hypothesized mechanism is that a decrease in ionic strength and protonation in soil water following recovery from acid deposition leads to increases in solubility and the mobilization of DOC to adjacent water bodies (Borken et al., 2011; De Wit et al., 2007; Evans et al., 2005; Hruška et al., 2009; Lawrence & Roy, 2021).

A suite of different hypotheses has been put forward to explain the increasing trends in DOC concentrations, in addition to declines in atmospheric deposition, each associated with global change. Mechanisms include increasing precipitation and runoff (De Wit et al., 2007; Stråät et al., 2018; Worrall et al., 2004), rising CO_2 and increased primary productivity (Freeman et al., 2004), enhanced microbial organic matter decomposition due to increased temperatures (De Wit et al., 2007; Finlay et al., 2006; Worrall et al., 2004), and permafrost thaw in northern high-latitude ecosystems (Frey & McClelland, 2009; Frey et al., 2007; Frey & Smith, 2005; Larouche et al., 2015).

DOC concentrations are not increasing everywhere, however. Declines in DOC concentration over time have been associated with decreasing soil organic matter solubility (Clair et al., 2008), declines in carbon inputs from upstream acidified lakes (Schindler et al., 1997), increases in soil aluminum pools (Löfgren et al., 2010), and greater adsorption of DOM to the mineral layer and infiltration of DOM deeper into permafrost soils (Kendrick et al., 2018; Striegl et al., 2005). Long-term stability in stream DOC concentrations has also been observed (Chow et al., 2017; Clair et al., 2008; Monteith et al., 2007; Worrall et al., 2004), even in some of the longest existing records of stream chemistry (e.g., since 1975; Räike et al., 2012). Trends in total organic carbon concentrations have even varied in direction within a continuous 35-year record (Erlandsson et al., 2008; Lepistö et al., 2008). Despite the evidence that a wide range of changes in DOC concentration can be expected, a broad multi-biome assessment of global DOC trends is lacking. A spatially distributed analysis would allow for the examination of trends along multiple environmental gradients and for the testing of coherent cross biome patterns (e.g., Dodds et al., 2019).

Concentrations of dissolved organic nitrogen (DON) are rarely measured in long-term studies of DOM. Changes in DON concentration can have critical implications for freshwater ecosystems, especially when DON serves as a primary source of N for biota (Kissman et al., 2017; Mackay et al., 2020). While analytical challenges exist in the assessment of DON, researchers often assume that the concentrations of DON track those of DOC (i.e., concentrations are

positively correlated; Campbell et al., 2000; Goodale et al., 2000; Kortelainen et al., 2006; Lepistö et al., 2008; Mann et al., 2012). Other lines of evidence, however, suggest that concentrations of DOC and DON can respond differently to environmental change such as changes in the concentrations of inorganic nutrients (Lutz et al., 2012; Wymore et al., 2015, 2021c; Yates et al., 2019) and seasonal variability in precipitation and stream runoff (Bernal et al., 2005). Recent evidence has pointed to the stream DOC:DON ratio varying according to the extent of nutrient enrichment in catchments, diverging from the soil DOC:DON ratio as systems become more nutrient-enriched through land-use change and increasing human population density (Yates et al., 2019). Such divergent trends in DOC and DON concentrations will lead to changes in DOM stoichiometry (i.e., DOC:DON ratios). DOC:DON ratios provide a relatively simple quantification of bulk DOM characteristics, which serves as an indicator of bioavailability (del Giorgio & Cole, 1998) and of changing OM sources within catchments (Yates et al., 2019). A broad assessment of how DOM stoichiometry changes concurrently with changes in concentrations of DOC and DON could provide insights into how the energy and nutrient balance of one of the larger pools of organic matter in freshwater ecosystems is changing with potential impacts on other biogeochemical reactions (e.g., Strauss & Lamberti, 2002; Wymore et al., 2019).

The objective of this study was to explore long-term trends in DOC and DON concentrations, and DOM stoichiometry in streams and rivers across biomes of the Northern Hemisphere. Our overarching hypothesis is that changes in concentrations of DON will track those of DOC and consequently the stoichiometry of DOM will remain consistent through time (Brookshire et al., 2007; Wymore et al., 2021c). We also hypothesize that sites historically affected by acid deposition will be associated with increases in concentrations of DOC and DON assuming the same external forces are acting on each of these components of the DOM pool (Deininger et al., 2020). A global assessment of how riverine DOM is responding to global change is essential for robust regional and global scale predictive ecosystem models and for future watershed management protocols.

2 | MATERIALS AND METHODS

2.1 | Data set compilation

We compiled long-term data on DOC and DON concentrations for 74 individual streams from 7 different sites (Table 1; Figure S1) in the Northern Hemisphere spanning 42 degrees of latitude (Tables S1 and S2). For each stream, DOC and DON data were collected at either weekly or monthly intervals, except for streams in a tallgrass prairie ecosystem (Konza Prairie: KNZ), for which we have limited DON data. For consistency across sites, we set minimum detection limits (MDL) for each solute: DOC (0.1 mg C/L), TDN (0.05 mg N/L), DON (0.01 mg N/L), NO_3^- (0.005 mg NO_3-N/L), and NH_4^+ (0.004 mg NH_4-N/L). In addition, we only used DON values that were 5% or more of the TDN pool, to account for analytical uncertainty (Lloyd

et al., 2016). For data points that were below the MDL, values were replaced with half the MDL. To estimate DOC and TDN from the Finnish data set, we multiplied TOC and TN by 0.95 (Kortelainen et al., 2006; Mattsson et al., 2005). These calculated TDN values for the Finnish data were then used to determine DON for these sites as: DON = TDN − (NO_3^- + NH_4^+). Molar DOC:DON ratios were determined from the final DOC and DON concentrations and were used to describe change over time in the DOM pool. For more details on analytical methods see Table S4. Concentrations used in this study were not flow-weighted as discharge data were not available for the same time frame as the chemistry time series nor available for all streams. Past work found that long-term data collection can account for the variety of discharge values that occur at a site, and in at least one of our sites DOC concentrations were not correlated with discharge (Coble et al., 2018; Rüegg et al., 2015).

2.2 | Time series and trend analyses

We examined time series from mean monthly DOC, DON, and DOC:DON values for each stream using the longest record possible from each site (Table S3) with the exception of the Arctic site, Caribou-Poker Creeks Research Watersheds (CPC) where data are only available from May to August which coincides with the freshet and summer base flow periods. Time series were used to calculate trends using Sen slope (Hirsch et al., 1982) obtained from the *trend* package (Pohlert, 2018) in R (R Core Team, 2016) for DOC, DON, and DOC:DON ratios in each stream. Sen slope is a robust nonparametric method of regression, with the slope similar to the regression slope but less sensitive to outliers and reports a median change on the given parameter over time. Sen slopes with *p*-value less than .05 were considered statistically significant indicators of either increasing or decreasing trends, while slopes with *p*-values greater than .05 were considered insignificant and replaced with zeros for further analysis. The length of the data records across the 74 streams ranged from 8 to 45 years, where the longest starts in 1975 and all end between 2010 and 2015. Changes in analytical methods have been previously evaluated to ensure consistency over time (LUQ: McDowell et al., 2021; LMP: Coble et al., 2018; Wymore et al., 2021a; AND: Johnson et al., 2021; HBF: Campbell et al., 2021). Although we recognize that length of the record can be an important factor in trends over time (Argerich et al., 2013), we found no clear relationships between length of the record and trends in DOC, DON, and DOC:DON across our sites (Figure S2).

We used mutual information (MI) to determine the degree to which DOC and DON covary in each stream over time with the *muti* package (Scheuerell, 2017) in R (R Core Team, 2016). Mutual information is a non-parametric method that characterizes the mutual dependence of two time series (Ardón et al., 2017; Cazelles, 2004). Here, we interpret that MI values closer to 1 indicate strong synchrony between DOC and DON where MI values closer to 0 indicate little dependency between the temporal dynamics of DOC and DON. Given that MI values do not provide information on the direction of the relationship, we

TABLE 1 Sites from which DOC, DON, and DOC:DON time series were obtained with the number of individual streams used from each site

Site	Site abbreviation	Biome	Acid deposition history	Individual streams
Finland	FIN	Boreal forest	Yes	32
Caribou Poker Creek, AK	CPC[a]	Boreal forest	No	9
Hubbard Brook Experimental Forest, NH	HBF[a]	Temperate deciduous forest	Yes	5
Lamprey River Basin, NH	LMP	Temperate deciduous forest	Yes	9
H.J. Andrews Experimental Forest, OR	AND[a]	Coniferous temperate forest	No	9
Konza Prairie, KS	KNZ[a]	Tallgrass Prairie	Yes	2
Luquillo Experimental Forest, PR	LUQ[a]	Tropical rainforest	No	8

Note: DOC, DON, and DOC:DON molar ratios median concentrations with minimum and maximum values, biome, geology, and soil type for each site.
'–' represents no data available.
[a]Sites that are part of the long-term ecological research network.

paired MI values with eight categorical descriptions of the DOC and DON directional trends based on their respective Sen slopes. These categorical descriptions were: increasing DOC and DON, declining DOC and DON, increasing DOC with no trend in DON, increasing DOC with declining DON, no trend in DOC and increasing DON, no trends in DOC and decline in DON, a decline in DOC and no trend in DON and no trend in DOC and DON.

We obtained data from the National Atmospheric Deposition Program (NADP; NRSP-3) to test the effect of atmospheric deposition on DOM trends for sites that have nearby NADP sampling locations (CPC, HBF, AND, KNZ, and LUQ). We used time series of NO_3^- and SO_4^{2-} fluxes to identify sites historically affected by atmospheric deposition (Figure S3). Sites showing a decline in atmospheric NO_3^- and SO_4^{2-} fluxes over time were classified as affected by atmospheric deposition and those that showed constant atmospheric NO_3^- and SO_4^{2-} fluxes were classified as sites that were not affected by acid deposition (Figure S3). We corroborated this approach with the expert knowledge of authors for their respective research sites. We used NADP data from HBF for LMP as these sites are in the same region. The sites across Finland were classified by their history in atmospheric acid deposition based on longitudinal patterns where southern Finland receives the greatest deposition (Ruoho-Airola et al., 2014, 2015; Vuorenmaa, 2004).

We determined potential predictor variables of DOC, DON, and DOC:DON trends via an elastic net analysis, which is a form of penalized regression that shrinks variables that do not influence the model (Zou & Hastie, 2005). Elastic net produces a parsimonious model with the most influential variables and is minimally influenced by collinearity among predictor variables (Finlay et al., 2015). Lambda and alpha values were determined by cross-validation and choosing the lowest mean squared error (Finlay et al., 2015). Lambda controls the shrinkage of variables while alpha selects the type of penalty where alpha values between 0 and 1 denote elastic net regression (Friedman et al., 2010). DOC, DON, and DOC:DON trends that were significant ($p < .05$) were included as the response

variables into three different models focused on either ambient stream chemistry, watershed characteristics, or acid deposition history to determine if trends in DOM were related to in-stream chemistry, the surrounding landscape or location, or atmospheric deposition history. The predictor variables for the ambient stream chemistry model were mean concentrations of DOC, DON, DOC:DON, NO_3^-, NH_4^+, Na^+, and Ca^{+2} for each stream. Predictor variables for the watershed characteristics model were mean annual temperature (MAT, °C), mean annual precipitations (MAP, mm), mean watershed elevation (m), and watershed area (km²). The predictor variables for the atmospheric deposition model were mean and peak NO_3^- and SO_4^{2-} atmospheric deposition. We also tested categorical variables such as soil type (i.e., clay, silt, loam, till, and moraine), watershed geology (i.e., granitic, andesite, and volcaniclastic), and forest type (i.e., evergreen, conifer, deciduous, and mixed forest) with a Kruskal–Wallis rank sum test due to uneven sample size between groups with the *Stats* package (R-Core-Team, 2016). These categorical variables were not included in the models because they are poorly balanced and lead to the overfitting of models. Watershed characteristics were obtained from the site description on each LTER's website and from Räike et al. (2012), Kortelainen et al. (2006), and Vuorenmaa (2004) for Finnish (FIN) sites. Atmospheric deposition values were obtained from the NAPD monitor site at the LTER sites, and models were fit using the *glmnet* package (Friedman et al., 2010) in R (R Core Team, 2016).

Differences in DOC, DON, and DOC:DON trends between acid deposition-affected and unaffected sites were explored with a Kruskal–Wallis rank sum test due to uneven sample size between groups. We also conducted a one-sample *t*-test to determine if the means of DOM trends, in sites affected and not affected from acid deposition, were different from 0. This test is especially important for DOC:DON ratios to indicate whether changes in DOC and DON are proportional. The one-sample *t*-test was performed using the *Stats* package. All statistical analyses were conducted in R (R Core Team, 2016) using RStudio (version 1.2.1335, RStudio, Inc. Team, 2016).

| DOC (mg/L)	DON (mg/L)	DOC:DON Molar ratios	Geology	Soil type
11.40 (1.9–78.85)	0.44 (0.02–12.40)	34.74 (20.89–74.47)	Granite	Ground moraine or silty clay
3.63 (0.27–29.44)	0.26 (0.02–1.91)	17.95 (10.98–19.78)	Quartz mica	Silt
2.29 (0.18–24.49)	0.08 (0.01–0.42)	32.59 (31.37–63.53)	Granite	Sandy loam
4.80 (0.04–18.43)	0.19 (0.02–0.89)	30.79 (21.51–36.44)	Granite	Glacial till
0.99 (0.19–4.27)	0.03 (0.01–0.15)	34.61 (26.60–66.50)	Andesite and volcaniclastic	Sandy loam
0.88 (0.10–11.98)	–	–	Limestone	Silty clay
1.05 (0.05–15.16)	0.05 (0.01–1.12)	23.67 (16.90–28.33)	Quartz diorite and volcaniclastic	Silty clay
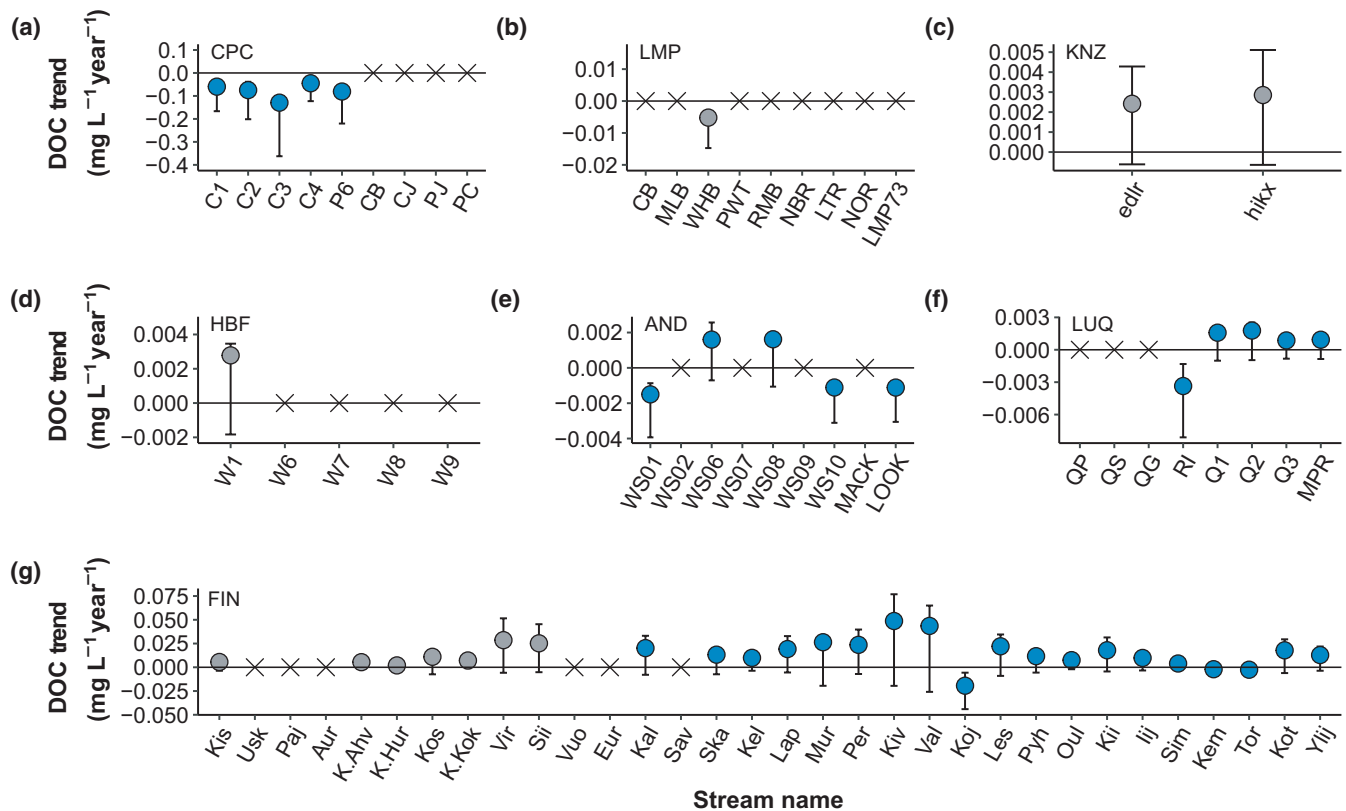
FIGURE 1 Sen slopes for DOC for each individual stream in (a) Caribou-Poker Creeks Research Watershed (CPC), (b) Lamprey River Basin (LMP), (c) Konza Prairie (KNZ), (d) Hubbard Brook Experimental Forest (HBF), (e) H.J. Andrews Experimental Forest (AND), (f) Luquillo Experimental Forest (LUQ), and (g) Finland (FIN). Circles denote streams DOC trends ($p < .05$) along with their respective 95% confidence intervals and the X are streams with no DOC trends ($p > .05$). Blue are sites not affected by acid deposition and grey are sites historically affected by acid deposition. Caribou-Poker Creeks, Lamprey, Hubbard Brook, and Andrews streams are ordered by watershed size from smallest to largest Luquillo streams are ordered by size within their respective major watersheds; Finland streams are ordered by latitude from South to North

3 | RESULTS

3.1 | DOC, DON, and DOC:DON trends

Long-term trends in concentrations of DOC (Figure 1) and DON (Figure 2) showed no consistent patterns across study sites. DOC trends ranged between −0.13 and 0.05 mg C/L per year

(median = 0.003 mg C/L per year) while DON trends ranged from −0.006 to 0.0009 mg N/L per year (median = −0.0002 mg C/L per year). Trends for DOC:DON ratios ranged between −0.05 and 0.96 per year (median = 0.02 per year).

The majority of the streams had no significant temporal trend for either DON (36 of 70; 51%) or DOC:DON ratio (42 of 70; 60%; Figure 4). For DOC, a large portion of streams showed
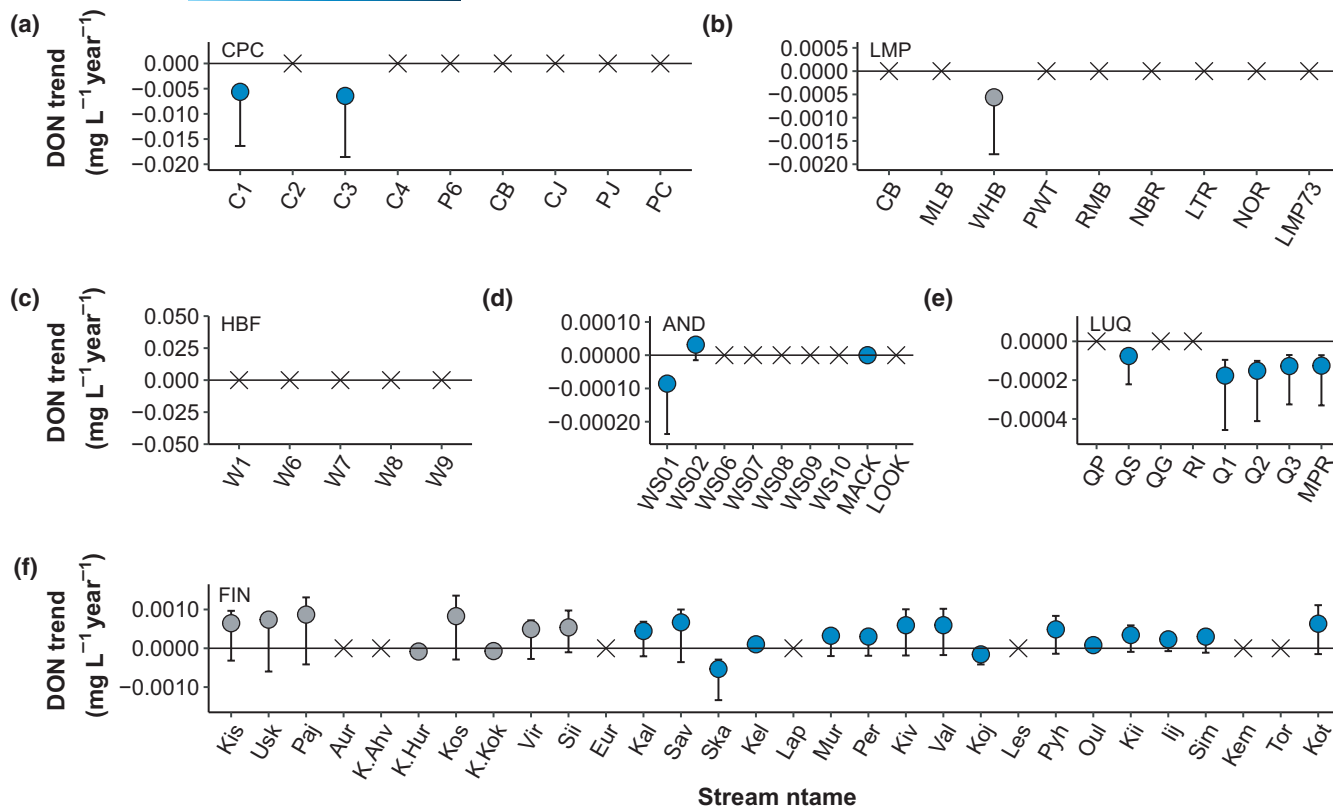
FIGURE 2 Sen slopes for DON for each individual stream in (a) Caribou-Poker Creeks (CPC), (b) Lamprey River Basin (LMP), (c) Hubbard Brook Forest (HBF), (d) H.J. Andrews Forest (AND), (e) Luquillo Experimental Forest (LUQ), and (f) Finland (FIN). Circles denote streams with DON trends ($p < .05$) with their respective 95% confidence intervals and X denote streams with no trends ($p > .05$). Note Konza and 2 Finnish streams (YLIJOKI 1 and Vuoksi Vastuupuomi 061) were excluded due to no DON data available for these streams. Blue represents sites not affected by acid deposition and grey are sites historically affected by acid deposition. Caribou-Poker Creeks, Lamprey, Hubbard Brook, and Andrews streams are ordered by watershed size; Luquillo streams are ordered by size within their respective major watersheds; Finland streams are ordered by latitude from South to North

increasing trends (32 of 74; 43%), followed by 29 streams (37%) with no trends, and 13 streams (18%) with decreasing trends (Figure 4a). For DON, 21 (30%) and 13 (19%) of the streams had significant increasing and decreasing trends, respectively (Figure 4b). For DOC:DON ratios, 20 (29%) and 8 (11%) of the streams had significant increasing or decreasing trends, respectively (Figure 4c).

The directionality of significant DOC trends was not consistent within the sites. At CPC, streams showed consistent decreasing DOC (Figure 1a) while KNZ and most of the FIN streams (44%) showed increases in DOC over time (Figure 1c,g). Other sites (LMP, AND, and LUQ; Figure 1b,e,f) exhibited variability in the direction of their significant DOC trends. Significant trends for DON were mostly declining across and within sites (Figure 2), except for FIN that had streams with both significantly increasing and declining DON trends (Figure 2f). DON trends were not significant at HBF (Figure 2c). Significant trends for DOC:DON ratios were generally positive (Figure 3) except for streams in LMP (Figure 3b) and FIN (Figure 3f), which showed declining stream DOC:DON ratios over time. There were no significant trends in DOC:DON ratios at CPC (Figure 3a).

3.2 | Synchronicity between DOC and DON

Contrary to our hypothesis, trends in DON concentrations did not consistently track those of DOC. In only five of 68 streams (7%) did DON and DOC track each other, with MI values greater than 0.5. Of these five streams, in only three did DOC and DON covary in the same direction, both increasing or both declining in BNZ and FIN (Figure 5a,f). There were also various streams (18 out of 68) across sites where DOC and DON changed in a similar direction (either increased or decreased), but concentrations did not strongly covary according to MI values (i.e., MI < 0.5; Figure 5a,b,e,f). For 23 streams (33%), DOC and DON trends were asynchronous (i.e., DOC and DON changed in the opposite direction and MI < 0.5).

3.3 | Acid deposition history

We did not find strong evidence to confirm our second hypothesis that DOC and DON would both increase in sites historically affected by atmospheric deposition. There was no difference in long-term trends in DOC concentration ($p = .38$; Figure 6a) between sites
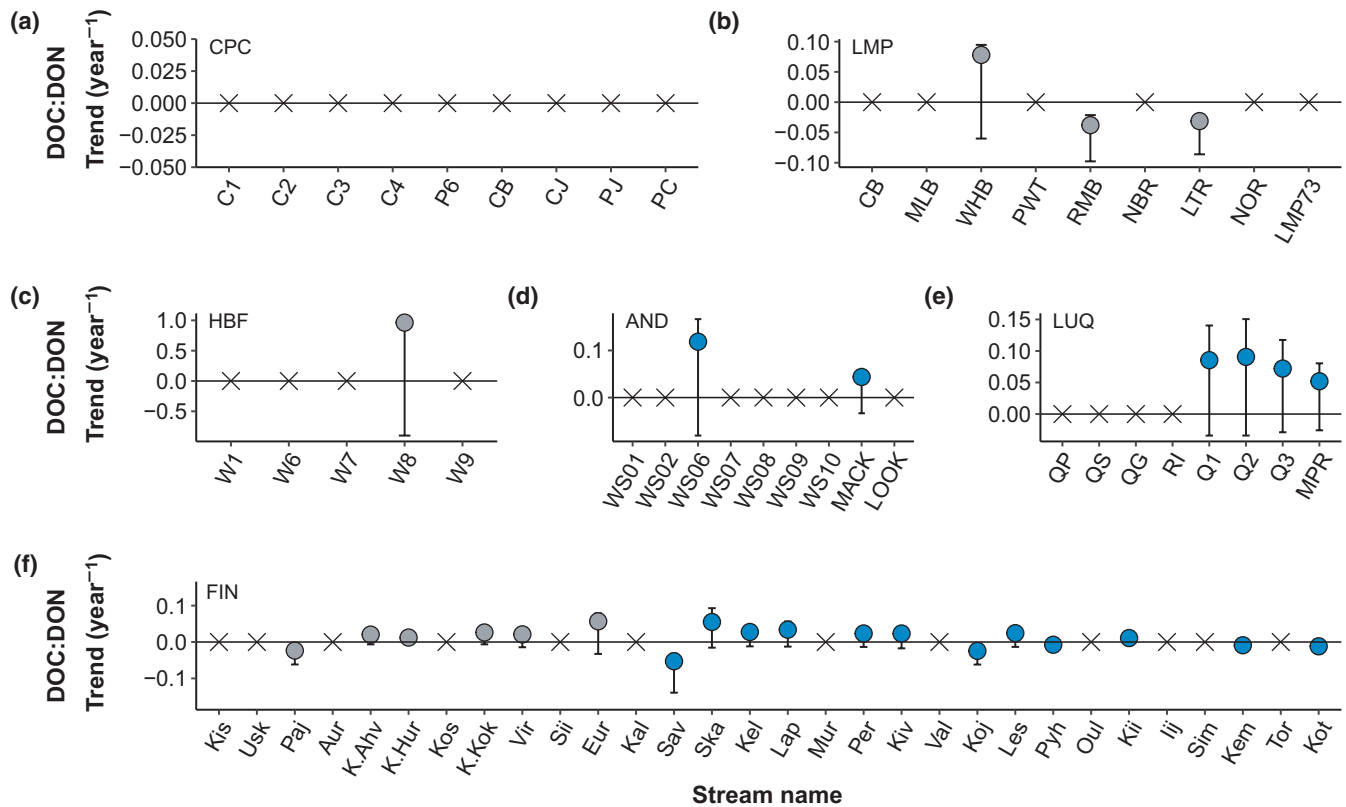
FIGURE 3 Sen slopes for DOC:DON molar ratios for each individual stream in (a) Caribou-Poker Creeks (CPC), (b) Lamprey River Basin (LMP), (c) Hubbard Brook Forest (HBF), (d) H.J. Andrews Forest (AND), (e) Luquillo Experimental Forest LUQ), and (f) Finland (FIN). Circles denote streams with DOC:DON trends ($p < .05$) with their respective 95% confidence intervals and X denote streams with no trends ($p > .05$). Note Konza and 2 Finnish streams (YLIJOKI 1 and Vuoksi Vastuupuomi 061) were excluded due to no DON data available for these streams. Blue represents sites not affected by acid deposition and grey are sites historically affected by acid deposition. Caribou-Poker Creeks, Lamprey, Hubbard Brook, and Andrews streams are ordered by watershed size; Luquillo streams are ordered by size within their respective major watersheds; Finland streams are ordered by latitude from South to North

historically affected by acid deposition (HBF, LMP, KNZ, and Southern FIN) and those not affected by acid deposition (CPC, AND, LUQ, and Northern FIN). The DOC Sen slope values for sites that were affected by acid deposition were different from zero (t-test $p = .008$), whereas those unaffected by acid deposition were not different from zero (t-test $p = .63$). Trends in DON differed with acid deposition history ($p = .05$, Figure 6b), with trends in acid deposition affected sites being greater than trends in sites not affected by acid deposition. The DON Sen slopes were different from zero for sites affected by atmospheric deposition (t-test $p = .05$), but not for unaffected sites (t-test $p = .35$). Trends in DOC:DON ratios did not differ in their response to acid deposition history ($p = .56$). DOC:DON Sens slopes for sites affected by acid deposition were not different from 0 (t-test $p = .33$), whereas DOC:DON Sens slopes were significantly different from zero in sites unaffected by acid deposition (t-test $p = .008$, Figure 6c).

3.4 | Predictor variables of DOM trends

The elastic net models for chemistry and watershed characteristics identified several predictor variables for DOC, DON, and DOC:DON

trends. For DOC trends, the ambient stream chemistry model accounted for a large percentage of variability, followed by acid deposition, and watershed characteristics: $r^2 = .66$, $r^2 = .34$, and $r^2 = .32$, respectively (Table 2). Variables selected for DOC trends were Ca^{2+} ($\beta = -.005$), Na^+ ($\beta = .002$), and DOC ($\beta = .002$) in the stream chemistry model; MAT ($\beta = .0006$) and elevation ($\beta = -.0001$) for watershed characteristics; mean ($\beta = -.004$) and peak ($\beta = .002$) SO_4^{2-} and peak NO_3^- ($\beta = -.0007$) deposition. DOC trends did not vary across different geology types (Figure S4a), but DOC trends were the greatest in streams draining moraine and clay soil types (Figure S5a) as well as conifer forests (Figure S6a).

For DON, the ambient stream chemistry and the acid deposition models explained 27% and 34% of the variability, respectively, in trends while the watershed characteristics model did not select any variables (Table 2). The highest β coefficients for the chemistry model were mean concentrations of DON ($\beta = .001$), NO_3^- ($\beta = .0002$), Na^+ ($\beta = .0001$), and Ca^{2+} ($\beta = -.0001$). For the acid deposition model, the variables selected were mean and peak SO_4^{2-} deposition ($\beta = -.0004$ and $.0003$, respectively). Significant DON trends were only found in volcaniclastic and granitic watersheds, but trends were more constrained in volcaniclastic areas (Figure S4b).

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TABLE 2 Results of elastic net models exploring the influence of ambient stream chemistry (DOC, DON, DOC:DON, NO_3^-, NH_4^+, Ca^{2+}, Na^+), watershed characteristics (mean annual temperature (MAT °C), mean annual precipitations (MAP, mm), mean watershed elevation, and watershed area (km^2)), and atmospheric acid deposition (mean and peak NO_3^- and SO_4^{2-} deposition (kg/ha)) on DOC, DON, and DOC:DON trends (for streams with significant Sen slopes) that were considered as response variables

DOC

Model parameters	Stream chemistry		Watershed characteristics		Acid deposition	
r^2	.66		.32		.34	
n	43		41		39	
Lambda	0.003		0.0002		0.0001	
Alpha	.96		.96		.96	
	Variable	β	Variable	β	Variable	β
	Ca^{2+}	−.005	MAT (°C)	.0006	Mean SO_4^{2-}	−.004
	Na^+	.002	Elev. (m)	−.0001	Peak SO_4^{2-}	.002
	DOC	.002			Peak NO_3^-	−.0007

DON

Model parameters	Stream chemistry		Watershed characteristics		Acid deposition	
r^2	.27				.34	
n	34				34	
Lambda	0.0004				0.00001	
Alpha	.21				.83	
	Variable	β			Variable	β
	DON	.001			Mean SO_4^{2-}	−.0004
	NO_3^-	.0002			Peak SO_4^{2-}	.0003
	Na^+	.0001				
	Ca^{2+}	−.0001				

DOC:DON

Model parameters	Stream chemistry		Watershed characteristics		Acid deposition	
r^2	.10		.18		.01	
n	28		26		28	
Lambda	0.05		0.07		0.06	
Alpha	.58		.19		.94	
	Variable	β	Variable	β	Variable	β
	DON	−.10	Elev. (m)	.0002	Peak NO_3^-	.0007
	Ca^{2+}	−.004				

Note: Lambda controls the shrinkage of variables while alpha selects the type of penalty where alpha values between 0 and 1 denote elastic net regression, and beta values are the model coefficients for the selected variables. KNZ was excluded for these models due to no DON data. No variables were selected in the DON trends watershed characteristics model.

Similar to DOC trends, DON trends were the greatest in streams draining moraine and clay soil types and mostly negative for loam, silt, and sandy watersheds (Figure S5b) as well as greater in conifer forests (Figure S6b).

Lastly, the goodness of fit of the models for DOC:DON ratios was low with the stream chemistry and watershed characteristics models explaining 10% and 18% of the variability in trends, respectively. The acid deposition model only explained 1% of the variance (Table 2). The predictor variables for DOC:DON trends in the stream chemistry model were DON ($\beta = -.10$), and Ca^{2+} ($\beta = -.004$),

elevation ($\beta = .0002$) in the watershed characteristics, and peak NO_3^- deposition ($\beta = .0007$) for the acid deposition model. See Figures S4–S6 for more details on watershed characteristic relationships. Opposite to DOC and DON trends, DOC:DON trends were mostly positive in volcaniclastic watersheds and showed greater variability in the granitic sites (Figure S4c). There were no statistical differences in DOC:DON trends across soil types (Figure S5c) and differences across forest types were minimal except comparing DOC:DON trends between evergreen and conifer forests (Figure S6c).
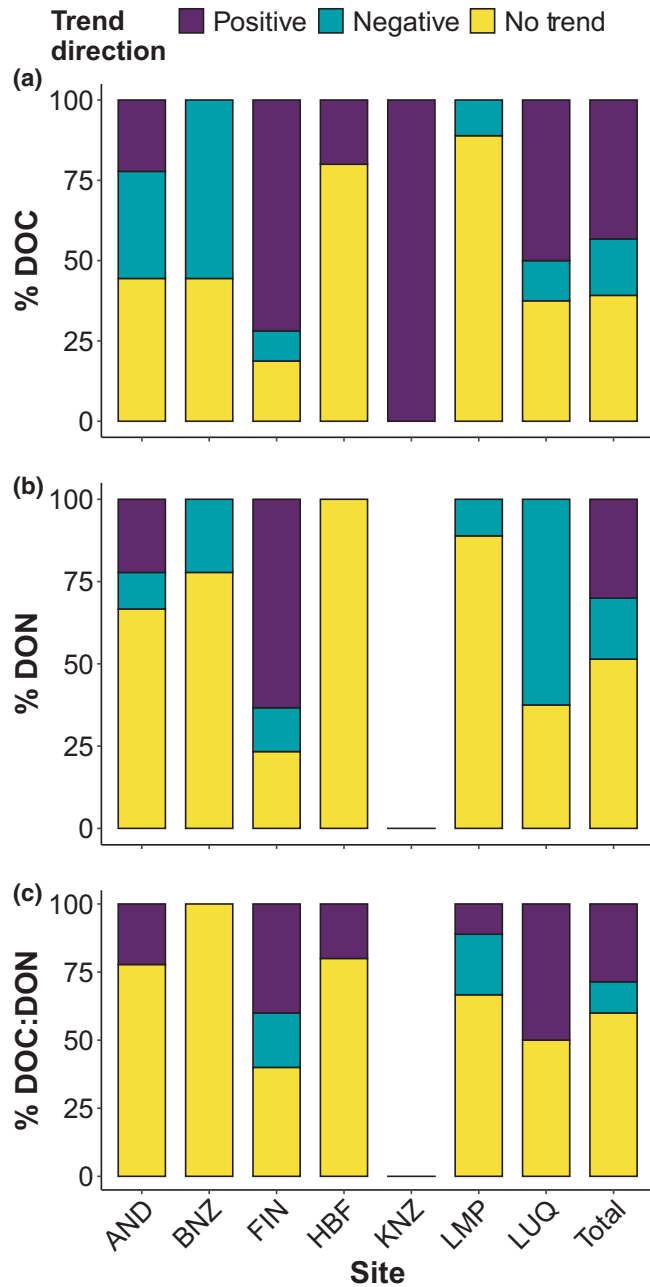
FIGURE 4 Percent of (a) DOC, (b) DON, and (c) DOC:DON ratios trends with positive (purple), negative (blue), or no trend (yellow) per site based on Sen slope *p* < .05. Note KNZ and 2 Finnish streams (YLIJOKI 1 and Vuoksi Vastuupuomi 061) were excluded from (b) and (c) due to no DON data available

4 | DISCUSSION

This is one of the first comprehensive studies in which time-series trends have been simultaneously determined for concentrations of DOC and DON and for DOM stoichiometry of the dissolved organic pool. We captured the inherent heterogeneity of DOM across a wide range of streams (74 individual streams) and six biomes by quantifying changes in three different metrics of the ambient DOM pool.

Contrary to expectations from earlier studies exploring increases in DOC concentrations in freshwater systems, primarily in temperate New England, the United Kingdom, and parts of Europe, concentrations of DOC and DON did not vary over time in any consistent pattern across study sites. Although we found 43% of our streams increasing in DOC (Figure 4), the majority of sites exhibited no significant long-term trends (Figure 4; Arvola et al., 2004; Clair et al., 2008; Coble et al., 2018; Räike et al., 2012; Rodríguez-Murillo et al., 2015), suggesting that increasing DOC is not ubiquitous across the landscape and that local context influences these long-term trends. Increasing DOC concentrations were also not exclusive to sites affected by acid deposition. For example, streams in the tropical rainforest site (LUQ) exhibit mostly positive trends in DOC concentrations that could be related to the high frequency of storm events (Wymore et al., 2017) that can also lead to an increase in the decomposition of organic matter (McDowell et al., 2013) rather than atmospheric deposition history. Another example of the unclear relationship between acid deposition and DOC trends is in the tallgrass prairie sites (KNZ) with positive DOC trends in streams affected by acid deposition. The site is in a karst landscape and well buffered against increases in hydrogen ion concentrations in soils and streams. Other directional changes at KNZ include increased woody vegetation in riparian zones (Veach et al., 2014) and increased drying in intermittent streams (Dodds et al., 2012) which could lead to changes in instream C concentrations (Rüegg et al., 2015).

A putative hypothesis about DOM properties is that concentrations of DOC and DON are highly correlated (e.g., Campbell et al., 2000; Goodale et al., 2000; Kortelainen et al., 2006; Lepistö et al., 2008; Mann et al., 2012). For those sites showing significant temporal trends, changes in concentrations of DON did not always track those of DOC, with decoupled trends found in over 50% of the analyses. The lack of temporal synchronicity in the changes of DOC and DON concentrations is likely the result of diverse sources of DOM captured among sites, the variable state factors (*sensu lato* Jenny, 1941) represented in this analysis, and variable biogeochemical processing along flow paths and stream networks (McDowell et al., 2004; Yates et al., 2019). Across the array of streams where DOM stoichiometry is significantly changing, DOM is becoming enriched with C and relatively depleted in N suggesting that fundamental changes in the energy and nutrient balance of freshwater ecosystems is occurring over large spatial scales.

4.1 | Cross biome patterns in DOC and DON concentration trends

Many studies examining the response of DOC over time are reported from regions exposed to significant amounts of acidic deposition (Driscoll et al., 2003; Hall et al., 2021; Hruška et al., 2009; Monteith et al., 2007; Worrall et al., 2004). Whereas these studies have informed the notion that DOC concentrations are increasing in northern temperate streams (and we present complementary results), we also show that the directional change in concentrations of DOC and DON is highly variable and site- and stream-specific. Our DOC Sen
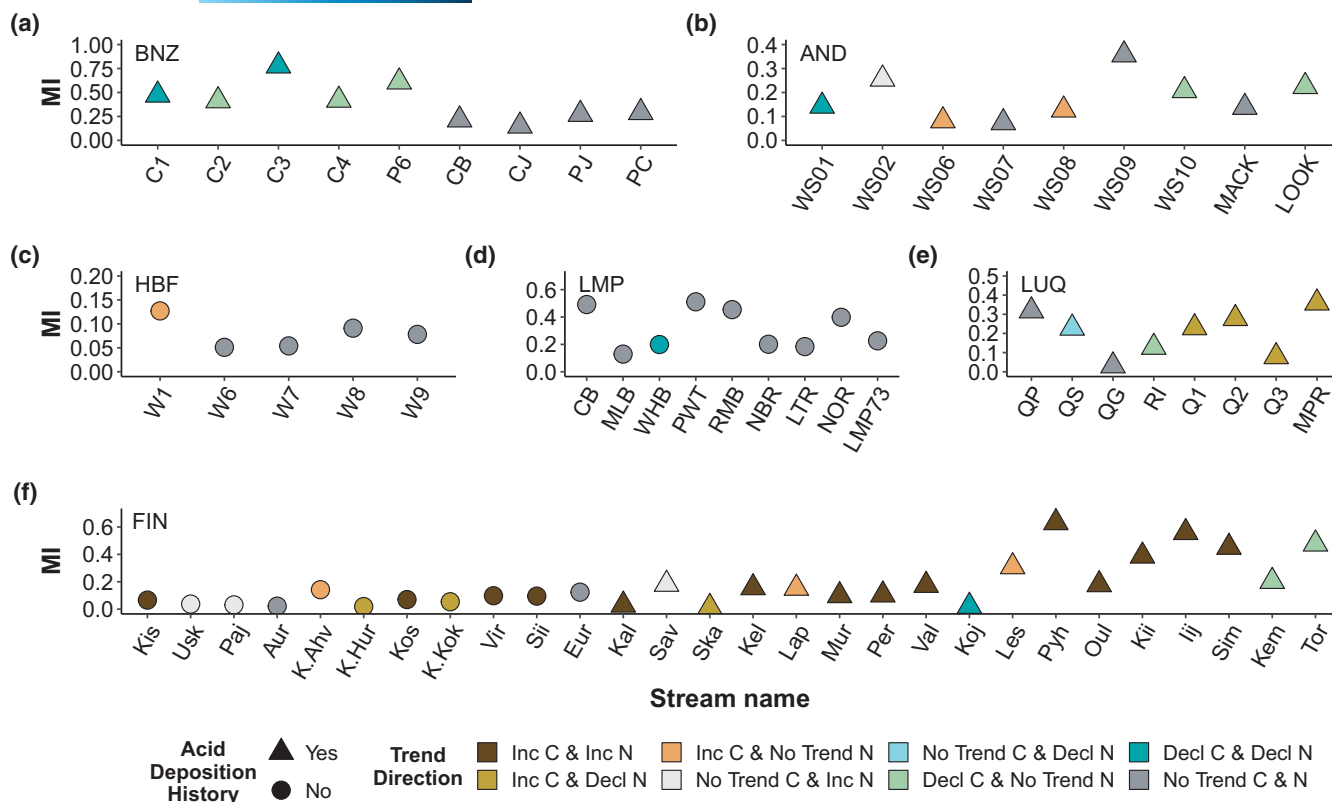
FIGURE 5 Mutual information values (MI) for DOC and DON. Shapes describe the acid deposition history by site, circles represent sites with a history of acid deposition and triangles are for sites that have not been affected by acid deposition. Colors represent the directional trend of DOC and DON based on their Sen slope where no trend are streams with a Sen slope with $p > .05$. Note Konza and 4 Finnish streams (YLIJOKI 1, Vuoksi Vastuupuomi 061, KOTIOJA 1, and Kivipuro 39) were excluded due to limited DON data available for these streams

slopes are within the range of variability reported from other studies that report values ranging between −0.25 and 0.51 mg C/L per year in streams primarily from northern latitudes (Clair et al., 2008; Coble et al., 2018; De Wit et al., 2007; Driscoll et al., 2003; Evans et al., 2005). And while the DON Sen slopes presented here are within the range of those reported earlier (0.0027–0.003 mg N/L per year in northern latitudes [Clair et al., 2008; Lepistö et al., 2008]), we also present negative DON trends. Studies addressing the long-term trends in DON are rarer than those of DOC, necessitating a broader assessment of DON trends. Our results suggest that changes in DOM composition may have the greatest impact in ecosystems with the lowest DOM concentrations such as tall grass prairies (KNZ) and tropical rainforest (LUQ). In these ecosystems with low DOM concentration, small changes in DOC and DON can create a large proportional change with potentially meaningful ramifications for stream metabolic regimes (Bernhardt et al., 2018) and biogeochemical reaction rates that are often limited by the availability of energy (Brailsford, Glanville, Golyshin, Johnes, et al., 2019; Brailsford, Glanville, Golyshin, Marshall, et al., 2019; Rodríguez-Cardona et al., 2021).

Contrary to our hypothesis, synchronous changes in concentrations of DOC and DON were only found in a small number of streams (Figure 5). Asynchronous changes in concentrations of DOC

and DON suggest different controls on the C-rich and N-rich fractions of the DOM pool and/or different drivers of DOC and DON flux to streams. We found numerous examples where concentrations of DOC and DON changed in opposite directions, demonstrating that the DOM pool as a whole is highly dynamic and that the different constituents of DOM do not always have the same ecological and biogeochemical sources and roles (e.g., Bernal et al., 2005; Brookshire et al., 2007; Lutz et al., 2011; McDowell et al., 2004; Wymore et al., 2015, 2018; Yates et al., 2019). For example, we found streams increasing in DOC but decreasing in DON (Figure 5) as well as sites that changed in either DOC or DON, but not in the other constituent. These scenarios suggest a biogeochemical decoupling of the C-rich and N-rich fractions of the DOM pool where DON cycling has little effect on the overall DOC pool. Changes in concentrations of DON with no significant trend in concentrations of DOC may be the result of DON being more mobile and reactive along flow paths relative to DOC due to its hydrophilic nature (Aiken et al., 1992; Hood et al., 2003; Inamdar et al., 2012;). Scenarios in which no significant trend in DOC concentrations occurs but DON concentrations decline could also occur in the nutrient limited systems where both terrestrial and aquatic biota mine the N contained within DOM (Brailsford, Glanville, Golyshin, Marshall, et al., 2019; Jones et al., 2005; Kissman et al., 2017; Mackay et al., 2020; Neff
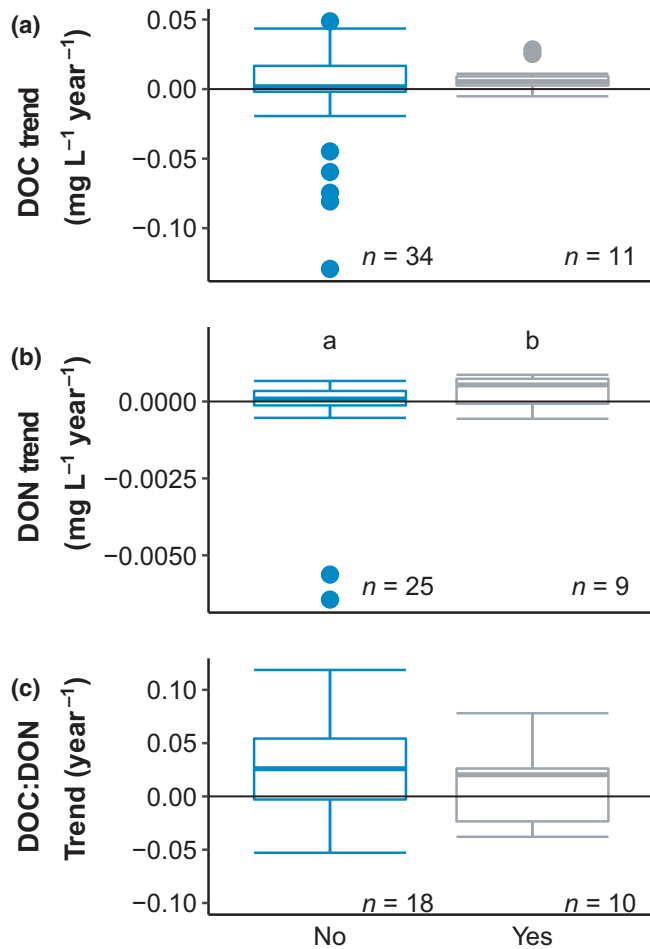
FIGURE 6 Significant Sen slopes ($p < .05$) in (a) DOC, (b) DON, and (c) DOC:DON ratios grouped by history of acid deposition where sites affected by acid deposition are in grey (FIN, HBF, LMP, KNZ) and sites not affected by acid deposition (CPC, AND, LUQ) are in blue. There is an outlier point in the DOC:DON trends for sites not affected by acid deposition that was excluded from the figure and statistics, the value is 0.96 year^{-1} from HBF. Letters denote statistically significant differences determined by Kruskall–Wallis rank-sum test (DOC $p = .38$; DON $p = .05$, and DOC:DON $p = .56$). p-values for one-sample t-test, to determine if means are different from 0 for DOC in acid deposition affected sites $p = .008$ and no acid deposition $p = .35$; DON in acid deposition affected sites $p = .05$ and no acid deposition $p = .41$; DOC:DON in acid deposition affected sites $p = .29$ and no acid deposition $p = .008$

et al., 2003; Wymore et al., 2015). We did not detect any instances where DOC concentration is declining but DON concentration is increasing, suggesting that autochthonous contributions to the DON pool are small compared to heterogeneous terrestrial inputs from the watershed, at least for the streams included in this study.

4.2 | A changing stoichiometry of the DOM pool

DOC and DON concentrations represent two ways to measure the composition of the DOM pool, yet few studies have used both bulk

elemental analyses as a way to describe the heterogenous DOM pool (McDowell et al., 2019). Although a stoichiometric approach to understanding nutrient and elemental cycling has a rich history (Elser et al., 2000; Redfield, 1958), the principles have seldom been applied to understanding changes in bulk DOM composition over time. For those sites where a significant change in DOC:DON stoichiometry was detected, the predominant direction of change reflected the C-enrichment or N-depletion of DOM. The exception to this general pattern was in streams at the LMP site, located in the temperate deciduous forests of New England (Wymore et al., 2021a), where DOC:DON ratios are decreasing, indicating the relative N-enrichment of DOM. These sites have a high percentage of wetlands (Flint & McDowell, 2015), which are likely contributing to these changing stoichiometric ratios (Coble et al., 2019). N-enriched DOM may provide additional nutrients to microbial communities making more NH_4^+ available through mineralization. In turn, competition for dissolved inorganic N may decline with higher rates of nitrification and increased NO_3^- production and export (Wymore et al., 2019), while increasing DON concentrations instream may provide an alternative nutrient resource for uptake by the primary producers (Mackay et al., 2020). In contrast, streams with increasing DOC:DON ratios may reflect increasing watershed N demand from greater retention in soils and increasing vegetative growth, possibly from CO_2 enrichment (Craine et al., 2018; Groffman et al., 2018; Huang et al., 2015). Just as instream primary producers can take up DON compounds directly as a nutrient resource, trees can bypass microbial symbionts taking up labile forms of DON directly from soils (Neff et al., 2003), which in turn would decrease DON exports to streams leading to increases in DOC:DON ratios. Changes in DOC:DON ratios can alter rates of N transformations including nitrification (Strauss & Lamberti, 2002), and NO_3^- concentrations (Bernhardt & McDowell, 2008). While the ecosystem and biogeochemical consequences of changes in DOC:DON is a relatively understudied topic, stoichiometric shifts in this particular compartment of organic matter will likely influence other biogeochemical cycles (Wymore et al., 2019; Yates et al., 2019), driving changes in the aquatic ecosystem and downstream, creating nutrient export regimes that can affect trophic assemblages in receiving bodies of water (Schade et al., 2005).

4.3 | Atmospheric deposition

In sites historically affected by acid deposition such as HBF, LMP, and Southern Finland, Sen slopes are mostly increasing for DOC and DON concentrations, consistent with previous studies in Northeast regions of the United States, Europe, and United Kingdom (Couture et al., 2012; Driscoll et al., 2003; Evans et al., 2005; Gavin et al., 2018; Monteith et al., 2007; Worrall et al., 2004). Similar trends for DOC and DON in these sites suggest analogous watershed sources, flow paths, and release mechanisms for both the C-rich and N-rich fractions of DOM. In these acid-impacted sites, the rates of change for DOC and DON concentrations remain proportional, leading to

a stoichiometrically stable DOM pool, despite the large changes in DOC concentrations (Wymore et al., 2021c). Sites affected by atmospheric acid deposition generally show increases in DON evidenced by the significant one-sample *t* tests (Figure 6).

Conversely, sites not affected by acid deposition generally show declines in DON, falling below the DON zero line (Figure 6). These results highlight the importance of DON as a component of the DOM pool, and its sensitivity to changes in N loading from the watershed. Sites unaffected by acid deposition exhibit the greatest change in DOC:DON ratios, very likely driven by larger declines in DON concentration relative to DOC, as demonstrated by the decoupling of DOC and DON (Figure 5). Recovery from atmospheric deposition plays an important role in the delivery of DOM to aquatic ecosystems but appears to have little effect on the stoichiometry of DOM.

4.4 | Predictors of DOM trends

The ambient stream chemistry models for all DOM trend models selected major dissolved ions such as Ca^{2+}. This result supports the idea that these streams are recovering from acid deposition and as soil Ca^{2+} recovers, DOM declines due to decreased DOM solubility (Miller et al., 2016). For both DOC and DON models, ambient mean DOC and DON concentrations, respectively, were selected suggesting that streams with greater DOC or DON concentrations will experience the greatest changes over time. Ambient NO_3^- concentrations had the second-highest beta coefficients for DON trends model, demonstrating the connection between the organic and inorganic N pool in streams and how DIN can influence concentrations of DON (Wymore et al., 2015). Either peak NO_3^- or SO_4^- deposition were selected for all DOM trends in the atmospheric acid deposition models demonstrating the lasting effects and recovery of acid deposition on aquatic ecosystems, but for DOC:DON trends this model explained very little of the variance. This result suggests that although atmospheric acid deposition can influence DOC and DON concentrations, the proportional changes might not be large enough to be detected in stoichiometry, at least for the subset of streams selected in this model.

In the watershed characteristics models, mean annual temperature (MAT) and watershed elevation were selected for DOC and DOC:DON trends demonstrating that the geographical location of the streams (MAT as a surrogate for latitudinal changes), can have a strong influence on DOM over time. DOC and DON trends were greatest in granitic watersheds as this bedrock has a poor buffering capacity (Robinson, 1997) allowing a greater release of DOM to adjacent aquatic systems. This translates to an opposite pattern for DOC:DON ratios where they were lower in granitic watersheds and greater in the volcaniclastic watersheds (Figure S4). The type of soil also played a role in DOM trends being streams in silty and sandy loam landscapes the ones showing the lowest DOC and DON trends (Figure S5). This finding suggests that the adsorption to silt particles can influence DOM availability by controlling the long-term storage and export of DOC and DON (Dosskey & Bertsch, 1997; Kaiser &

Guggenberger, 2000). The higher trends of DOC and DON in moraine sites (Figure S5) could be due to greater OM availability and associated microbial decomposition activity (Bruhn et al., 2021). Collectively, the results of these models support the hypothesis that regional state factors such as geology and soil type are important controls of stream long-term DOM trends.

5 | CONCLUSION

This study adds to the growing body of literature on long-term trends of stream water DOM by expanding the scope of past studies through the inclusion of underrepresented biomes and ecosystems including tropical rainforests, arctic taiga, and tallgrass prairie. Our study also provides one of the first large-scale assessments of long-term trends in concentrations of DON and DOM stoichiometry in streams. We demonstrated increases in DOC concentrations in sites recovering from acid deposition, similar to previous findings, and we have shown that those are accompanied by proportional increases in DON. In addition, there can be increasing trends in DOC in sites with no atmospheric acid deposition history where in these cases, trends are associated with local state factors such as soil and geology. Although we have shown that positive trends in DOC can occur regardless of the acid deposition history, we also demonstrate that increases in DOC are not ubiquitous across broad latitudinal gradients. Declining trends in DON suggest on the differential cycling of DOC and DON in soils and within streams. The biomes in which streams are embedded are expected to influence the biogeochemistry of those systems (Dodds et al., 2019), but exactly how is poorly known. Changes in DOC and DON concentrations will have implications for in-stream biogeochemical processes as well as the bulk composition of DOM exports to receiving bodies of water, especially those systems where changes in DOC and DON are decoupled. Continued monitoring of these long-term trends in DOM concentration and stoichiometry in response to climatic and landscape attributes is important to better understand the ultimate fate of DOM and nutrients in freshwater ecosystems in the face of global change.

AUTHOR CONTRIBUTIONS

Bianca M. Rodríguez-Cardona and Adam S. Wymore conceived the project. Bianca M. Rodríguez-Cardona, Adam S. Wymore, Ashley A. Coble, and Carla López-Lloreda, organized and synthesized the data, and Jeremy B. Jones, Sherri L. Johnson, Pirkko Kortelainen, Walter K. Dodds, and William H. McDowell provided data. Bianca M. Rodríguez-Cardona, Adam S. Wymore, Alba Argerich analyzed the data. All authors helped to interpret that data. Bianca M. Rodríguez-Cardona wrote the initial draft of the manuscript with significant input from Adam S. Wymore, Robert G. M. Spencer, Ashley M. Helton, Susana Bernal, and William H. McDowell. All co-authors discussed hypotheses, data and results, and commented and revised the manuscript.

DATA AVAILABILITY STATEMENT

The data used in these analyses represent a synthesis of multiple data sets. The individual data sets and their associated repositories and references can be found in Tables S4 and S5. The archived data set (Wymore et al., 2021b) is openly shared at the Environmental Data Initiative (EDI) according to FAIR principles of data sharing (https://environmentaldatainitiative.org). Data can be accessed here: https://doi.org/10.6073/pasta/50965f9e091ffa833da3c73bce2467fa.

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REFERENCES

Aiken, G. R., Mcknight, I. D. M., Thorn, I. K. A., & Thurman, E. M. (1992). Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Organic Geochemistry*, *18*, 567–573. https://doi.org/10.1016/0146-6380(92)90119-I

Ardón, M., Helton, A. M., Scheuerell, M. D., & Bernhardt, E. S. (2017). Fertilizer legacies meet saltwater incursion: Challenges and constraints for coastal plain wetland restoration. *Elementa*, *5*. https://doi.org/10.1525/elementa.236

Argerich, A., Johnson, S. L., Sebestyen, S. D., Rhoades, C. C., Greathouse, E., Knoepp, J. D., Adams, M. B., Likens, G. E., Campbell, J. L., McDowell, W. H., Scatena, F. N., & Ice, G. G. (2013). Trends in stream nitrogen concentrations for forested reference catchments across the USA. *Environmental Research Letters*, *8*, 1–8. https://doi.org/10.1088/1748-9326/8/1/014039

Arvola, L., Räike, A., Kortelainen, P., & Järvinen, M. (2004). The effect of climate and landuse on TOC concentrations and loads in Finnish rivers. *Boreal Environment Research*, *9*, 381–387.

Bernal, S., Butturini, A., & Sabater, F. (2005). Seasonal variations of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream. *Biogeochemistry*, *75*, 351–372. https://doi.org/10.1007/s10533-005-1246-7

Bernhardt, E. S., Heffernan, J. B., Grimm, N. B., Stanley, E. H., Harvey, J. W., Arroita, M., Appling, A. P., Cohen, M. J., McDowell, W. H., Hall, R. O., Read, J. S., Roberts, B. J., Stets, E. G., & Yackulic, C. B. (2018). The metabolic regimes of flowing waters. *Limnology and Oceanography*, *63*, S99–S118. https://doi.org/10.1002/lno.10726

Bernhardt, E. S., & McDowell, W. H. (2008). Twenty years apart: Comparisons of DOM uptake during leaf leachate releases to Hubbard Brook Valley streams in 1979 versus 2000. *Journal of Geophysical Research*, *113*, G03032. https://doi.org/10.1029/2007jg000618

Borken, W., Ahrens, B., Schulz, C., & Zimmermann, L. (2011). Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils. *Global Change Biology*, *17*, 2428–2443. https://doi.org/10.1111/j.1365-2486.2011.02390.x

Brailsford, F. L., Glanville, H. C., Golyshin, P. N., Johnes, P. J., Yates, C. A., & Jones, D. L. (2019a). Microbial uptake kinetics of dissolved organic carbon (DOC) compound groups from river water and sediments. *Scientific Reports*, *9*, 11229. https://doi.org/10.1038/s41598-019-47749-6

Brailsford, F. L., Glanville, H. C., Golyshin, P. N., Marshall, M. R., Lloyd, C. E., Johnes, P. J., & Jones, D. L. (2019b). Nutrient enrichment induces a shift in dissolved organic carbon (DOC) metabolism in oligotrophic freshwater sediments. *Science of the Total Environment*, *690*, 1131–1139. https://doi.org/10.1016/j.scitotenv.2019.07.054

Brookshire, E. N. J., Valett, H. M., Thomas, S. A., & Webster, J. R. (2007). Atmospheric N deposition increases organic N loss from temperate forests. *Ecosystems*, *10*, 252–262. https://doi.org/10.1016/j.scitotenv.2019.07.054

Bruhn, A. D., Stedmon, C. A., Comte, J., Matsuoka, A., Speetjens, N. J., Tanski, G., Vonk, J. E., & Sjöstedt, J. (2021). Terrestrial dissolved organic matter mobilized from eroding permafrost controls microbial community composition and growth in Arctic coastal zones. *Frontiers in Earth Science*, *9*, 1–20. https://doi.org/10.3389/feart.2021.640580

Campbell, J. L., Hornbeck, J. W., McDowell, W. H., Buso, D. C., Shanley, J. B., & Likens, G. E. (2000). Dissolved organic nitrogen budgets for upland, forested ecosystems in New England. *Biogeochemistry*, *49*, 123–142. https://doi.org/10.1023/A:1006383731753

Campbell, J. L., Rustad, L. E., Bailey, S. W., Bernhardt, E. S., Driscoll, C. T., Green, M. B., Groffman, P. M., Lovett, G. M., McDowell, W. H., McGuire, K. J., & Rosi, E. J. (2021). Watershed studies at the Hubbard Brook Experimental Forest: Building on a long legacy of research with new approaches and sources of data. *Hydrological Processes*, 35, 1–5. https://doi.org/10.1002/hyp.14016

Cazelles, B. (2004). Symbolic dynamics for identifying similarity between rhythms of ecological time series. *Ecology Letters*, 7, 755–763. https://doi.org/10.1111/j.1461-0248.2004.00629.x

Chow, M. F., Lai, C. C., Kuo, H. Y., Lin, C. H., Chen, T. Y., & Shiah, F. K. (2017). Long term trends and dynamics of dissolved organic carbon (DOC) in a subtropical Reservoir basin. *Water*, 9, 1–14. https://doi.org/10.3390/w9070545

Clair, T. A., Dennis, I. F., Vet, R., & Laudon, H. (2008). Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. *Biogeochemistry*, 87, 83–97. https://doi.org/10.1007/s10533-007-9170-7

Coble, A. A., Koenig, L. E., Potter, J. D., Parham, L. M., & McDowell, W. H. (2019). Homogenization of dissolved organic matter within a river network occurs in the smallest headwaters. *Biogeochemistry*, 143, 85–104. https://doi.org/10.1007/s10533-019-00551-y

Coble, A. A., Wymore, A. S., Shattuck, M. D., Potter, J. D., & McDowell, W. H. (2018). Multiyear trends in solute concentrations and fluxes from a suburban watershed: Evaluating effects of 100-year flood events. *Journal of Geophysical Research: Biogeosciences*, 123, 3072–3087. https://doi.org/10.1029/2018JG004657

Couture, S., Houle, D., & Gagnon, C. (2012). Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada. *Environmental Science and Pollution Research*, 19, 361–371. https://doi.org/10.1007/s11356-011-0565-6

Craine, J. M., Elmore, A. J., Wang, L., Aranibar, J., Bauters, M., Boeckx, P., Crowley, B. E., Dawes, M. A., Delzon, S., Fajardo, A., Fang, Y., Fujiyoshi, L., Gray, A., Guerrieri, R., Gundale, M. J., Hawke, D. J., Hietz, P., Jonard, M., Kearsley, E., ... Zmudczyńska-Skarbek, K. (2018). Isotopic evidence for oligotrophication of terrestrial ecosystems. *Nature Ecology & Evolution*, 2, 1735–1744. https://doi.org/10.1038/s41559-018-0694-0

De Wit, H. A., Mulder, J., Hindar, A., & Hole, L. (2007). Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environmental Science and Technology*, 41, 7706–7713. https://doi.org/10.1021/es070557f

De Wit, H. A., Valinia, S., Weyhenmeyer, G. A., Futter, M. N., Kortelainen, P., Austnes, K., Hessen, D. O., Räike, A., Laudon, H., & Vuorenmaa, J. (2016). Current browning of surface waters will be further promoted by wetter climate. *Environmental Science and Technology Letters*, 3, 430–435. https://doi.org/10.1021/acs.estlett.6b00396

Deininger, A., Kaste, Ø., Frigstad, H., & Austnes, K. (2020). Organic nitrogen steadily increasing in Norwegian rivers draining to the Skagerrak coast. *Scientific Reports*, 10, 1–9. https://doi.org/10.1038/s41598-020-75532-5

Del Giorgio, P. A., & Cole, J. J. (1998). Bacterial growth efficiency in natural aquatic systems. *Annual Review of Ecology and Systematics*, 29, 503–541. https://doi.org/10.1146/annurev.ecolsys.29.1.503

Dodds, W. K., Bruckerhoff, L., Batzer, D., Schechner, A., Pennock, C., Renner, E., Tromboni, F., Bigham, K., & Grieger, S. (2019). The freshwater biome gradient framework: Predicting macroscale properties based on latitude, altitude, and precipitation. *Ecosphere*, 10, 1–33. https://doi.org/10.1002/ecs2.2786

Dodds, W. K., Robinson, C. T., Gaiser, E. E., Hansen, G. J. A., Powell, H., Smith, J. M., Morse, N. B., Johnson, S. L., Gregory, S. V., Bell, T., Kratz, T. K., & McDowell, W. H. (2012). Surprises and insights from long-term aquatic data sets and experiments. *BioScience*, 62, 709–721. https://doi.org/10.1525/bio.2012.62.8.4

Dosskey, M. G., & Bertsch, P. M. (1997). Transport of dissolved organic matter through a sandy forest soil. *Soil Science Society of America Journal*, 61, 920–927. https://doi.org/10.2136/sssaj1997.03615995006100030030x

Driscoll, C. T., Driscoll, K. M., Roy, K. M., & Mitchell, M. J. (2003). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environmental Science and Technology*, 37, 2036–2042. https://doi.org/10.1021/es020924h

Elser, J. J., Sterner, R. W., Gorokhova, E., Fagan, W. F., Markow, T. A., Cotner, J. B., Harrison, J. F., Hobbie, S. E., Odell, G. M., & Weider, L. W. (2000). Biological stoichiometry from genes to ecosystems. *Ecology Letters*, 3, 540–550. https://doi.org/10.1046/j.1461-0248.2000.00185.x

Erlandsson, M., Buffam, I., Fölster, J., Laudon, H., Temnerud, J., Weyhenmeyer, G. A., & Bishop, K. (2008). Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biology*, 14, 1191–1198. https://doi.org/10.1111/j.1365-2486.2008.01551.x

Evans, C. D., Monteith, D. T., & Cooper, D. M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*, 137, 55–71. https://doi.org/10.1016/j.envpol.2004.12.031

Finlay, J., Neff, J., Zimov, S., Davydova, A., & Davydov, S. (2006). Snowmelt dominance of dissolved organic carbon in high-latitude watersheds: Implications for characterization and flux of river DOC. *Geophysical Research Letters*, 33, 2–6. https://doi.org/10.1029/2006GL025754

Finlay, K., Vogt, R. J., Bogard, M. J., Wissel, B., Tutolo, B. M., Simpson, G. L., & Leavitt, P. R. (2015). Decrease in CO_2 efflux from northern hardwater lakes with increasing atmospheric warming. *Nature*, 519, 215–218. https://doi.org/10.1038/nature14172

Flint, S. A., & McDowell, W. H. (2015). Effects of headwater wetlands on dissolved nitrogen and dissolved organic carbon concentrations in a suburban New Hampshire watershed. *Freshwater Science*, 34, 456–471. https://doi.org/10.1086/680985

Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., Lock, M. A., Sleep, D., Hughes, S., & Hudson, J. (2004). Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature*, 430, 59–61. https://doi.org/10.1038/nature02707

Frey, K. E., & McClelland, J. W. (2009). Impacts of permafrost degradation on arctic river biogeochemistry. *Hydrological Processes*, 23, 169–182. https://doi.org/10.1002/hyp.7196

Frey, K. E., McClelland, J. W., Holmes, R. M., & Smith, L. G. (2007). Impacts of climate warming and permafrost thaw on the riverine transport of nitrogen and phosphorus to the Kara Sea. *Journal of Geophysical Research: Biogeosciences*, 112, 1–10. https://doi.org/10.1029/2006JG000369

Frey, K. E., & Smith, L. C. (2005). Amplified carbon release from vast West Siberian peatlands by 2100. *Geophysical Research Letters*, 32, 1–4. https://doi.org/10.1029/2004GL022025

Friedman, J., Hastie, T., & Tibshirani, R. (2010). Regularization paths for generalized linear models via coordinate descent. *Journal of Statistical Software*, 33, 1–22. https://doi.org/10.18637/jss.v033.i01

Gavin, A. L., Nelson, S. J., Klemmer, A. J., Fernandez, I. J., Strock, K. E., & McDowell, W. H. (2018). Acidification and climate linkages to increased dissolved organic carbon in high-elevation lakes. *Water Resources Research*, 54, 5376–5393. https://doi.org/10.1029/2017WR020963

Goodale, C. L., Aber, J. D., & McDowell, W. H. (2000). The long-term effects of disturbance on organic and inorganic nitrogen export in the White Mountains, New Hampshire. *Ecosystems*, 3, 433–450. https://doi.org/10.1007/s100210000039

Groffman, P. M., Driscoll, C. T., Durán, J., Campbell, J. L., Christenson, L. M., Fahey, T. J., Fisk, M. C., Fuss, C., Likens, G. E., Lovett, G., Rustad, L., & Templer, P. H. (2018). Nitrogen oligotrophication in northern hardwood forests. *Biogeochemistry*, 141, 523–539. https://doi.org/10.1007/s10533-018-0445-y

Hall, L. J., Emilson, E. J. S., Edwards, B., & Watmough, S. A. (2021). Patterns and trends in lake concentrations of dissolved organic carbon in a landscape recovering from environmental degradation and widespread acidification. *Science of the Total Environment*, 765. https://doi.org/10.1016/j.scitotenv.2020.142679

Hirsch, R. M., Slack, J. R., & Smith, R. A. (1982). Techniques of trend detection for monthly water quality data. *Water Resources Research*, 18, 107–121. https://doi.org/10.1029/WR018i001p00107

Hood, E., McKnight, D. M., & Williams, M. W. (2003). Sources and chemical character of dissolved organic carbon across an alpine/subalpine ecotone, Green Lakes Valley, Colorado Front Range, United States. *Water Resources Research*, 39, 1–12. https://doi.org/10.1029/2002WR001738

Hruška, J., Krám, P., McDowell, W. H., & Oulehle, F. (2009). Increased dissolved organic carbon (doc) in central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environmental Science & Technology*, 43, 4320–4326. https://doi.org/10.1021/es803645w

Huang, W., Houlton, B. Z., Marklein, A. R., Liu, J., & Zhou, G. (2015). Plant stoichiometric responses to elevated CO_2 vary with nitrogen and phosphorus inputs: Evidence from a global-scale meta-analysis. *Scientific Reports*, 5, 1–8. https://doi.org/10.1038/srep18225

Inamdar, S., Finger, N., Singh, S., Mitchell, M., Levia, D., Bais, H., Scott, D., & McHale, P. (2012). Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. *Biogeochemistry*, 108, 55–76. https://doi.org/10.1007/s10533-011-9572-4

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W. H., & Campbell, J. L. (2008). Spatial and temporal variations in DOM composition in ecosystems: The importance of long-term monitoring of optical properties. *Journal of Geophysical Research: Biogeosciences*, 113, 1–15. https://doi.org/10.1029/2008JG000683

Jenny, H. (1941). *Factors of soil formation: A system of quantitative pedology*. Dover Publications.

Johnson, S. L., Henshaw, D., Downing, G., Wondzell, S., Schulze, M., Kennedy, A., Cohn, G., Schmidt, S. A., & Jones, J. A. (2021). Long-term hydrology and aquatic biogeochemistry data from H. J. Andrews Experimental Forest, Cascade Mountains, Oregon. *Hydrological Processes*, 35, 1–9. https://doi.org/10.1002/hyp.14187

Jones, D. L., Healey, J. R., Willett, V. B., Farrar, J. F., & Hodge, A. (2005). Dissolved organic nitrogen uptake by plants—An important N uptake pathway? *Soil Biology and Biochemistry*, 37, 413–423. https://doi.org/10.1016/j.soilbio.2004.08.008

Kaiser, K., & Guggenberger, G. (2000). The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry*, 31, 711–725. https://doi.org/10.1016/S0146-6380(00)00046-2

Kendrick, M. R., Huryn, A. D., Bowden, W. B., Deegan, L. A., Findlay, R. H., Hershey, A. E., Peterson, B. J., Beneš, J. P., & Schuett, E. B. (2018). Linking permafrost thaw to shifting biogeochemistry and food web resources in an arctic river. *Global Change Biology*, 24, 5738–5750. https://doi.org/10.1111/gcb.14448

Kissman, C. E. H., Williamson, C. E., Rose, K. C., & Saros, J. E. (2017). Nutrients associated with terrestrial dissolved organic matter drive changes in zooplankton:phytoplankton biomass ratios in an alpine lake. *Freshwater Biology*, 62, 40–51. https://doi.org/10.1111/fwb.12847

Kortelainen, P., Mattsson, T., Finér, L., Ahtiainen, M., Saukkonen, S., & Sallantaus, T. (2006). Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland. *Aquatic Sciences*, 68, 453–468. https://doi.org/10.1007/s00027-006-0833-6

Larouche, J. R., Abbott, B. W., Bowden, W. B., & Jones, J. B. (2015). The role of watershed characteristics, permafrost thaw, and wildfire on dissolved organic carbon biodegradability and water chemistry in Arctic headwater streams. *Biogeosciences Discussions*, 12, 4021–4056. https://doi.org/10.5194/bgd-12-4021-2015

Lawrence, G. B., & Roy, K. M. (2021). Ongoing increases in dissolved organic carbon are sustained by decreases in ionic strength rather than decreased acidity in waters recovering from acidic deposition. *Science of the Total Environment*, 766, 142529. https://doi.org/10.1016/j.scitotenv.2020.142529

Lawrence, G. B., Simonin, H. A., Baldigo, B. P., Roy, K. M., & Capone, S. B. (2011). Changes in the chemistry of acidified Adirondack streams from the early 1980s to 2008. *Environmental Pollution*, 159, 2750–2758. https://doi.org/10.1016/j.envpol.2011.05.016

Lepistö, A., Kortelainen, P., & Mattsson, T. (2008). Increased organic C and N leaching in a northern boreal river basin in Finland. *Global Biogeochemical Cycles*, 22, 1–10. https://doi.org/10.1029/2007GB003175

Lloyd, C. E. M., Freer, J. E., Johnes, P. J., Coxon, G., & Collins, A. L. (2016). Discharge and nutrient uncertainty: Implications for nutrient flux estimations in small streams. *Hydrological Processes*, 30, 135–152. https://doi.org/10.1002/hyp.10574

Löfgren, S., Gustafsson, J. P., & Bringmark, L. (2010). Decreasing DOC trends in soil solution along the hillslopes at two IM sites in southern Sweden—Geochemical modeling of organic matter solubility during acidification recovery. *Science of the Total Environment*, 409, 201–210. https://doi.org/10.1016/j.scitotenv.2010.09.023

Lutz, B., Bernhardt, E., Roberts, B., Cory, R., & Mulholland, P. (2012). Distinguishing dynamics of dissolved organic matter components in a forested stream using kinetic enrichments. *Limnology and Oceanography*, 57, 76–89. https://doi.org/10.4319/lo.2012.57.1.0076

Lutz, B. D., Bernhardt, E. S., Roberts, B. J., & Mulholland, P. J. (2011). Examining the coupling of carbon and nitrogen cycles in Appalachian streams: The role of dissolved organic nitrogen. *Ecology*, 92, 720–732. https://doi.org/10.1890/10-0899.1

Mackay, E. B., Feuchtmayr, H., De Ville, M. M., Thackeray, S. J., Callaghan, N., Marshall, M., Rhodes, G., Yates, C. A., Johnes, P. J., & Maberly, S. C. (2020). Dissolved organic nutrient uptake by riverine phytoplankton varies along a gradient of nutrient enrichment. *Science of the Total Environment*, 722, 137837. https://doi.org/10.1016/j.scitotenv.2020.137837

Mann, P. J., Davydova, A., Zimov, N., Spencer, R. G. M., Davydov, S., Bulygina, E., Zimov, S., & Holmes, R. M. (2012). Controls on the composition and lability of dissolved organic matter in Siberia's Kolyma River basin. *Journal of Geophysical Research: Biogeosciences*, 117, G01028. https://doi.org/10.1029/2011JG001798

Mattsson, T., Kortelainen, P., & Räike, A. (2005). Export of DOM from boreal catchments: Impacts of land use cover and climate. *Biogeochemistry*, 76, 373–394. https://doi.org/10.1007/s10533-005-6897-x

McArthur, J. V., Marzolf, G. R., & Urban, J. E. (1985). Response of bacteria isolated from a pristine prairie stream to concentration and source of soluble organic carbon. *Applied and Environmental Microbiology*, 49, 238–241. https://doi.org/10.1128/aem.49.1.238-241.1985

McDowell, W. H., Brereton, R. L., Scatena, F. N., Shanley, J. B., Brokaw, N. V., & Lugo, A. E. (2013). Interactions between lithology and biology drive the long-term response of stream chemistry to major hurricanes in a tropical landscape. *Biogeochemistry*, 116, 175–186. https://doi.org/10.1007/s10533-013-9916-3

McDowell, W. H., Leon, M. C., Shattuck, M. D., Potter, J. D., Heartsill-Scalley, T., González, G., Shanley, J. B., & Wymore, A. S. (2021). Luquillo experimental forest: Catchment science in the montane tropics. *Hydrological Processes*, 35, 1–10. https://doi.org/10.1002/hyp.14146

McDowell, W. H., Magill, A. H., Aitkenhead-Peterson, J. A., Aber, J. D., Merriam, J. L., & Kaushal, S. S. (2004). Effects of chronic nitrogen amendment on dissolved organic matter and inorganic nitrogen in

soil solution. *Forest Ecology and Management*, 196, 29–41. https://doi.org/10.1016/j.foreco.2004.03.010

McDowell, W. H., McDowell, W. G., Potter, J. D., & Ramírez, A. (2019). Nutrient export and elemental stoichiometry in an urban tropical river. *Ecological Applications*, 29, 1–15. https://doi.org/10.1002/eap.1839

Miller, M. P., Boyer, E. W., McKnight, D. M., Brown, M. G., Gabor, R. S., Hunsaker, C. T., Iavorivska, L., Inamdar, S., Johnson, D. W., Kaplan, L. A., Lin, H., McDowell, W. H., & Perdrial, J. N. (2016). Variation of organic matter quantity and quality in streams at Critical Zone Observatory watersheds. *Water Resources Research*, 52, 8202–8216. https://doi.org/10.1002/2016WR018970

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., & Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, 450, 537–540. https://doi.org/10.1038/nature06316

Neff, J. C., Chapin, F. S., & Vitousek, P. M. (2003). Breaks in the cycle: Dissolved organic nitrogen in terrestrial ecosystems. *Frontiers in Ecology and the Environment*, 1, 205–211.

Pagano, T., Bida, M., & Kenny, J. (2014). Trends in levels of allochthonous dissolved organic carbon in natural water: A review of potential mechanisms under a changing climate. *Water*, 6, 2862–2897. https://doi.org/10.3390/w6102862

Pohlert, T. (2018). *Trend: Non-parametric trend tests and change-point detection*. R package version 1.1.0.

Räike, A., Kortelainen, P., Mattsson, T., & Thomas, D. N. (2012). 36 year trends in dissolved organic carbon export from Finnish rivers to the Baltic Sea. *Science of the Total Environment*, 435–436, 188–201. https://doi.org/10.1016/j.scitotenv.2012.06.111

R-Core-Team. (2016). *R: A language and environment for statistical computing*. R Foundation for Statistical Computing.

Redfield, A. C. (1958). The biological control of chemical factors in the environment. *American Scientist*, 46, 230A, 205–221.

Robinson, G. R. (1997). *Portraying chemical properties of bedrock for water quality and ecosystem analysis: An approach for the New England region*. USGS. https://doi.org/10.3133/ofr97154

Rodríguez-Cardona, B. M., Wymore, A. S., & McDowell, W. H. (2021). Nitrate uptake enhanced by availability of dissolved organic matter in tropical montane streams. *Freshwater Science*, 40, 65–76. https://doi.org/10.1086/713070

Rodríguez-Murillo, J. C., Zobrist, J., & Filella, M. (2015). Temporal trends in organic carbon content in the main Swiss rivers, 1974–2010. *Science of the Total Environment*, 502, 206–217. https://doi.org/10.1086/713070

Rüegg, J., Eichmiller, J. J., Mladenov, N., & Dodds, W. K. (2015). Dissolved organic carbon concentration and flux in a grassland stream: Spatial and temporal patterns and processes from long-term data. *Biogeochemistry*, 125, 393–408. https://doi.org/10.1007/s10533-015-0134-z

Ruoho-Airola, T., Anttila, P., Hakola, H., Ryyppö, T., & Tuovinen, J. P. (2015). Trends in the bulk deposition and atmospheric concentration of air pollutants in the Finnish Integrated Monitoring catchment Pallas during 1992–2012. *Boreal Environment Research*, 20, 553–569.

Ruoho-Airola, T., Hatakka, T., Kyllönen, K., Makkonen, U., & Porvari, P. (2014). Temporal trends in the bulk deposition and atmospheric concentration of acidifying compounds and trace elements in the Finnish Integrated Monitoring catchment Valkea-Kotinen during 1988–2011. *Boreal Environment Research*, 19, 31–46.

Schade, J. D., Espeleta, J. F., Klausmeier, C. A., Megan, E., Thomas, S. A., & Zhang, L. (2005). A conceptual framework for ecosystem stoichiometry: Balancing resource supply and demand. *Oikos*, 109, 40–51. https://doi.org/10.1111/j.0030-1299.2005.14050.x

Scheuerell, M. (2017). *muti: Calculates the mutual information between two vectors*. R package version 1.0.0. https://doi.org/10.5281/zenodo.439391

Schindler, D. W., Curtis, P. J., Bayley, S. E., Parker, B. R., Beaty, K. G., & Stainton, M. P. (1997). Climate-induced changes in the dissolved organic carbon budgets of boreal lakes. *Biogeochemistry*, 36, 9–28. https://doi.org/10.1023/A:1005792014547

Strååt, K. D., Mörth, C.-M., & Undeman, E. (2018). Future export of particulate and dissolved organic carbon from land to coastal zones of the Baltic Sea. *Journal of Marine Systems*, 177, 8–20. https://doi.org/10.1016/j.jmarsys.2017.09.002

Strauss, E. A., & Lamberti, G. A. (2002). Effect of dissolved organic carbon quality on microbial decomposition and nitrification rates in stream sediments. *Freshwater Biology*, 47, 65–74. https://doi.org/10.1046/j.1365-2427.2002.00776.x

Striegl, R. G., Aiken, G. R., Dornblaser, M. M., Raymond, P. A., & Wickland, K. P. (2005). A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. *Geophysical Research Letters*, 32, 1–4. https://doi.org/10.1029/2005GL024413

Veach, A. M., Dodds, W. K., & Skibbe, A. (2014). Fire and grazing influences on rates of riparian woody plant expansion along grassland streams. *PLoS One*, 9, 1–8. https://doi.org/10.1371/journal.pone.0106922

Vuorenmaa, J. (2004). Long-term changes of acidiyfing deposition in Finland (1973–2000). *Envrionmentl Pollution*, 128, 351–362. https://doi.org/10.1016/j.envpol.2003.09.014

Webster, J. R., & Meyer, J. L. (1997). Organic matter budgets for streams: A synthesis. *Journal of the North American Benthological Society*, 16, 141–161. https://doi.org/10.2307/1468247

Worrall, F., Harriman, R., Evans, C. D., Watts, C. D., Adamson, J., Neal, C., Tipping, E., Burt, T., Grieve, I., Monteith, D., Naden, P. S., Nisbet, T., Reynolds, B., & Stevens, P. (2004). Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry*, 70, 369–402. https://doi.org/10.1007/s10533-004-8131-7

Wymore, A. S., Brereton, R. L., Ibarra, D. E., Maher, K., & McDowell, W. H. (2017). Critical zone structure controls concentration-discharge relationships and solute generation in forested tropical montane watersheds. *Water Resources Research*, 53, 6279–6295. https://doi.org/10.1002/2016WR020016

Wymore, A. S., Johnes, P. J., Bernal, S., Brookshire, E. N. J., Fazekas, H. M., Helton, A. M., Argerich, A., Barnes, R. T., Coble, A. A., Dodds, W. K., Haq, S., Johnson, S. L., Jones, J. B., Kaushal, S. S., Kortelainen, P., López-Lloreda, C., Rodríguez-Cardona, B., Spencer, R. G. M., Sullivan, P. L., … McDowell, W. H. (2021c). Gradients of anthropogenic nutrient enrichment alter N composition and DOM stoichiometry in freshwater ecosystems. *Global Biogeochemical Cycles*, 35, e2021GB006953. https://doi.org/10.1029/2021GB006953

Wymore, A. S., Johnes, P. J., Bernal, S., Brookshire, E. N. J., Fazekas, H. M., Helton, A. M., Argerich, A., Barnes, R. T., Coble, A. A., Dodds, W. K., Haq, S., Johnson, S. L., Jones, J. B., Kaushal, S. S., Kortelainen, P., López-Lloreda, C., Rodríguez-Cardona, B. M., Spencer, R. G. M., Yates, C. A., & McDowell, W. H. (2021b). Stream Elemental Cycling (LTER Synthesis Working Group) ver 1. *Environmental Data Initiative*. https://doi.org/10.6073/pasta/50965f9e091ffa833da3c73bce2467fa

Wymore, A. S., Potter, J., Rodríguez-Cardona, B. M., & McDowell, W. H. (2018). Using in situ optical sensors to understand the biogeochemistry of dissolved organic matter across a stream network. *Water Resources Research*, 54, 2949–2958. https://doi.org/10.1002/2017WR022168

Wymore, A. S., Rodríguez-Cardona, B. M., Herreid, A., & McDowell, W. H. (2019). LINX I and II: Lessons learned and emerging questions. *Frontiers in Environmental Science*, 7, 181. https://doi.org/10.3389/fenvs.2019.00181

Wymore, A. S., Rodríguez-Cardona, B. M., & McDowell, W. H. (2015). Direct response of dissolved organic nitrogen to nitrate availability in headwater streams. *Biogeochemistry*, *126*, 1–10. https://doi.org/10.1007/s10533-015-0153-9

Wymore, A. S., Shattuck, M. D., Potter, J. D., Snyder, L., & McDowell, W. H. (2021a). The Lamprey River Hydrological Observatory: Suburbanization and changing seasonality. *Hydrological Processes*, *35*, 4. https://doi.org/10.1002/hyp.14131

Yates, C. A., Johnes, P. J., Owen, A. T., Brailsford, F. L., Glanville, H. C., Evans, C. D., Marshall, M. R., Jones, D. L., Lloyd, C. E. M., Jickells, T., & Evershed, R. P. (2019). Variation in dissolved organic matter (DOM) stoichiometry in U.K. freshwaters: Assessing the influence of land cover and soil C:N ratio on DOM composition. *Limnology and Oceanography*, *64*, 2328–2340. https://doi.org/10.1002/lno.11186

Zou, H., & Hastie, T. (2005). Regularization and variable selection via the elastic net. *Journal of the Royal Statistical Society. Series B: Statistical Methodology*, *67*, 301–320. https://doi.org/10.1111/j.1467-9868.2005.00503.x

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