Long-term change in the concentration-discharge relationship reveals controls on watershed exports of dissolved organic carbon

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Abstract

Dissolved organic carbon (DOC) export from watersheds by streams is an important, changing component of the global carbon cycle. We examined the controls on DOC export by quantifying changes in the DOC concentration-discharge relationship from 1992 through 2022 for nine forested headwater catchments at the Hubbard Brook Experimental Forest in the northeastern United States. We observed a strong increase in the intercept of the log-log concentration-discharge relationship between 2005 and 2017 and a weak increase in the slope of that relationship between 2002 and 2021, along with seasonal and watershed-level differences. The intercept, which indicates the average stream DOC concentration at a given discharge, was strongly and inversely related to ionic strength of the soil solution as predicted by electrolyte solubility theory. This relationship varied among watersheds, perhaps because of soil pH. The intercept was not strongly related to annual precipitation or air temperature. DOC export ranged from 13 to 153 kg C ha-1 y-1 among study watersheds and years, and was correlated with annual precipitation and discharge. Historical data suggest that DOC export has probably increased over the past 50 years, likely due both to increases in precipitation and runoff and to increases in the intercept and slope of the concentration-discharge relationship. Our results suggest the potential for long-term legacy effects of acidification on DOC solubility and stream DOC concentrations in acid-sensitive watersheds, despite reductions in acid deposition, as mineral weathering slowly replenishes the ionic strength of soil solutions.

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Key points

- We quantified long-term changes, and their causes, in the dissolved organic carbon concentration-discharge relationship in nine watersheds.
- The intercept of the log-log concentration-discharge relationship, and to some extent the slope, increased over the past 20 years.
- The ionic strength of the soil solution plays a central role in controlling watershed exports of dissolved organic carbon.

Abstract

Dissolved organic carbon (DOC) export from watersheds by streams is an important, changing component of the global carbon cycle. We examined the controls on DOC export by quantifying changes in the DOC concentration-discharge relationship from 1992 through 2022 for nine forested headwater catchments at the Hubbard Brook Experimental Forest in the northeastern United States. We observed a strong increase in the intercept of the log-log concentration-discharge relationship between 2005 and 2017 and a weak increase in the slope of that relationship between 2002 and 2021, along with seasonal and watershed-level differences. The intercept, which indicates the average stream DOC concentration at a given discharge, was strongly and inversely related to ionic strength of the soil solution as predicted by electrolyte solubility theory. This relationship varied among watersheds, perhaps because of soil pH. The intercept was not strongly related to annual precipitation or air temperature. DOC export ranged from 13 to 153 kg C ha^{-1} y^{-1} among study watersheds and years, and was correlated with annual precipitation and discharge. Historical data suggest that DOC export has probably increased over the past 50 years, likely due both to increases in precipitation and runoff and to increases in the intercept and slope of the concentration-discharge relationship. Our results suggest the potential for long-term legacy effects of acidification on DOC solubility and stream DOC concentrations in acid-sensitive watersheds, despite reductions in acid deposition, as mineral weathering slowly replenishes the ionic strength of soil solutions.

Plain language summary

Some of the organic carbon that plants produce via photosynthesis makes its way in dissolved form to streams, which carry it to the ocean. This movement of dissolved organic carbon is an important component of the global carbon cycle and strongly influences the structure and function of aquatic ecosystems. Over the past several decades, the amount of dissolved organic carbon that streams carry has been increasing in many parts of the world. We measured dissolved organic carbon in nine streams over three decades, and compared the patterns that we observed to data on climate and soil chemistry to understand what drives variation in dissolved organic carbon export. We observed substantial changes in the average dissolved organic carbon concentration of these streams over time. As predicted by theory, these changes were strongly related to the abundance of ions in the soil water. Our results help inform how dissolved organic carbon export from the land to streams and oceans will continue to change over the decades to come.

Introduction

The fluvial export of dissolved organic carbon (DOC) from watersheds is an important and changing component of terrestrial and aquatic carbon cycles. As a global flux it is similar in magnitude to net terrestrial C uptake and comprises roughly one third of the total carbon flux of 5.1 Pg C y^{-1} from terrestrial to aquatic ecosystems (Stets and Striegl 2012, Butman et al. 2016, Drake et al. 2018, Hararuk et al. 2022, Friedlingstein et al. 2023). Furthermore, once DOC is transported to aquatic ecosystems it plays a major role in controlling primary and secondary productivity and a host of other ecosystem processes (Jones 1992, Karlsson et al. 2009, Solomon et al. 2015, Creed et al. 2018, Olson et al. 2020). For both of these reasons there has been substantial interest in understanding ongoing long-term changes in DOC exports, which have been reflected in widespread increases in stream and lake DOC concentrations over the past several decades at a rate averaging around 1% per year across broad areas of northeastern North America and northern Europe (Monteith et al. 2007, de Wit et al. 2021, Rodríguez-Cardona et al. 2022).

Observed long-term changes in DOC concentrations of streams and lakes have been attributed to a variety of mechanisms that control inputs to and losses from the soil organic matter pool (Figure 1A). The relative importance of these mechanisms varies spatially and temporally (Clark et al. 2010). Two mechanisms that are particularly important for describing observed patterns are the effects of soil ionic strength and soil pH on the solubility and thus the mobility of organic matter in soils (de Wit et al. 2007, Monteith et al. 2007, 2023, Hruška et al. 2009, Lawrence and Roy 2021). The effects of these two mechanisms can be difficult to differentiate, because ionic strength and pH often covary and are to some extent intrinsically linked (Monteith et al. 2023). Decreases in ionic strength increase organic matter solubility because they lead to expansion of the diffuse double layer around organic colloids, making those colloids more polar (Thurman 1985, Tipping and Hurley 1988, Tipping and Woof 1991). Similarly, decreases in acidity (i.e. lower H^+ concentration and higher pH) increase organic matter solubility by favoring the deprotonation of weakly acidic functional groups, resulting in greater negatively charged sites and more polar behavior (Fakhraei and Driscoll 2015). Decreases in acidity also increase organic matter solubility via interactions with aluminum, an important coagulant of organic matter, which is less soluble at neutral pH (Cronan and Schofield 1990, Tipping and Woof 1991, Li and Johnson 2016). Decreases in soil ionic strength and increases in pH driven by decreases in atmospheric deposition of strong acids (and also of sea salt in some places) seem to be important drivers of observed increases in DOC concentrations of surface waters over the past several decades, particularly in watersheds where acid deposition was high and where low base cation availability makes soils sensitive to that deposition (Monteith et al. 2007, Driscoll et al. 2016, de Wit et al. 2021). Additional mechanisms that can contribute to changing surface water DOC concentrations include changes in soil organic matter inputs or losses driven by changes in terrestrial productivity, land use, and both the temperature and precipitation components of climate change (Erlandsson et al. 2008, Larsen et al. 2011, Singh et al. 2016, Kritzberg 2017, de Wit et al. 2021), and other processes that control the dynamics of organic matter within the soil (Kalbitz et al. 2000, Kaiser and Kalbitz 2012). Recent syntheses suggest that the effects of ionic strength, rather than pH, on organic matter solubility may be the primary control on observed long-term changes in stream DOC concentrations, and that climate-related mechanisms may be becoming more important as the scope for further reductions in atmospheric deposition of strong acids (and thus also changes in soil ionic strength) declines (de Wit et al. 2021, Monteith et al. 2023).

Because fluvial DOC export is the (time-integrated) product of stream discharge and DOC concentration, any mechanism that alters export must manifest in one of three ways: as a change in discharge, in the average DOC concentration at a given discharge, or in the rate at which DOC concentration changes with discharge. The latter two quantities are represented by the scaling coefficient and exponent of a power-law concentration-discharge relationship, or equivalently by the intercept and slope of the log-log transformed version of this relationship, which we will focus on here. These two parameters should vary systematically in response to the mechanistic controls on DOC export (Figure 1B). For instance, one useful distinguishing feature of DOC concentration-discharge relationships is whether they have positive, zero, or negative slopes. The DOC concentration-discharge relationship is typically positive in watersheds where organo-mineral soils predominate, because as the volume of water draining off the landscape increases, the proportion of water transported through organic-rich surface soils increases relative to the proportion through deeper mineral soils with lower concentrations of soil organic matter which is more strongly retained by mineral surfaces (McDowell and Wood 1984, Sebestyen et al. 2008, Pellerin et al. 2012). In contrast, the concentration-discharge relationship is generally flat or even negative in organic peat soils, where the dependency of DOC yield on the depth of flowpaths is weaker but where high runoff may flush pore waters more rapidly than they can accumulate new DOC (McDowell and Likens 1988, Schiff et al. 1998, Clark et al. 2010). Beyond these coarse differences in the sign of the slope, the actual magnitude of both the slope and the intercept of the concentration-discharge (or flux-discharge) relationship are related to watershed properties such as topography and land cover, and to climatic conditions (Zarnetske et al. 2018).

In this study we explored the effects of long-term environmental change on DOC export by examining variation in the concentration-discharge relationship for DOC, and variation in stream discharge itself, in nine watersheds over a period of 30 years at the Hubbard Brook Experimental Forest, NH. A number of previous studies have examined changes in DOC concentration-discharge relationships over shorter periods to reveal important controls on DOC export (e.g. Ågren et al. 2010), and data on long-term changes in DOC concentrations are relatively abundant (e.g. de Wit et al. 2021). Yet consideration of changes in DOC concentration-discharge relationships over multiple decades is exceedingly rare, despite the demonstrated utility of such analyses for understanding the dynamics of DOC and other solutes (Huntington and Shanley 2022, Creed et al. 2025). During the study period all watersheds experienced similar changes in large-scale drivers of DOC export such as acid deposition and climate, and some were subjected to watershed-scale experimental manipulations that may also have altered DOC export. We therefore tested two specific hypotheses concerning the effects of long-term change and inter-watershed differences on DOC export. First, we hypothesized that the intercept of the DOC concentration-discharge relationship would increase through time in all watersheds. We anticipated that this increase would be driven largely by changes in DOM mobility resulting from the long-term trajectory of acid deposition and recovery in these watersheds, and that therefore the intercept of the concentration-discharge relationship would be correlated with increasing soil pH and decreasing soil ionic strength. We also expected that the intercept might vary with mean annual temperature or precipitation, given the potential effects of these climate variables on inputs to and respiratory losses from the soil organic matter pool (Figure 1) and recent observations of increasing climate dependence of DOC concentration trends (de Wit et al. 2021). Second, we hypothesized that the slope of the DOC concentration-discharge relationship might also change through time, due to differential changes in the DOC yield of frequently- and rarely-connected contributing areas, or to changes in average flow paths (Figure 1B). Finally, in addition to testing these hypotheses we combined our estimates of the DOC concentration-discharge relationship with data on stream discharge to estimate DOC export and explore inter-annual variation in export.

Methods

Study system

We studied nine forested, headwater watersheds at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, USA (43° 56′ N, 71° 45′ W). The area of these watersheds ranges from 11.8 to 77.4 ha. Elevations range from 442 to 685 m at the watershed outlets, and from 716 to 910 m at the ridgetops. Watersheds 1 through 6 are south-facing, while Watersheds 7 through 9 are north-facing; all drain to the mainstem Hubbard Brook, and almost all drainage from the watersheds occurs as streamflow, not groundwater flow (Verry 2003, Likens 2013). Aside from a small wetland in the upper portion of Watershed 9 (0.8 ha; 1.2% of watershed), land cover is predominantly northern hardwood forest, with spruce-fir forest at higher elevations (van Doorn et al. 2011, Cawley et al. 2014). The soils are relatively shallow Spodosols developed on glacial till, which vary with landscape position due to the effects of lateral water flow on soil development (Bailey et al. 2014). The climate is cool, humid, and continental, and temperature, precipitation, and streamflow have been increasing over the long term (Campbell et al. 2021, 2022). Additional details about the site are available elsewhere (e.g. Likens 2013).

Long-term changes, natural disturbances, and experimental manipulations, all of which might influence DOC exports, have occurred in the study watersheds. All of the study watersheds have been exposed to multi-decadal changes in atmospheric acid deposition, which peaked in the 1960s and 1970s and has since declined substantially (Likens et al. 2021). This legacy of acid deposition has severely depleted available base cations from the soils, among other impacts (Likens et al. 1996, 1998). Watershed 2 was clear-cut in autumn 1965, and subsequently treated with herbicide for three growing seasons to suppress regrowth (Likens et al. 1970). Watershed 4 was strip-cut between 1970 and 1974 (Hornbeck et al. 1986). A whole-tree harvest of Watershed 5 was conducted in 1983-1984 (Dahlgren and Driscoll 1994). A severe ice storm occurred in January 1998, causing severe canopy damage in portions of the south-facing watersheds (Rhoads et al. 2002, Houlton et al. 2003). Finally, pelletized wollastonite ($CaSiO_3$) was applied by helicopter to Watershed 1 in November 1999 (Shao et al. 2015).

Our study period extends from the beginning of regular DOC monitoring in these watersheds on 31 August 1992, through the end of the 2021 water year on 31 May 2022. The water year in our study system is usually defined as running from 1 June through 31 May, and we use this convention here (Likens 2013).

Stream discharge and DOC concentration

The hydrologic discharge of the stream draining each of the watersheds is measured continuously at the outlet of each watershed with a V-notch weir, and a San Dimas flume in some instances, and total daily discharge is calculated by integration (USDA Forest Service, Northern Research Station 2022). To facilitate comparisons among watersheds of different drainage areas we use the specific discharge (discharge divided by watershed area; units mm y^{-1}).

The DOC concentration of each stream is measured at least weekly whenever the stream is flowing, in samples collected just upstream of the weir (HBWatER 2023). These routine weekly DOC measurements began in August 1992 in Watershed 6, and in May 1995 in Watersheds 7 through 9. Watersheds 1 through 5 were added to the sampling regime later, and all nine watersheds have been included since December 2012. Before May 1995 DOC was measured by colorimetric CO_2 detection on a Technicon II after persulfate digestion. Since June 1995, DOC has been measured by infrared CO_2 detection on a Shimadzu total organic carbon analyzer after high-temperature combustion. The first method has a negative bias of 0.17 mg C L^{-1} relative to the second, perhaps because of incomplete digestion (Buso et al. 2000); we corrected for this bias before conducting our statistical analyses. Water samples for DOC analysis were unfiltered in the early years of the sampling program, but beginning between January and March 2005 all samples have been filtered through pre-combusted Whatman GF/F 0.7 μm pore size filters prior to analysis. We did not correct measured concentrations for this change in filtering because analysis of paired samples indicated that DOC concentrations after filtering were on average 98.8 to 99.6% of concentrations before filtering (Buso, unpublished). Buso et al. (2000) provide additional details on analytical methods.

For some water year by watershed combinations fewer than 52 measurements of DOC were available, for instance when regular sampling in that watershed started part way through a water year or when stream discharge ceased during the summer. We eliminated from our analysis ten water year by watershed combinations for which fewer than 26 DOC measurements were available, leaving 182 water year by watershed combinations with between 26 and 296 DOC measurements each (mean 59, median 53; total number of measurements across all water years = 10,759).

Soil solution chemistry

We sampled freely-draining soil solutions approximately monthly using tension-free lysimeters installed in Watershed 1 and adjacent to Watershed 6 (Fuss et al. 2015, LoRusso et al. 2021, Driscoll 2025a, 2025b). In each watershed, lysimeters were installed in organic and mineral soil horizons in each of three different elevation zones; we focus on lysimeters installed below the Oa horizon in high-elevation spruce-fir-beech habitats because these areas make important contributions to stream DOC in our study region (Gannon et al. 2015), but note that patterns in ionic strength and pH were similar in other elevation zones and soil horizons (Figure S1, Figure S2). We calculated the ionic strength of the soil solution from the concentrations of the ions Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, H^+, SO_4^{2-}, NO_3^-, HCO_3^-, Cl^-, and F^-, as:

$$[1] \qquad ionic\ strength = 0.5 * \Sigma c_i (z_i)^2$$

where c_i is the concentration (mol L^{-1}) and z_i the charge of ionic solute i. The HCO_3^- concentration was estimated from the measured DIC concentration and pH using the AquaEnv package (Hofmann et al. 2010), the H^+ concentration was calculated from the measured pH, and the Al^{3+} concentration was estimated as the difference between measurements of total monomeric aluminum and organic monomeric aluminum; all the other ions were directly measured. Methods for chemical analysis are described by Driscoll (2025a, 2025b).

Climate

Daily precipitation was estimated in each watershed from a network of rain gauges, using the Thiessen means method through 2014 and an inverse distance weighting method thereafter (USDA Forest Service, Northern Research Station 2024a). We summed these daily estimates to obtain total precipitation in each watershed and water year. We also calculated mean air temperature for each water year from daily temperature measurements taken near the base of the south-facing watersheds (USDA Forest Service, Northern Research Station 2024b).

Statistical analysis

We fit four candidate models to describe the relationship between DOC concentration and stream discharge. All statistical analyses were performed in R (R Core Team 2023). The most complex model was a hierarchical or mixed-effects regression:

$$[2] \qquad \log_e([DOC]_{ijk}) = \beta_{0,jk} + \beta_{1,jk}\log_e(Q_{ijk} + 0.0001) + \beta_2 \sin(2\pi i) + \beta_3 \cos(2\pi i)$$

Where [DOC] is the dissolved organic carbon concentration in mg L^{-1}, Q is the specific discharge in mm d^{-1}, $\log_e()$ indicates the natural logarithm, and the subscripts *i, j*, and *k* indicate respectively the day of the water year expressed as a fraction between 0 and 1; the water year; and the watershed. This model allows the intercept (β_0) and slope (β_1) of the log-log concentration-discharge relationship to vary by water year, watershed, and the interaction of water year and watershed, and assumes that those random effects are normally distributed with a mean of zero. It also includes, in the last two terms, a sinusoidal seasonal cycle in the average log([DOC]) at a given discharge (Cohn et al. 1992). As alternatives, we considered a hierarchical model identical to Model 1 but lacking the seasonal component; a fixed-effects model including the seasonal component but allowing only a single β_0 and a single β_1 across all water years and watersheds; and a fixed effects model with a single β_0, single β_1, and no seasonal component. We fit the hierarchical models by maximum likelihood using the lmer() function (Bates et al. 2015), and the fixed-effects models by least squares using the lm() function, and then compared the predictive power of the models using AIC. The most complex hierarchical model was far superior to the others, and we re-fit this model using restricted maximum likelihood to ensure that we reported unbiased variance estimates.

We used standard regression models to test our hypothesis that changes in the intercept of the DOC concentration-discharge relationship would be related to changes in soil solution chemistry and climate. We constrained this analysis to Watersheds 1 and 6, because these were the only two watersheds for which long-term soil solution chemistry data are available. The response variable in these models was the set of watershed- and year-specific estimates of β_0 from the hierarchical concentration-discharge model described above, weighted by their inverse variances. The predictor variables included the inverse square root of soil solution ionic strength (Debye and Hückel 1923, Monteith et al. 2023), soil solution pH, total annual precipitation, mean annual temperature, watershed, and the interaction of watershed with each of the continuous predictors. We fit the full model and all of its subsets on the Z-transformed variables, and examined in more detail the model with the lowest AICc and all other models within 4 AICc units of that best model (Barton 2024). For completeness we used the same procedure to consider models for β_1, the slope of the DOC concentration-discharge relationship.

Results

Concentration-discharge relationships

The concentration-discharge relationship for DOC varied among watersheds and years, as well as seasonally (Figure 2, Table 1). The model that allowed the intercept and slope of the concentration-discharge relationship to vary by watershed, year, and watershed:year, and included seasonal effects, was far superior to any of the other candidate models that we considered (ΔAIC > 6000). This model explains 90% of the variance in the log-transformed DOC concentration. Variation in the slope and intercept of the concentration-discharge relationship among watersheds and years accounts for most of the explained variance; only 15% of the variance in log-transformed DOC is attributable to the fixed intercept, slope, and seasonal effects. Estimates of the intercept ranged from 0.15 to 2.21, and estimates of the slope from 0.05 to 0.25, depending on the watershed and water year and setting aside the seasonal effect (Figure S3; note that units of these parameters are on the scale of the $\log_e$-transformed concentration and discharge). The fitted seasonal trend indicates that the DOC concentration at a given discharge reaches a maximum in late August and a minimum in late February, on average, and the amplitude of this seasonal cycle (the difference in $\log_e$(DOC) between the peak and midpoint of the cycle) is 0.25.

Among watersheds there were substantial differences in the intercept, and smaller differences in the slope, of the concentration-discharge relationship for an average year (Figure 3). The intercept, which indicates the average DOC concentration at a given discharge, was very high in Watershed 9, somewhat high in Watershed 8, and somewhat low in Watershed 2, relative to the other watersheds (Figure 3A). The slope, which indicates the rate at which DOC concentration increases with increasing discharge, was very high in Watershed 8, somewhat high in Watershed 9, and somewhat low in Watershed 2, relative to the other watersheds (Figure 3B).

The intercept of the concentration-discharge relationship, and to some extent the slope, also changed considerably through time (Figure 4). The intercept fluctuated between 1992 and 2003, declined between 2003 and 2005, and increased fairly steadily from 2005 through 2017 (Figure 4A). In contrast, temporal patterns in the slope were much less pronounced relative to their average values and uncertainties, but there is some suggestion of a decline and recovery between 1997 and 1999, and a weak upward trend from 2002 through 2021 (Figure 4B, Figure S3). Changes in the concentration-discharge relationship through time were similar, but not identical, across the different watersheds (Figure S3).

Environmental conditions

Soil solution chemistry and climatic conditions varied substantially over the study period (Figure 5). Ionic strength of the soil solution decreased at a similar rate in both watersheds, to approximately $1.8*10^{-4}$ in Watershed 1 and $1.4*10^{-4}$ in Watershed 6 by 2021. This decrease occurred largely during the middle portion of the study period, and ionic strength was relatively stable beginning around 2015. Soil acidity also decreased (pH increased), particularly in Watershed 1 after the 1999 wollastonite addition. Mean annual temperature and total annual precipitation also increased over the study period. Stream discharge was highly correlated with precipitation ($r=0.86$ to 0.94 across the nine watersheds).

Drivers of change in concentration-discharge relationships

The ionic strength of the soil solution was a strong predictor of variation in the intercept (β_0) of the DOC concentration-discharge relationship among watersheds and water years (Figure 6). This result indicates that the average DOC concentration at any given level of discharge increases as the ionic strength of the soil solution decreases. A model including only ionic strength and watershed as predictors, and allowing the effect of ionic strength to vary among watersheds, had the highest predictive ability among all the candidate models that we considered ($\Delta AICc \geq 0.98$, $R^2=0.56$; Table S1). All other plausible models (those with $\Delta AICc < 4$) also included the ionic strength and watershed terms, sometimes in combination with terms for pH, annual precipitation, mean annual temperature, or their interactions with watershed. These additional terms did not substantially increase the explained variance, and with the exception of a positive pH term and a pH:watershed term in some models, their confidence intervals overlapped zero.

As expected, variation in the slope (β_1) of the DOC concentration-discharge relationship was not strongly related to soil ionic strength, soil pH, annual precipitation, or mean annual temperature. The best model of variation in the slope included only a term for watershed and had low explanatory power ($\Delta AICc \geq 1.13$, $R^2=0.19$, Table S2).

Export

Export of DOC from the study watersheds varied among watersheds and water years (Figure 7). The median annual export was 104 kg C ha^{-1} in Watershed 9, 42 kg C ha^{-1} in Watershed 8, and 15-26 kg C ha^{-1} in the other watersheds. There was a slight increasing trend in export through time, although this trend did not explain a significant portion of the variation in export in a linear model that also included watershed as a predictor (estimated slope of log(export) on year = 0.0048 ± 0.0021 SE; $F_{1,172}$=2.1, p=0.15). Inter-annual variability in export was substantial (CV 19-26%, depending on watershed), and was highly correlated with total annual discharge or precipitation (r>0.93, p<0.0001; Figure 5). Median annual DOC concentrations ranged from approximately 1 to 10 mg C L^{-1}, depending on the watershed and year (Figure S4).

Discussion

By quantifying changes in the DOC concentration-discharge relationship through time in multiple watersheds and relating those changes to hypothesized drivers within a mechanistic framework, we gained new insights into the controls on DOC export in our study ecosystem. Our results provide strong evidence that soil ionic strength, and to a lesser extent soil pH, control the solubility of soil organic matter and thus the average stream DOC concentration at any level of stream discharge. These effects of soil solution chemistry on the intercept of the concentration-discharge relationship, combined with smaller changes in the slope of that relationship and with the important effects of total discharge, controlled patterns of DOC export across space and time.

Our finding that soil ionic strength was the best predictor of variation in the intercept of the concentration-discharge relationship is consistent with the model of DOC solubility recently proposed by Monteith et al. (2023). This model assumes that ionic strength is a primary regulator of organic matter solubility in soils, and that solubility increases in proportion to the inverse square root of ionic strength (Debye and Hückel 1923). Monteith and colleagues tested this model in European streams, and found the electrical conductivity of precipitation, as a proxy for soil ionic strength, explained most of the observed long-term change in stream DOC concentrations. Our study finds a similar pattern but takes a step closer to the hypothesized mechanism by relating the average stream DOC concentration at a given discharge to actual soil solution ionic strength measurements rather than the proxy (we also found that these measurements and the proxy are reasonably well correlated at the annual scale, Spearman's ρ=0.58). Unlike the analysis by Monteith and colleagues, our analysis does not suggest that the effects of temperature-dependent microbial degradation are an important control on organic matter solubility in the soil horizons that contribute DOC to the stream, but this may be because we considered mean annual temperature while they focused on shorter time windows.

Our results also provide compelling evidence of the effects of soil pH on organic matter solubility, separate from the effects of soil ionic strength. Separating these effects has often been challenging in previous studies, because many regions impacted by acid deposition have experienced simultaneous changes in both the ionic strength and the pH of the soil solution. In our analysis we were able to address this limitation by comparing Watershed 1, which was experimentally enriched with wollastonite to increase its soil calcium and alkalinity, to Watershed 6, a nearby unmanipulated reference watershed. The rate at which the intercept of the DOC concentration-discharge relationship changed with a given change in soil ionic strength was higher in Watershed 1 than in Watershed 6 (Table S1, Figure 6), and we hypothesize that this difference reflects the effects of pH. Soil pH was substantially higher in Watershed 1 than in Watershed 6, particularly after the wollastonite addition midway through the 1999 water year (Figure 5). Furthermore, in Watershed 1 the increase in pH over time kept pace with the decrease in ionic strength, whereas in Watershed 6 after about 2005 the increase in pH was limited relative to the decrease in ionic strength (Figure 5, Figure S5). Higher soil pH might increase organic matter mobility in Watershed 1 in at least two ways: by enhancing dissociation of weak organic acids (Fakhraei and Driscoll 2015), and by increasing rates of microbial activity and thus the availability of more soluble, microbially-processed humic materials (LoRusso et al. 2021, Possinger et al. 2025). In some soils higher pH also limits coagulation of organic matter by aluminum, but this may be a minor effect currently in our watersheds because inorganic aluminum concentrations are low following recovery from acidification (Fuss et al. 2015).

The wollastonite addition also likely explains one puzzling anomaly that we observed: a substantial increase in the intercept of the concentration-discharge relationship in Watershed 1 between the 1998 and 1999 water years, even as the intercept in all the other watersheds decreased (Figure S3). This pattern does not seem to be attributable to the effects of the wollastonite addition on the ionic strength and pH of the soil solution, because in the immediate aftermath of the addition the increase in pH in Watershed 1 was not substantially different from the trend in reference Watershed 6, and the ionic strength may have decreased (Figure 5, Figure S1). Instead, we suspect that the increase in the DOC concentration-discharge intercept in Watershed 1 during this period was due to the mobilization of the organic carbon in the highly water-soluble lignin sulfonate binder that was used to help pelletize the finely ground wollastonite in the experimental treatment (Peters et al. 2004).

A gradual increase in the slope of the DOC concentration-discharge relationship beginning around the mid-2000s may be a regional phenomenon. A study at Sleepers River, Vermont, 60 km from our study site, found that the slope of the concentration-discharge relationship was steeper when fit to recent observations between 2002 and 2018 than when fit to earlier ones between 1991 and 2002 (Huntington and Shanley 2022). If we compare our estimates of the slope for the period starting in 2002 to those for the period up to and including 2002, we see some evidence of a similar, albeit small, steepening (mean slope of 0.13 during the recent period and 0.12 during the earlier period; $t_{20.9}$=-1.89, p=0.07). This steepening indicates an increase in the rate at which the mean DOC yield of the soil units contributing to stream flow increases as water yield from the landscape increases, which could be occurring for either or both of two reasons (Figure 1). First, average flow paths could be changing, routing a higher proportion of runoff through organic-rich soils (e.g. Gannon et al. 2015). Increasing frequency and intensity of summer storms at our study site could contribute to such a change, although analysis of storm recession curves does not suggest any change in flow paths over the period of record (Green and Bernhardt unpublished). Second, the DOC yield of these soil units that contribute to stream flow only under high flow conditions might be increasing faster than (or decreasing slower than) the DOC yield of soil units that regularly contribute to stream flow. Decreases in soil ionic strength and increases in pH could produce this pattern if they progressed faster in the rarely-contributing O horizon than in lower soil horizons, but we see no evidence for this pattern in our data (Figure S1, Figure S2). Alternatively, inputs to or losses from the soil organic matter pool, or soil frost effects on the availability of organic matter for export, might be changing differently in rarely-contributing soil units than in regularly contributing ones (Tiwari et al. 2018, Huntington and Shanley 2022).

The inter-watershed patterns that we observed in the intercept and slope of the DOC concentration-discharge relationship (Figure 3) were broadly consistent with previous literature. An analysis of over 1000 first- through tenth-order streams across the conterminous United States identified steepness, wetland cover, mean annual precipitation, and deciduous forest cover as the most important controls on the intercept of the log-log relationship between discharge and DOC flux (i.e. concentration multiplied by discharge; Zarnetske et al. 2018). The one watershed in our study for which the intercept of the concentration-discharge relationship was substantially higher than the others, Watershed 9, also has substantially lower steepness, higher wetland cover, and substantially lower deciduous forest cover than all the other watersheds (Cawley et al. 2014). For each of these three predictors, the difference between Watershed 9 and the other watersheds is consistent with a higher predicted intercept in the model of Zarnetske et al. (2018). Inter-watershed differences in the slope of the concentration-discharge relationship among our study watersheds were not as pronounced as differences in the intercept, but

Watershed 8, and to some extent Watershed 9, did have a markedly higher slope than the other watersheds, perhaps due to their high evergreen forest cover (90% and 96%, respectively). Evergreen forest cover was one of the strongest predictors of the slope of the DOC flux-discharge relationship in the analysis of Zarnetske et al. (2018). Those authors saw that watersheds which exceeded 50% evergreen cover tended to have positive flux-discharge slopes and attributed this pattern to the effects of evergreen forest cover on DOC production. Our conceptual model suggests a slight modification to that interpretation, emphasizing that it is not just the production of DOC that matters, but the differential production (and respiration and mobility) of DOC in soil units that are rarely or regularly connected to the hydrologic network (Figure 1). Positive, "transport-limited" concentration-discharge relationships arise not from increases in organic matter inputs to soils per se, but rather because those inputs are concentrated in soil units, like the O horizon, which become connected to the hydrologic network only under water-rich conditions that also lead to high stream discharge. Furthermore, while watersheds with <50% evergreen cover or <20% wetland cover tend to show "source-limited" negative relationships between DOC flux and discharge (Zarnetske et al. 2018), our results in Watersheds 1 through 6, all of which have ≤19% evergreen cover and 0% wetland cover, emphasize that "transport limitation" does occur under such conditions. In our watersheds this may be in part because organic, shallow-to-bedrock soils in the upper reaches of the watershed quickly saturate during precipitation events and deliver DOC to channel heads without substantial interactions with mineral soil in which DOC might be immobilized (Gannon et al. 2015, LoRusso et al. 2021). A corollary point is that so-called "source-limited", negative concentration-discharge relationships may not necessarily arise from an actual limitation of DOC sources; even if carbon sources are abundant on the landscape, a negative concentration-discharge relationship can occur if adding water to the landscape does not change which soil units are hydrologically connected in such a way as to increase the mean DOC yield of all contributing areas.

Exports of DOC from watersheds to surface waters have changed substantially over the past several decades and are likely to continue to change in complex ways for decades to come. Between 1976 and 1980, DOC export from the Bear Brook watershed, which is mostly comprised of Watersheds 5 and 6, ranged from 17 to 24 kg C ha^{-1} y^{-1} (McDowell and Likens 1988). Since 2005, however, export from Watershed 6 has exceeded 24 kg C ha^{-1} y^{-1} in half of all years, and the mean export from Watersheds 5 and 6 was 21 and 25 kg ha^{-1} y^{-1}, respectively (Figure 7). This apparent long-term increase in DOC export arises both from an increase in precipitation and runoff (Green et al. 2021) and from an increase in the average amount of DOC that the watersheds yield at any level of runoff, driven largely by changes in soil ionic strength (Figure 4). More generally, future long-term trends in the average stream DOC concentration at a given discharge may vary from one watershed to the next, despite identical changes in atmospheric deposition, climate, and other drivers, due to differences in soil properties or history of acidification. In watersheds like those at Hubbard Brook, where previous acid deposition has stripped available nutrient cations from the soil and greatly reduced soil ionic strength, DOC solubility and stream DOC concentrations may decline from their current elevated levels only very gradually over many years, despite substantial reduction in acid deposition and recovery of soil pH, as soil ionic strength is very gradually replenished by the slow process of mineral weathering (Lawrence and Roy 2021). Watersheds that experienced smaller changes in soil ionic strength, due to better initial buffering or lower acid deposition, should see more rapid recovery from any small increases in DOC solubility and stream concentration. Both acid-sensitive and acid-resistant watersheds are also experiencing ongoing climate change, which may impact DOC exports via the intercept or slope of the DOC concentration-discharge relationship or via changes in discharge itself. Our analysis suggests that these climate effects may manifest first via the effects of hydrologic intensification on average flowpaths (and thus the slope of the concentration-discharge relationship) and total discharge, but ultimately changes in precipitation and temperature may also influence both the slope and intercept of the concentration-discharge relationship via effects on primary production, respiration, and the size and nature of soil organic matter pools. Building a mechanistic and predictive understanding of these complex dynamics remains an important challenge for future research.

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Data availability statement

All of the data used in this paper are available in public repositories with DOIs, which are cited throughout the manuscript and code. All code to access those data and reproduce the analyses and figures is available at https://github.com/ctsolomon/HB-DOC (doi: 10.5281/zenodo.15882497)

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Table 1. Summary of the model describing the relationship between DOC concentration and stream discharge (Equation 2, fit by restricted maximum likelihood to log-transformed concentration and discharge). Point estimates ± 1 SE are shown for the fixed effects, followed by the standard deviations of any random effects. The model was fit to 10,759 observations of DOC concentration across 30 water years, 9 watersheds, and 182 water year by watershed combinations.

Model component		Estimate
Intercept	β_0	0.825 ± 0.165
Water year	σ_j	0.086
Watershed	σ_k	0.493
Water year : Watershed	σ_{jk}	0.061
Slope	β_1	0.127 ± 0.013
Water year	σ_j	0.016
Watershed	σ_k	0.039
Water year : Watershed	σ_{jk}	0.019
Seasonal cycle	β_2	0.249 ± 0.003
	β_3	0.032 ± 0.003
$\sigma_{residual}$		0.182
marginal R^2=0.145, conditional R^2=0.905		

Figure 1

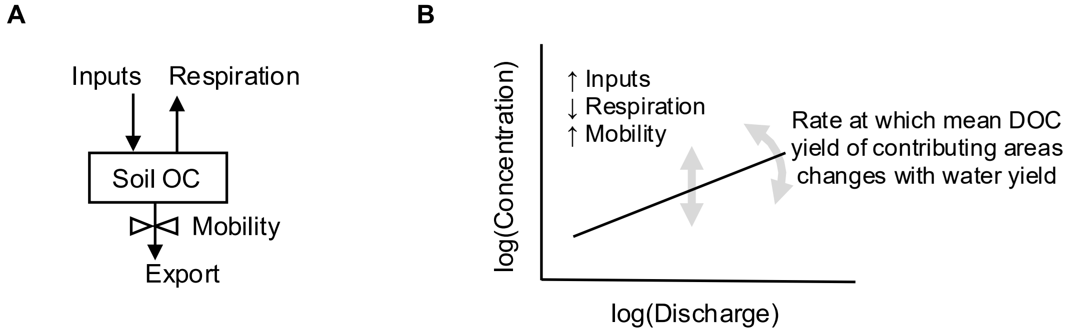

Figure 1. (A) DOC exports from watersheds depend mechanistically on inputs to, respiratory losses from, and thus the size of the soil organic matter pool; on chemical reactions that control organic matter mobility; and on hydrologic flows and flowpaths (see e.g. Kalbitz et al. 2000, Futter et al. 2007, Clark et al. 2010). (B) Differences in these mechanisms across space or time are manifested in the concentration-discharge relationship. The intercept of the log-log concentration-discharge relationship shifts upwards in response to greater inputs, lower respiratory losses, or higher DOM mobility across all contributing areas. The slope pivots upwards if there is an increase in the rate at which the mean DOC yield of all contributing areas increases with water yield from the landscape; this could occur due to differential changes in the DOC yield of frequently- and rarely-connected contributing areas, or due to changes in average flow paths.

Figure 2

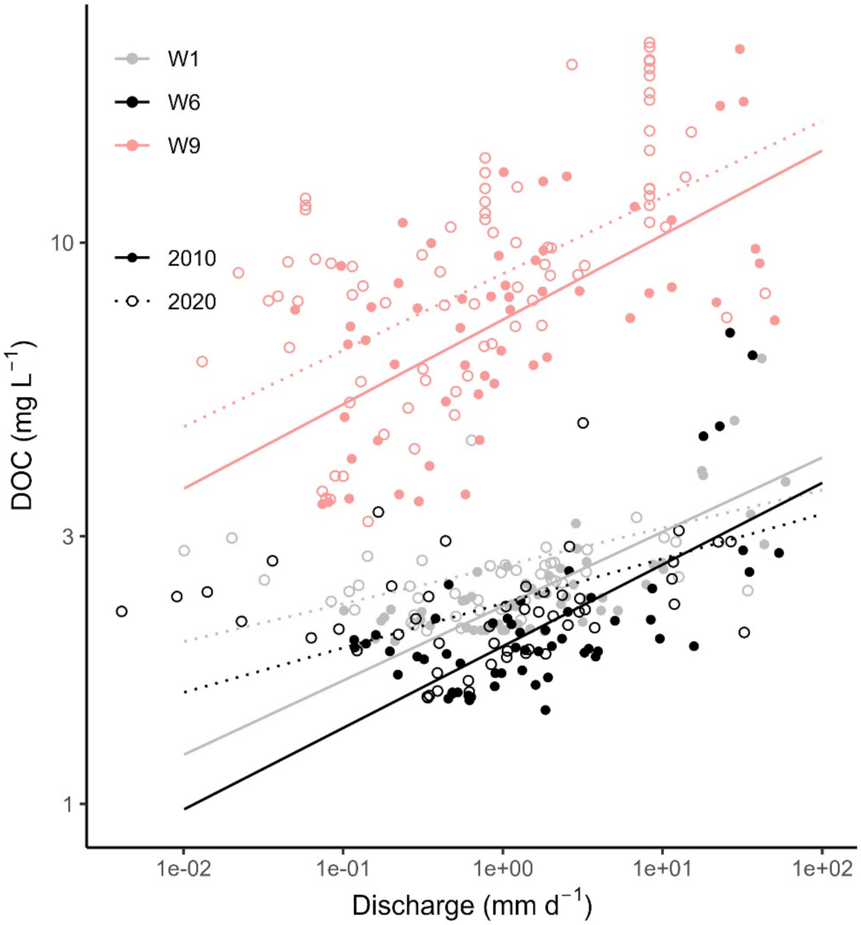

Figure 2. Data and model fits for three watersheds in two water years, to illustrate the full data set and model (which include 9 watersheds, 30 water years, and 182 water year by watershed combinations). For each watershed-year combination, the line gives the model fit at the midpoint of the seasonal cycle; additional variation parallel to the fitted line is accounted for by the seasonal cycle, which is not shown here. Filled points and solid lines indicate data and fits for 2010; hollow points and dotted lines indicate data and fits for 2020; and colors indicate different watersheds.

Figure 3

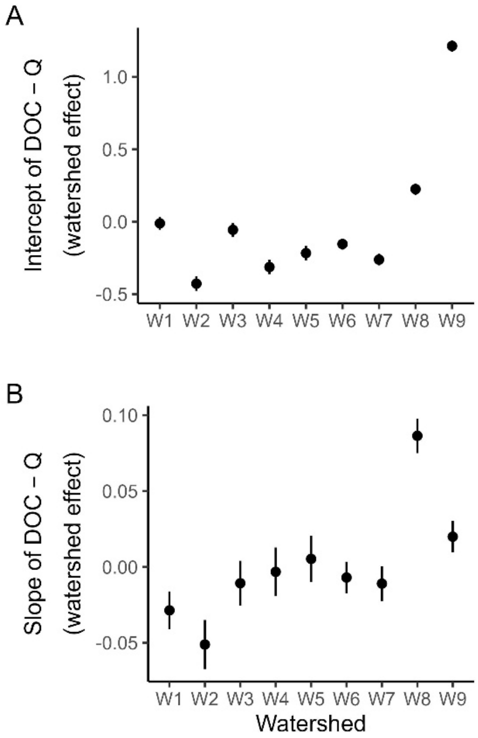

Figure 3. Differences among watersheds in the relationship between DOC concentration and stream discharge. Points are the estimated watershed effects, for the average water year and at the midpoint of the seasonal cycle, on the intercept (A) and slope (B) of the concentration-discharge relationship (see Fig. 4 for estimated water year effects, and Fig. S3 for the full coefficient estimates including watershed, water year, and interaction effects). Error bars indicate 95% confidence intervals; note that in panel A the confidence intervals are narrow and largely hidden by the points.

Figure 4

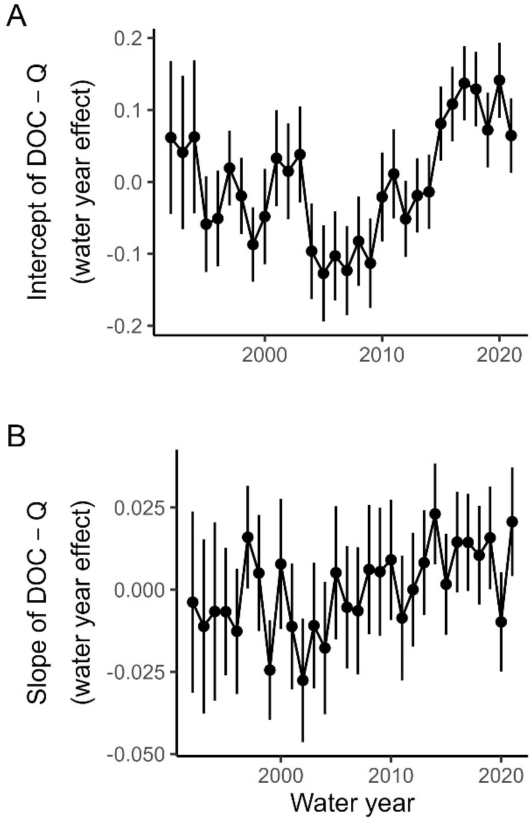

Figure 4. Differences among years in the relationship between DOC concentration and stream discharge. Points are the estimated year effects, for the average watershed and at the midpoint of the seasonal cycle, on the intercept (A) and slope (B) of the concentration-discharge relationship (see Fig. 3 for estimated watershed effects, and Fig. S3 for the full coefficient estimates including watershed, water year, and interaction effects). Error bars indicate 95% confidence intervals.

Figure 5

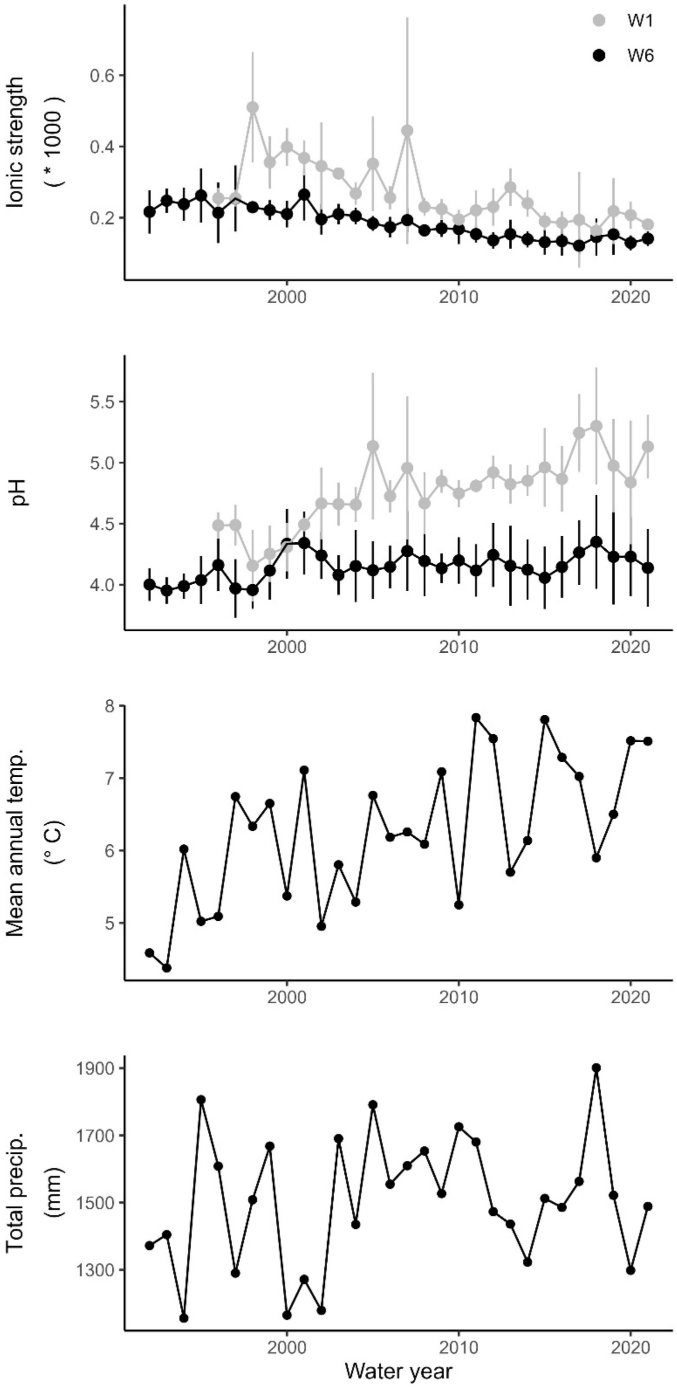

Figure 5. Soil solution ionic strength, soil solution pH, mean annual temperature, and total annual

795 precipitation in the study watersheds. Soil solution data are shown for watersheds 1 and 6. Error bars indicate ± 1 SD.

Figure 6

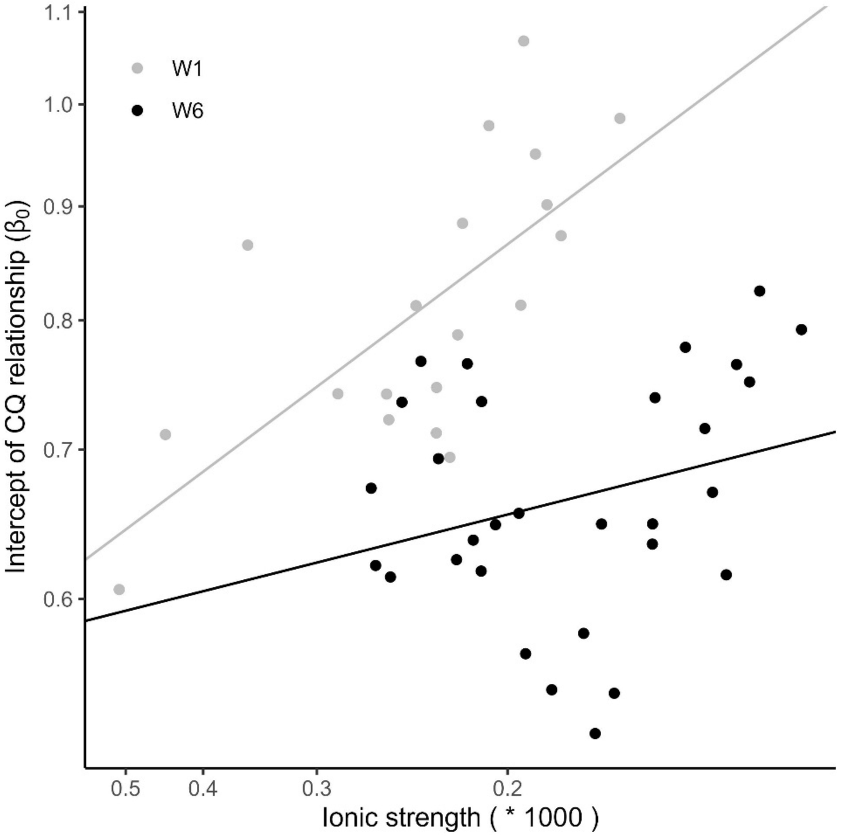

Figure 6. In Watersheds 1 and 6, variation among watersheds and water years in the intercept of the DOC concentration-discharge relationship (β_0; y-axis) is related to the ionic strength of the soil solution (x-axis). Lines show fits from the model with the highest ability to predict variation in β_0 (Model 1 in Table S1). Note that ionic strength is plotted on an inverse square root scale, in keeping with the theoretically expected relationship between organic matter solubility and ionic strength (Debye and Hückel 1923, Monteith et al. 2023); thus low values of ionic strength are at the right of the figure.

Figure 7

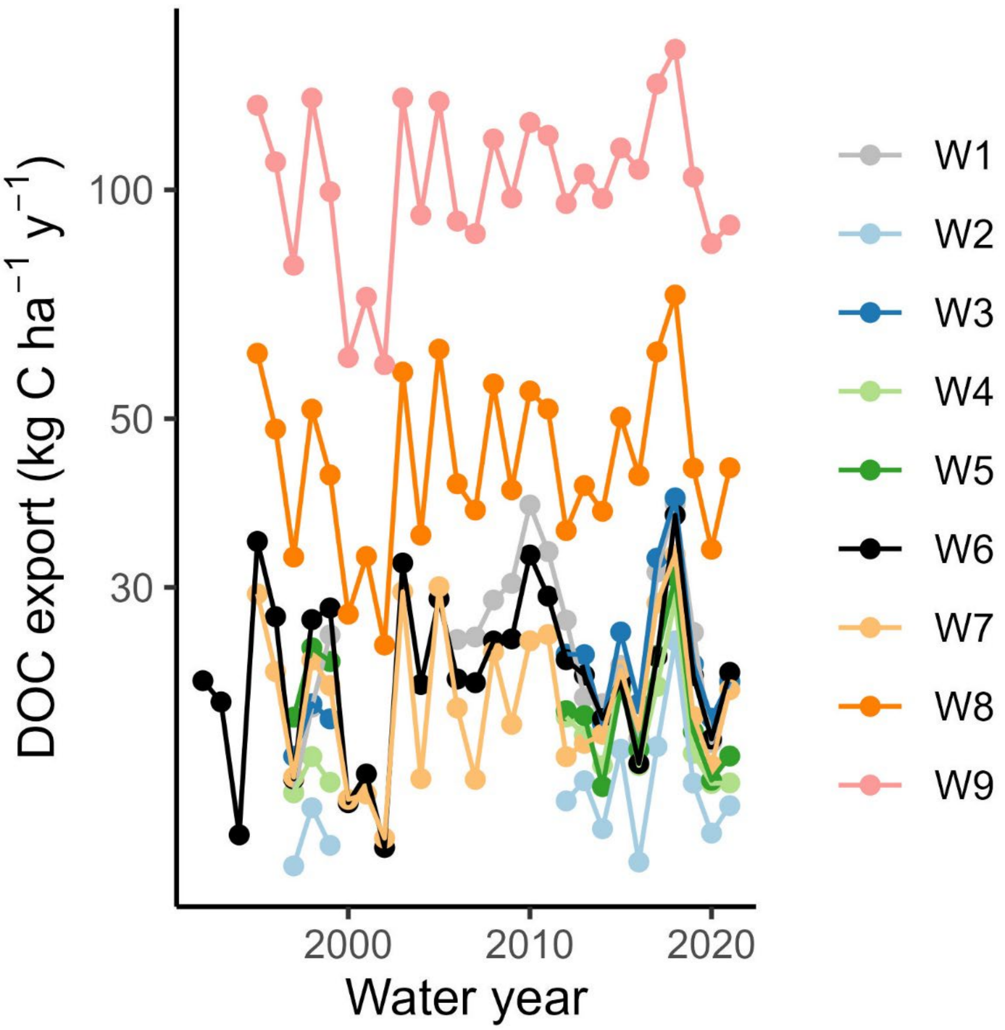

Figure 7. Export of dissolved organic carbon from each watershed in each water year.

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Supplementary material

Table S1. Summary of models explaining variation in the intercept of the DOC concentration-discharge relationship (β_0) among watersheds and water years. The model with the best predictive ability appears at the top, and alternative models within 4 AICc units of that best model appear below that, ranked by ΔAICc. Coefficient estimates (with standard errors) are given for each term included in each model. In addition to an overall intercept, candidate predictor variables included an intercept term describing the offset of Watershed 6 from Watershed 1, the inverse square root of soil solution ionic strength, soil solution pH, total annual precipitation, mean annual temperature, and interaction terms allowing the ionic strength, pH, precipitation, and temperature effects to vary by watershed. All of the continuous predictors were Z-transformed prior to fitting, and soil ionic strength was multiplied by 1000 prior to inverse square root transformation. Models were fit to estimates of β_0, weighted by the inverse of their variances, from Watersheds 1 and 6 only, where soil solution chemistry data were available.

Model rank	ΔAICc	intercept	watershed	ionic strength	ionic strength : watershed	pH	pH : watershed	precipitation	precipitation : watershed	temperature	temperature : watershed	R^2
1	0.00	1.06 (0.17)	-1.67 (0.23)	0.81 (0.19)	-0.56 (0.25)							0.56
2	0.94	0.38 (0.31)	-1.46 (0.56)	0.38 (0.14)		0.50 (0.24)	-1.01 (0.48)					0.58
3	1.93	1.07 (0.17)	-1.68 (0.23)	0.83 (0.20)	-0.57 (0.25)			-0.08 (0.11)				0.57
4	2.33	0.90 (0.36)	-1.41 (0.58)	0.72 (0.26)	-0.50 (0.28)	0.13 (0.25)						0.56
5	2.45	0.36 (0.31)	-1.43 (0.56)	0.39 (0.14)		0.54 (0.24)	-1.04 (0.48)	-0.11 (0.11)				0.59
6	2.60	1.06 (0.18)	-1.68 (0.26)	0.81 (0.20)	-0.56 (0.26)					-0.01 (0.12)		0.56
7	2.79	0.93 (0.17)	-1.66 (0.24)	0.46 (0.13)								0.51
8	2.83	0.61 (0.41)	-1.59 (0.58)	0.58 (0.27)	-0.28 (0.32)	0.35 (0.30)	-0.78 (0.55)					0.58
9	3.04	0.55 (0.31)	-0.97 (0.53)	0.35 (0.15)		0.33 (0.23)						0.53
10	3.39	1.04 (0.18)	-1.66 (0.23)	0.78 (0.20)	-0.51 (0.26)			0.10 (0.21)	-0.26 (0.24)			0.58
11	3.59	0.41 (0.33)	-1.50 (0.59)	0.40 (0.16)		0.50 (0.24)	-1.01 (0.49)			-0.03 (0.12)		0.58

Table S2. Summary of models explaining variation in the slope of the DOC concentration-discharge relationship (β_1) among watersheds and water years. The model with the best predictive ability appears at the top, and alternative models within 4 AICc units of that best model appear below that, ranked by ΔAICc. Coefficient estimates (with standard errors) are given for each term included in each model. In addition to an overall intercept, candidate predictor variables included an intercept term describing the offset of Watershed 6 from Watershed 1, the inverse square root of soil solution ionic strength, soil solution pH, total annual precipitation, mean annual temperature, and interaction terms allowing the ionic strength, pH, precipitation, and temperature effects to vary by watershed. All of the continuous predictors were Z-transformed prior to fitting, and soil ionic strength was multiplied by 1000 prior to inverse square root transformation. Models were fit to estimates of β_1, weighted by the inverse of their variances, from Watersheds 1 and 6 only, where soil solution chemistry data were available.

Model rank	ΔAICc	intercept	watershed	ionic strength	ionic strength : watershed	pH	pH : watershed	precipitation	precipitation : watershed	temperature	temperature : watershed	R^2
1	0.00	-0.55 (0.21)	0.90 (0.27)									0.19
2	1.13	-0.84 (0.34)	1.40 (0.53)			0.28 (0.25)						0.21
3	1.57	-0.56 (0.21)	0.89 (0.27)					0.12 (0.14)				0.20
4	1.87	-0.51 (0.22)	0.79 (0.31)	0.11 (0.17)								0.20
5	2.29	-0.53 (0.22)	0.88 (0.28)							-0.04 (0.14)		0.19
6	2.97	-0.42 (0.24)	0.77 (0.29)							-0.34 (0.27)	0.41 (0.32)	0.22
7	3.13	-0.80 (0.34)	1.33 (0.54)			0.24 (0.26)		0.10 (0.15)				0.22
8	3.41	-0.89 (0.36)	1.27 (0.61)			0.33 (0.28)	-0.29 (0.66)					0.21
9	3.43	-0.83 (0.34)	1.39 (0.54)			0.29 (0.26)				-0.06 (0.14)		0.21
10	3.59	-0.80 (0.41)	1.33 (0.71)	0.03 (0.20)		0.25 (0.30)						0.21
11	3.73	-0.52 (0.22)	0.81 (0.32)	0.09 (0.17)				0.11 (0.15)				0.21
12	3.84	-0.74 (0.34)	1.33 (0.53)			0.32 (0.26)				-0.39 (0.27)	0.45 (0.32)	0.24
13	3.87	-0.45 (0.24)	0.69 (0.35)	0.17 (0.19)						-0.11 (0.16)		0.20
14	3.88	-0.46 (0.24)	0.79 (0.32)	0.26 (0.27)	-0.23 (0.34)							0.20
15	4.00	-0.54 (0.22)	0.88 (0.28)					0.12 (0.14)		-0.03 (0.14)		0.20

Figure S1

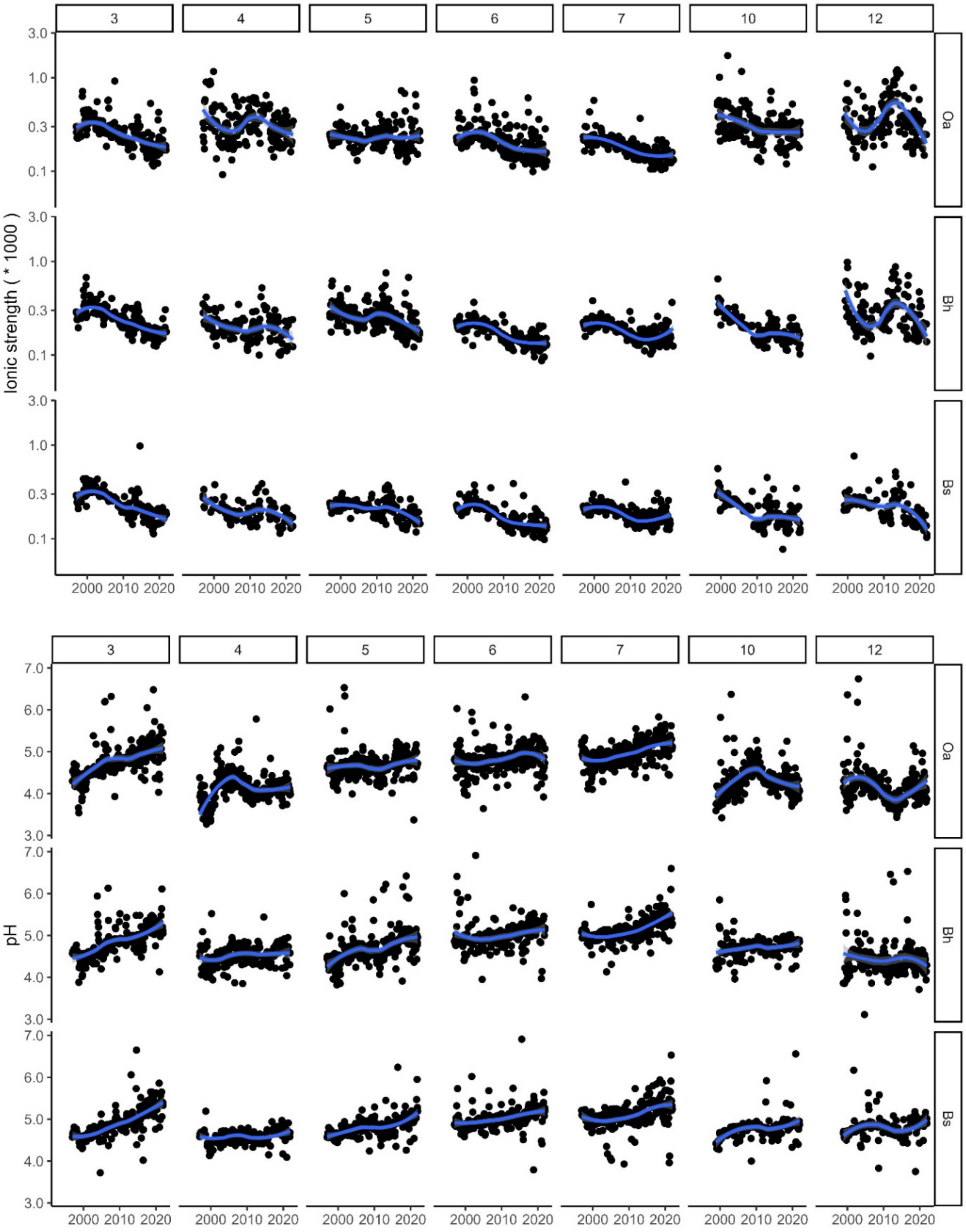

Figure S1. Ionic strength (top) and pH (bottom) of the soil solution in Watershed 1. Each panel displays data for a particular location (columns, numbered 3 through 12) and soil horizon (rows). Note that the y-axis limits exclude a few outlying observations.

Figure S2

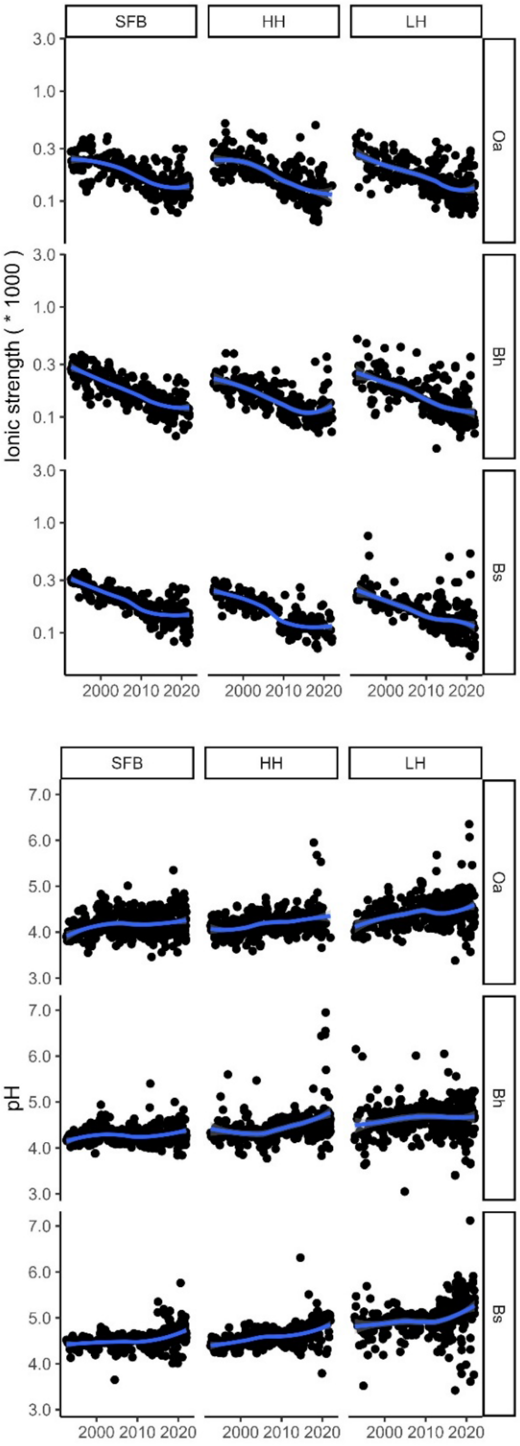

Figure S2. Ionic strength (top) and pH (bottom) of the soil solution in Watershed 6. Each panel displays data for a particular location (columns, SFB=spruce-fir-birch zone, HH=high hardwood zone, LH=low hardwood zone) and soil horizon (rows). Note that the y-axis limits exclude one outlying observation.

Figure S3

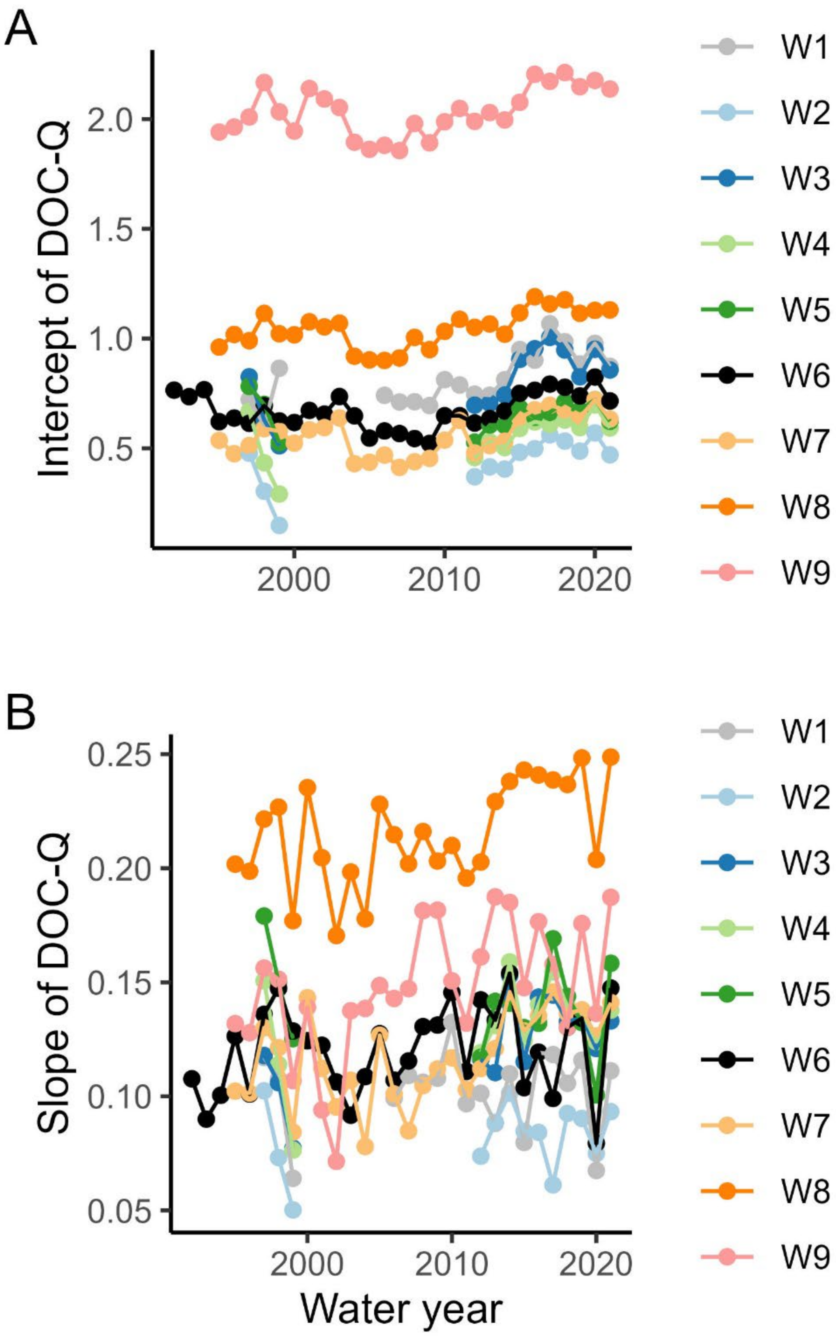

Figure S3. Estimated intercept (A) and slope (B) of the $\log_e$-$\log_e$ relationship between DOC concentration (mg L^{-1}) and stream discharge (mm d^{-1}) for each watershed by water year combination, at the midpoint of the seasonal cycle. These estimates include watershed effects (Figure 3), water year effects (Figure 4), and watershed by water year interaction effects.

Figure S4

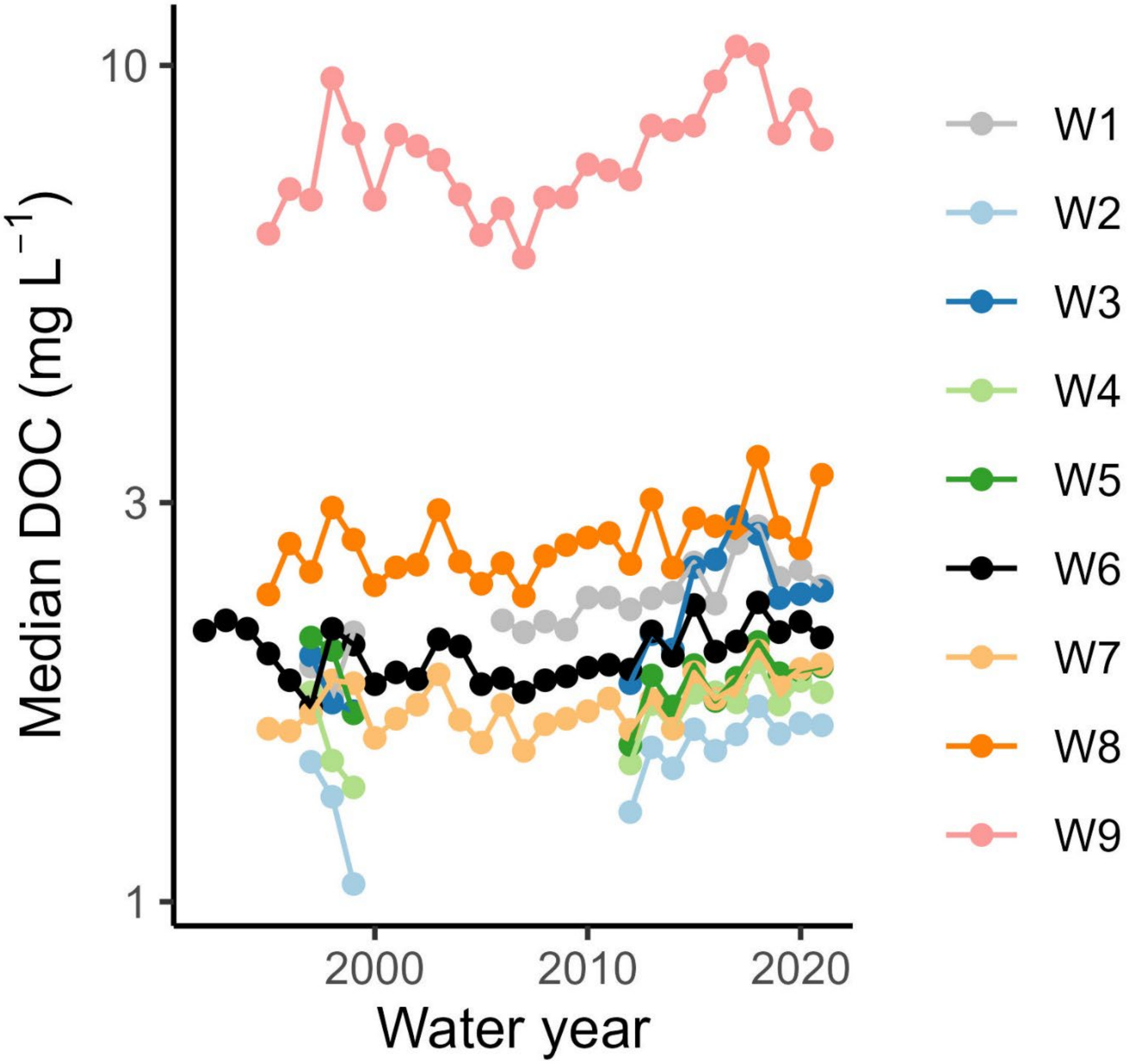

Figure S4. Median DOC concentration for each watershed in each water year (excluding 10 watershed-years for which fewer than 26 observations of DOC concentration were available).

Figure S5

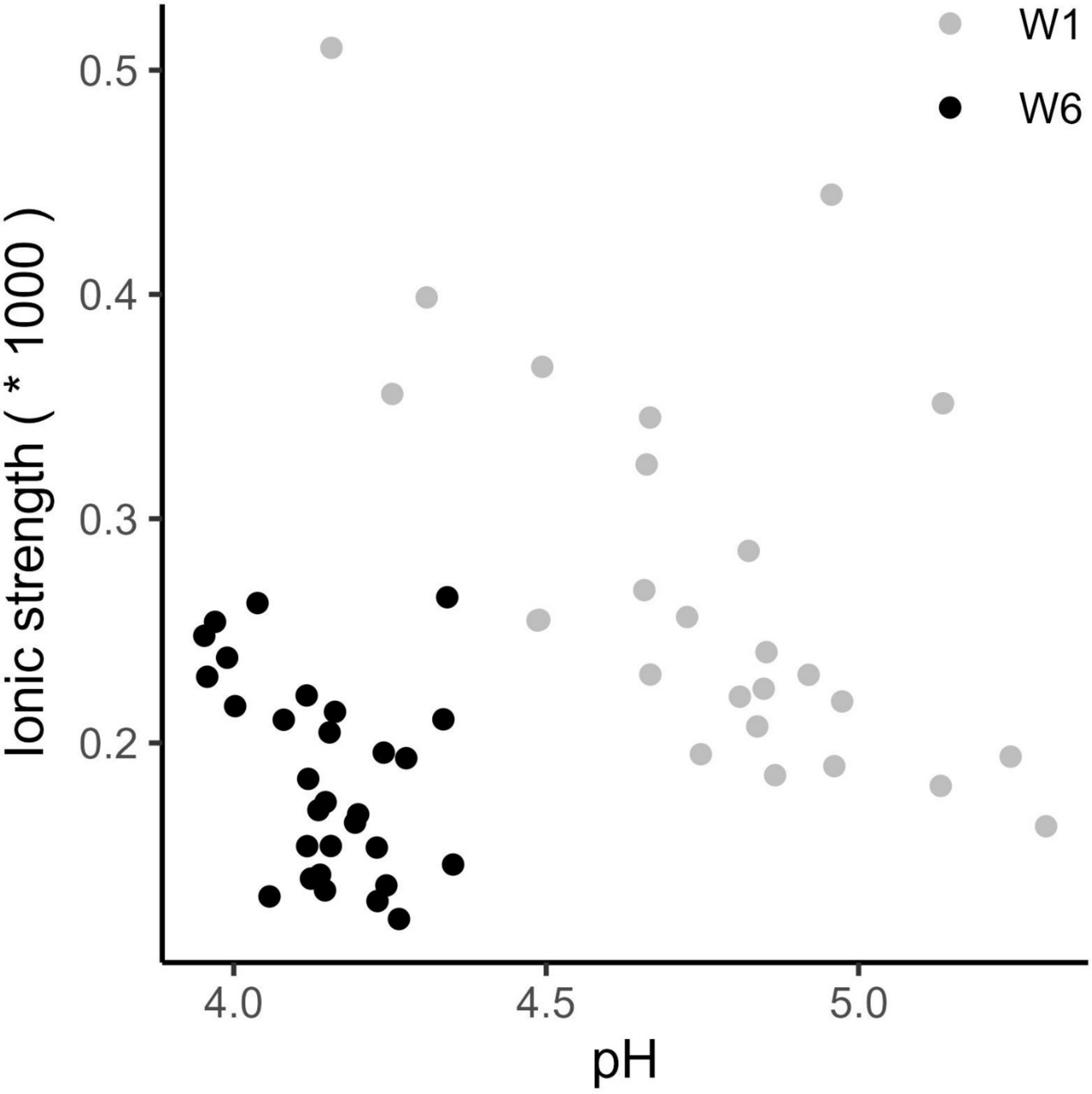

Figure S5. Ionic strength and pH of the soil solution in Watersheds 1 and 6 over the course of the study period. Each point represents an annual mean. In Watershed 1 the ionic strength declines at a fairly constant rate relative to the increase in pH – that is, all the points cluster around a single line with negative slope. In Watershed 6 there seems to be a breakpoint in this relationship around 2005, after which ionic strength declines and then levels out without substantial increases in pH.

Long-term change in the concentration-discharge relationship reveals controls on watershed exports of dissolved organic carbon

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Key points

- We quantified long-term changes, and their causes, in the dissolved organic carbon concentration-discharge relationship in nine watersheds.
- The intercept of the log-log concentration-discharge relationship, and to some extent the slope, increased over the past 20 years.
- The ionic strength of the soil solution plays a central role in controlling watershed exports of dissolved organic carbon.

Abstract

Dissolved organic carbon (DOC) export from watersheds by streams is an important, changing component of the global carbon cycle. We examined the controls on DOC export by quantifying changes in the DOC concentration-discharge relationship from 1992 through 2022 for nine forested headwater catchments at the Hubbard Brook Experimental Forest in the northeastern United States. We observed a strong increase in the intercept of the log-log concentration-discharge relationship between 2005 and 2017 and a weak increase in the slope of that relationship between 2002 and 2021, along with seasonal and watershed-level differences. The intercept, which indicates the average stream DOC concentration at a given discharge, was strongly and inversely related to ionic strength of the soil solution as predicted by electrolyte solubility theory. This relationship varied among watersheds, perhaps because of soil pH. The intercept was not strongly related to annual precipitation or air temperature. DOC export ranged from 13 to 153 kg C ha^{-1} y^{-1} among study watersheds and years, and was correlated with annual precipitation and discharge. Historical data suggest that DOC export has probably increased over the past 50 years, likely due both to increases in precipitation and runoff and to increases in the intercept and slope of the concentration-discharge relationship. Our results suggest the potential for long-term legacy effects of acidification on DOC solubility and stream DOC concentrations in acid-sensitive watersheds, despite reductions in acid deposition, as mineral weathering slowly replenishes the ionic strength of soil solutions.

Plain language summary

Some of the organic carbon that plants produce via photosynthesis makes its way in dissolved form to streams, which carry it to the ocean. This movement of dissolved organic carbon is an important component of the global carbon cycle and strongly influences the structure and function of aquatic ecosystems. Over the past several decades, the amount of dissolved organic carbon that streams carry has been increasing in many parts of the world. We measured dissolved organic carbon in nine streams over three decades, and compared the patterns that we observed to data on climate and soil chemistry to understand what drives variation in dissolved organic carbon export. We observed substantial changes in the average dissolved organic carbon concentration of these streams over time. As predicted by theory, these changes were strongly related to the abundance of ions in the soil water. Our results help inform how dissolved organic carbon export from the land to streams and oceans will continue to change over the decades to come.

Introduction

The fluvial export of dissolved organic carbon (DOC) from watersheds is an important and changing component of terrestrial and aquatic carbon cycles. As a global flux it is similar in magnitude to net terrestrial C uptake and comprises roughly one third of the total carbon flux of 5.1 Pg C y^{-1} from terrestrial to aquatic ecosystems (Stets and Striegl 2012, Butman et al. 2016, Drake et al. 2018, Hararuk et al. 2022, Friedlingstein et al. 2023). Furthermore, once DOC is transported to aquatic ecosystems it plays a major role in controlling primary and secondary productivity and a host of other ecosystem processes (Jones 1992, Karlsson et al. 2009, Solomon et al. 2015, Creed et al. 2018, Olson et al. 2020). For both of these reasons there has been substantial interest in understanding ongoing long-term changes in DOC exports, which have been reflected in widespread increases in stream and lake DOC concentrations over the past several decades at a rate averaging around 1% per year across broad areas of northeastern North America and northern Europe (Monteith et al. 2007, de Wit et al. 2021, Rodríguez-Cardona et al. 2022).

Observed long-term changes in DOC concentrations of streams and lakes have been attributed to a variety of mechanisms that control inputs to and losses from the soil organic matter pool (Figure 1A). The relative importance of these mechanisms varies spatially and temporally (Clark et al. 2010). Two mechanisms that are particularly important for describing observed patterns are the effects of soil ionic strength and soil pH on the solubility and thus the mobility of organic matter in soils (de Wit et al. 2007, Monteith et al. 2007, 2023, Hruška et al. 2009, Lawrence and Roy 2021). The effects of these two mechanisms can be difficult to differentiate, because ionic strength and pH often covary and are to some extent intrinsically linked (Monteith et al. 2023). Decreases in ionic strength increase organic matter solubility because they lead to expansion of the diffuse double layer around organic colloids, making those colloids more polar (Thurman 1985, Tipping and Hurley 1988, Tipping and Woof 1991). Similarly, decreases in acidity (i.e. lower H^+ concentration and higher pH) increase organic matter solubility by favoring the deprotonation of weakly acidic functional groups, resulting in greater negatively charged sites and more polar behavior (Fakhraei and Driscoll 2015). Decreases in acidity also increase organic matter solubility via interactions with aluminum, an important coagulant of organic matter, which is less soluble at neutral pH (Cronan and Schofield 1990, Tipping and Woof 1991, Li and Johnson 2016). Decreases in soil ionic strength and increases in pH driven by decreases in atmospheric deposition of strong acids (and also of sea salt in some places) seem to be important drivers of observed increases in DOC concentrations of surface waters over the past several decades, particularly in watersheds where acid deposition was high and where low base cation availability makes soils sensitive to that deposition (Monteith et al. 2007, Driscoll et al. 2016, de Wit et al. 2021). Additional mechanisms that can contribute to changing surface water DOC concentrations include changes in soil organic matter inputs or losses driven by changes in terrestrial productivity, land use, and both the temperature and precipitation components of climate change (Erlandsson et al. 2008, Larsen et al. 2011, Singh et al. 2016, Kritzberg 2017, de Wit et al. 2021), and other processes that control the dynamics of organic matter within the soil (Kalbitz et al. 2000, Kaiser and Kalbitz 2012). Recent syntheses suggest that the effects of ionic strength, rather than pH, on organic matter solubility may be the primary control on observed long-term changes in stream DOC concentrations, and that climate-related mechanisms may be becoming more important as the scope for further reductions in atmospheric deposition of strong acids (and thus also changes in soil ionic strength) declines (de Wit et al. 2021, Monteith et al. 2023).

Because fluvial DOC export is the (time-integrated) product of stream discharge and DOC concentration, any mechanism that alters export must manifest in one of three ways: as a change in discharge, in the average DOC concentration at a given discharge, or in the rate at which DOC concentration changes with discharge. The latter two quantities are represented by the scaling coefficient and exponent of a power-law concentration-discharge relationship, or equivalently by the intercept and slope of the log-log transformed version of this relationship, which we will focus on here. These two parameters should vary systematically in response to the mechanistic controls on DOC export (Figure 1B). For instance, one useful distinguishing feature of DOC concentration-discharge relationships is whether they have positive, zero, or negative slopes. The DOC concentration-discharge relationship is typically positive in watersheds where organo-mineral soils predominate, because as the volume of water draining off the landscape increases, the proportion of water transported through organic-rich surface soils increases relative to the proportion through deeper mineral soils with lower concentrations of soil organic matter which is more strongly retained by mineral surfaces (McDowell and Wood 1984, Sebestyen et al. 2008, Pellerin et al. 2012). In contrast, the concentration-discharge relationship is generally flat or even negative in organic peat soils, where the dependency of DOC yield on the depth of flowpaths is weaker but where high runoff may flush pore waters more rapidly than they can accumulate new DOC (McDowell and Likens 1988, Schiff et al. 1998, Clark et al. 2010). Beyond these coarse differences in the sign of the slope, the actual magnitude of both the slope and the intercept of the concentration-discharge (or flux-discharge) relationship are related to watershed properties such as topography and land cover, and to climatic conditions (Zarnetske et al. 2018).

In this study we explored the effects of long-term environmental change on DOC export by examining variation in the concentration-discharge relationship for DOC, and variation in stream discharge itself, in nine watersheds over a period of 30 years at the Hubbard Brook Experimental Forest, NH. A number of previous studies have examined changes in DOC concentration-discharge relationships over shorter periods to reveal important controls on DOC export (e.g. Ågren et al. 2010), and data on long-term changes in DOC concentrations are relatively abundant (e.g. de Wit et al. 2021). Yet consideration of changes in DOC concentration-discharge relationships over multiple decades is exceedingly rare, despite the demonstrated utility of such analyses for understanding the dynamics of DOC and other solutes (Huntington and Shanley 2022, Creed et al. 2025). During the study period all watersheds experienced similar changes in large-scale drivers of DOC export such as acid deposition and climate, and some were subjected to watershed-scale experimental manipulations that may also have altered DOC export. We therefore tested two specific hypotheses concerning the effects of long-term change and inter-watershed differences on DOC export. First, we hypothesized that the intercept of the DOC concentration-discharge relationship would increase through time in all watersheds. We anticipated that this increase would be driven largely by changes in DOM mobility resulting from the long-term trajectory of acid deposition and recovery in these watersheds, and that therefore the intercept of the concentration-discharge relationship would be correlated with increasing soil pH and decreasing soil ionic strength. We also expected that the intercept might vary with mean annual temperature or precipitation, given the potential effects of these climate variables on inputs to and respiratory losses from the soil organic matter pool (Figure 1) and recent observations of increasing climate dependence of DOC concentration trends (de Wit et al. 2021). Second, we hypothesized that the slope of the DOC concentration-discharge relationship might also change through time, due to differential changes in the DOC yield of frequently- and rarely-connected contributing areas, or to changes in average flow paths (Figure 1B). Finally, in addition to testing these hypotheses we combined our estimates of the DOC concentration-discharge relationship with data on stream discharge to estimate DOC export and explore inter-annual variation in export.

Methods

Study system

We studied nine forested, headwater watersheds at the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, USA (43° 56′ N, 71° 45′ W). The area of these watersheds ranges from 11.8 to 77.4 ha. Elevations range from 442 to 685 m at the watershed outlets, and from 716 to 910 m at the ridgetops. Watersheds 1 through 6 are south-facing, while Watersheds 7 through 9 are north-facing; all drain to the mainstem Hubbard Brook, and almost all drainage from the watersheds occurs as streamflow, not groundwater flow (Verry 2003, Likens 2013). Aside from a small wetland in the upper portion of Watershed 9 (0.8 ha; 1.2% of watershed), land cover is predominantly northern hardwood forest, with spruce-fir forest at higher elevations (van Doorn et al. 2011, Cawley et al. 2014). The soils are relatively shallow Spodosols developed on glacial till, which vary with landscape position due to the effects of lateral water flow on soil development (Bailey et al. 2014). The climate is cool, humid, and continental, and temperature, precipitation, and streamflow have been increasing over the long term (Campbell et al. 2021, 2022). Additional details about the site are available elsewhere (e.g. Likens 2013).

Long-term changes, natural disturbances, and experimental manipulations, all of which might influence DOC exports, have occurred in the study watersheds. All of the study watersheds have been exposed to multi-decadal changes in atmospheric acid deposition, which peaked in the 1960s and 1970s and has since declined substantially (Likens et al. 2021). This legacy of acid deposition has severely depleted available base cations from the soils, among other impacts (Likens et al. 1996, 1998). Watershed 2 was clear-cut in autumn 1965, and subsequently treated with herbicide for three growing seasons to suppress regrowth (Likens et al. 1970). Watershed 4 was strip-cut between 1970 and 1974 (Hornbeck et al. 1986). A whole-tree harvest of Watershed 5 was conducted in 1983-1984 (Dahlgren and Driscoll 1994). A severe ice storm occurred in January 1998, causing severe canopy damage in portions of the south-facing watersheds (Rhoads et al. 2002, Houlton et al. 2003). Finally, pelletized wollastonite ($CaSiO_3$) was applied by helicopter to Watershed 1 in November 1999 (Shao et al. 2015).

Our study period extends from the beginning of regular DOC monitoring in these watersheds on 31 August 1992, through the end of the 2021 water year on 31 May 2022. The water year in our study system is usually defined as running from 1 June through 31 May, and we use this convention here (Likens 2013).

Stream discharge and DOC concentration

The hydrologic discharge of the stream draining each of the watersheds is measured continuously at the outlet of each watershed with a V-notch weir, and a San Dimas flume in some instances, and total daily discharge is calculated by integration (USDA Forest Service, Northern Research Station 2022). To facilitate comparisons among watersheds of different drainage areas we use the specific discharge (discharge divided by watershed area; units mm y^{-1}).

The DOC concentration of each stream is measured at least weekly whenever the stream is flowing, in samples collected just upstream of the weir (HBWatER 2023). These routine weekly DOC measurements began in August 1992 in Watershed 6, and in May 1995 in Watersheds 7 through 9. Watersheds 1 through 5 were added to the sampling regime later, and all nine watersheds have been included since December 2012. Before May 1995 DOC was measured by colorimetric CO_2 detection on a Technicon II after persulfate digestion. Since June 1995, DOC has been measured by infrared CO_2 detection on a Shimadzu total organic carbon analyzer after high-temperature combustion. The first method has a negative bias of 0.17 mg C L^{-1} relative to the second, perhaps because of incomplete digestion (Buso et al. 2000); we corrected for this bias before conducting our statistical analyses. Water samples for DOC analysis were unfiltered in the early years of the sampling program, but beginning between January and March 2005 all samples have been filtered through pre-combusted Whatman GF/F 0.7 μm pore size filters prior to analysis. We did not correct measured concentrations for this change in filtering because analysis of paired samples indicated that DOC concentrations after filtering were on average 98.8 to 99.6% of concentrations before filtering (Buso, unpublished). Buso et al. (2000) provide additional details on analytical methods.

For some water year by watershed combinations fewer than 52 measurements of DOC were available, for instance when regular sampling in that watershed started part way through a water year or when stream discharge ceased during the summer. We eliminated from our analysis ten water year by watershed combinations for which fewer than 26 DOC measurements were available, leaving 182 water year by watershed combinations with between 26 and 296 DOC measurements each (mean 59, median 53; total number of measurements across all water years = 10,759).

Soil solution chemistry

We sampled freely-draining soil solutions approximately monthly using tension-free lysimeters installed in Watershed 1 and adjacent to Watershed 6 (Fuss et al. 2015, LoRusso et al. 2021, Driscoll 2025a, 2025b). In each watershed, lysimeters were installed in organic and mineral soil horizons in each of three different elevation zones; we focus on lysimeters installed below the Oa horizon in high-elevation spruce-fir-beech habitats because these areas make important contributions to stream DOC in our study region (Gannon et al. 2015), but note that patterns in ionic strength and pH were similar in other elevation zones and soil horizons (Figure S1, Figure S2). We calculated the ionic strength of the soil solution from the concentrations of the ions Al^{3+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, H^{+}, SO_4^{2-}, NO_3^{-}, HCO_3^{-}, Cl^{-}, and F^{-}, as:

[1] $ionic\ strength = 0.5 * \Sigma c_i (z_i)^2$

where c_i is the concentration (mol L^{-1}) and z_i the charge of ionic solute i. The HCO_3^{-} concentration was estimated from the measured DIC concentration and pH using the AquaEnv package (Hofmann et al. 2010), the H^{+} concentration was calculated from the measured pH, and the Al^{3+} concentration was estimated as the difference between measurements of total monomeric aluminum and organic monomeric aluminum; all the other ions were directly measured. Methods for chemical analysis are described by Driscoll (2025a, 2025b).

Climate

Daily precipitation was estimated in each watershed from a network of rain gauges, using the Thiessen means method through 2014 and an inverse distance weighting method thereafter (USDA Forest Service, Northern Research Station 2024a). We summed these daily estimates to obtain total precipitation in each watershed and water year. We also calculated mean air temperature for each water year from daily temperature measurements taken near the base of the south-facing watersheds (USDA Forest Service, Northern Research Station 2024b).

Statistical analysis

We fit four candidate models to describe the relationship between DOC concentration and stream discharge. All statistical analyses were performed in R (R Core Team 2023). The most complex model was a hierarchical or mixed-effects regression:

$$[2] \qquad \log_e\left([DOC]_{ijk}\right) = \beta_{0,jk} + \beta_{1,jk}\log_e\left(Q_{ijk} + 0.0001\right) + \beta_2\sin(2\pi i) + \beta_3\cos(2\pi i)$$

Where [DOC] is the dissolved organic carbon concentration in mg L^{-1}, Q is the specific discharge in mm d^{-1}, $\log_e()$ indicates the natural logarithm, and the subscripts *i, j*, and *k* indicate respectively the day of the water year expressed as a fraction between 0 and 1; the water year; and the watershed. This model allows the intercept (β_0) and slope (β_1) of the log-log concentration-discharge relationship to vary by water year, watershed, and the interaction of water year and watershed, and assumes that those random effects are normally distributed with a mean of zero. It also includes, in the last two terms, a sinusoidal seasonal cycle in the average log([DOC]) at a given discharge (Cohn et al. 1992). As alternatives, we considered a hierarchical model identical to Model 1 but lacking the seasonal component; a fixed-effects model including the seasonal component but allowing only a single β_0 and a single β_1 across all water years and watersheds; and a fixed effects model with a single β_0, single β_1, and no seasonal component. We fit the hierarchical models by maximum likelihood using the lmer() function (Bates et al. 2015), and the fixed-effects models by least squares using the lm() function, and then compared the predictive power of the models using AIC. The most complex hierarchical model was far superior to the others, and we re-fit this model using restricted maximum likelihood to ensure that we reported unbiased variance estimates.

We used standard regression models to test our hypothesis that changes in the intercept of the DOC concentration-discharge relationship would be related to changes in soil solution chemistry and climate. We constrained this analysis to Watersheds 1 and 6, because these were the only two watersheds for which long-term soil solution chemistry data are available. The response variable in these models was the set of watershed- and year-specific estimates of β_0 from the hierarchical concentration-discharge model described above, weighted by their inverse variances. The predictor variables included the inverse square root of soil solution ionic strength (Debye and Hückel 1923, Monteith et al. 2023), soil solution pH, total annual precipitation, mean annual temperature, watershed, and the interaction of watershed with each of the continuous predictors. We fit the full model and all of its subsets on the Z-transformed variables, and examined in more detail the model with the lowest AICc and all other models within 4 AICc units of that best model (Barton 2024). For completeness we used the same procedure to consider models for β_1, the slope of the DOC concentration-discharge relationship.

Results

Concentration-discharge relationships

The concentration-discharge relationship for DOC varied among watersheds and years, as well as seasonally (Figure 2, Table 1). The model that allowed the intercept and slope of the concentration-discharge relationship to vary by watershed, year, and watershed:year, and included seasonal effects, was far superior to any of the other candidate models that we considered (ΔAIC > 6000). This model explains 90% of the variance in the log-transformed DOC concentration. Variation in the slope and intercept of the concentration-discharge relationship among watersheds and years accounts for most of the explained variance; only 15% of the variance in log-transformed DOC is attributable to the fixed intercept, slope, and seasonal effects. Estimates of the intercept ranged from 0.15 to 2.21, and estimates of the slope from 0.05 to 0.25, depending on the watershed and water year and setting aside the seasonal effect (Figure S3; note that units of these parameters are on the scale of the $\log_e$-transformed concentration and discharge). The fitted seasonal trend indicates that the DOC concentration at a given discharge reaches a maximum in late August and a minimum in late February, on average, and the amplitude of this seasonal cycle (the difference in $\log_e$(DOC) between the peak and midpoint of the cycle) is 0.25.

Among watersheds there were substantial differences in the intercept, and smaller differences in the slope, of the concentration-discharge relationship for an average year (Figure 3). The intercept, which indicates the average DOC concentration at a given discharge, was very high in Watershed 9, somewhat high in Watershed 8, and somewhat low in Watershed 2, relative to the other watersheds (Figure 3A). The slope, which indicates the rate at which DOC concentration increases with increasing discharge, was very high in Watershed 8, somewhat high in Watershed 9, and somewhat low in Watershed 2, relative to the other watersheds (Figure 3B).

The intercept of the concentration-discharge relationship, and to some extent the slope, also changed considerably through time (Figure 4). The intercept fluctuated between 1992 and 2003, declined between 2003 and 2005, and increased fairly steadily from 2005 through 2017 (Figure 4A). In contrast, temporal patterns in the slope were much less pronounced relative to their average values and uncertainties, but there is some suggestion of a decline and recovery between 1997 and 1999, and a weak upward trend from 2002 through 2021 (Figure 4B, Figure S3). Changes in the concentration-discharge relationship through time were similar, but not identical, across the different watersheds (Figure S3).

Environmental conditions

Soil solution chemistry and climatic conditions varied substantially over the study period (Figure 5). Ionic strength of the soil solution decreased at a similar rate in both watersheds, to approximately $1.8*10^{-4}$ in Watershed 1 and $1.4*10^{-4}$ in Watershed 6 by 2021. This decrease occurred largely during the middle portion of the study period, and ionic strength was relatively stable beginning around 2015. Soil acidity also decreased (pH increased), particularly in Watershed 1 after the 1999 wollastonite addition. Mean annual temperature and total annual precipitation also increased over the study period. Stream discharge was highly correlated with precipitation (r=0.86 to 0.94 across the nine watersheds).

Drivers of change in concentration-discharge relationships

The ionic strength of the soil solution was a strong predictor of variation in the intercept (β_0) of the DOC concentration-discharge relationship among watersheds and water years (Figure 6). This result indicates that the average DOC concentration at any given level of discharge increases as the ionic strength of the soil solution decreases. A model including only ionic strength and watershed as predictors, and allowing the effect of ionic strength to vary among watersheds, had the highest predictive ability among all the candidate models that we considered (ΔAICc ≥ 0.98, $R^2=0.56$; Table S1). All other plausible models (those with ΔAICc < 4) also included the ionic strength and watershed terms, sometimes in combination with terms for pH, annual precipitation, mean annual temperature, or their interactions with watershed. These additional terms did not substantially increase the explained variance, and with the exception of a positive pH term and a pH:watershed term in some models, their confidence intervals overlapped zero.

As expected, variation in the slope (β_1) of the DOC concentration-discharge relationship was not strongly related to soil ionic strength, soil pH, annual precipitation, or mean annual temperature. The best model of variation in the slope included only a term for watershed and had low explanatory power (ΔAICc ≥ 1.13, $R^2=0.19$, Table S2).

Export

Export of DOC from the study watersheds varied among watersheds and water years (Figure 7). The median annual export was 104 kg C ha^{-1} in Watershed 9, 42 kg C ha^{-1} in Watershed 8, and 15-26 kg C ha^{-1} in the other watersheds. There was a slight increasing trend in export through time, although this trend did not explain a significant portion of the variation in export in a linear model that also included watershed as a predictor (estimated slope of log(export) on year = 0.0048 ± 0.0021 SE; $F_{1,172}$=2.1, p=0.15). Inter-annual variability in export was substantial (CV 19-26%, depending on watershed), and was highly correlated with total annual discharge or precipitation ($r>0.93$, $p<0.0001$; Figure 5). Median annual DOC concentrations ranged from approximately 1 to 10 mg C L^{-1}, depending on the watershed and year (Figure S4).

Discussion

By quantifying changes in the DOC concentration-discharge relationship through time in multiple watersheds and relating those changes to hypothesized drivers within a mechanistic framework, we gained new insights into the controls on DOC export in our study ecosystem. Our results provide strong evidence that soil ionic strength, and to a lesser extent soil pH, control the solubility of soil organic matter and thus the average stream DOC concentration at any level of stream discharge. These effects of soil solution chemistry on the intercept of the concentration-discharge relationship, combined with smaller changes in the slope of that relationship and with the important effects of total discharge, controlled patterns of DOC export across space and time.

Our finding that soil ionic strength was the best predictor of variation in the intercept of the concentration-discharge relationship is consistent with the model of DOC solubility recently proposed by Monteith et al. (2023). This model assumes that ionic strength is a primary regulator of organic matter solubility in soils, and that solubility increases in proportion to the inverse square root of ionic strength (Debye and Hückel 1923). Monteith and colleagues tested this model in European streams, and found the electrical conductivity of precipitation, as a proxy for soil ionic strength, explained most of the observed long-term change in stream DOC concentrations. Our study finds a similar pattern but takes a step closer to the hypothesized mechanism by relating the average stream DOC concentration at a given discharge to actual soil solution ionic strength measurements rather than the proxy (we also found that these measurements and the proxy are reasonably well correlated at the annual scale, Spearman's ρ=0.58). Unlike the analysis by Monteith and colleagues, our analysis does not suggest that the effects of temperature-dependent microbial degradation are an important control on organic matter solubility in the soil horizons that contribute DOC to the stream, but this may be because we considered mean annual temperature while they focused on shorter time windows.

Our results also provide compelling evidence of the effects of soil pH on organic matter solubility, separate from the effects of soil ionic strength. Separating these effects has often been challenging in previous studies, because many regions impacted by acid deposition have experienced simultaneous changes in both the ionic strength and the pH of the soil solution. In our analysis we were able to address this limitation by comparing Watershed 1, which was experimentally enriched with wollastonite to increase its soil calcium and alkalinity, to Watershed 6, a nearby unmanipulated reference watershed. The rate at which the intercept of the DOC concentration-discharge relationship changed with a given change in soil ionic strength was higher in Watershed 1 than in Watershed 6 (Table S1, Figure 6), and we hypothesize that this difference reflects the effects of pH. Soil pH was substantially higher in Watershed 1 than in Watershed 6, particularly after the wollastonite addition midway through the 1999 water year (Figure 5). Furthermore, in Watershed 1 the increase in pH over time kept pace with the decrease in ionic strength, whereas in Watershed 6 after about 2005 the increase in pH was limited relative to the decrease in ionic strength (Figure 5, Figure S5). Higher soil pH might increase organic matter mobility in Watershed 1 in at least two ways: by enhancing dissociation of weak organic acids (Fakhraei and Driscoll 2015), and by increasing rates of microbial activity and thus the availability of more soluble, microbially-processed humic materials (LoRusso et al. 2021, Possinger et al. 2025). In some soils higher pH also limits coagulation of organic matter by aluminum, but this may be a minor effect currently in our watersheds because inorganic aluminum concentrations are low following recovery from acidification (Fuss et al. 2015).

The wollastonite addition also likely explains one puzzling anomaly that we observed: a substantial increase in the intercept of the concentration-discharge relationship in Watershed 1 between the 1998 and 1999 water years, even as the intercept in all the other watersheds decreased (Figure S3). This pattern does not seem to be attributable to the effects of the wollastonite addition on the ionic strength and pH of the soil solution, because in the immediate aftermath of the addition the increase in pH in Watershed 1 was not substantially different from the trend in reference Watershed 6, and the ionic strength may have decreased (Figure 5, Figure S1). Instead, we suspect that the increase in the DOC concentration-discharge intercept in Watershed 1 during this period was due to the mobilization of the organic carbon in the highly water-soluble lignin sulfonate binder that was used to help pelletize the finely ground wollastonite in the experimental treatment (Peters et al. 2004).

A gradual increase in the slope of the DOC concentration-discharge relationship beginning around the mid-2000s may be a regional phenomenon. A study at Sleepers River, Vermont, 60 km from our study site, found that the slope of the concentration-discharge relationship was steeper when fit to recent observations between 2002 and 2018 than when fit to earlier ones between 1991 and 2002 (Huntington and Shanley 2022). If we compare our estimates of the slope for the period starting in 2002 to those for the period up to and including 2002, we see some evidence of a similar, albeit small, steepening (mean slope of 0.13 during the recent period and 0.12 during the earlier period; $t_{20.9}$=-1.89, p=0.07). This steepening indicates an increase in the rate at which the mean DOC yield of the soil units contributing to stream flow increases as water yield from the landscape increases, which could be occurring for either or both of two reasons (Figure 1). First, average flow paths could be changing, routing a higher proportion of runoff through organic-rich soils (e.g. Gannon et al. 2015). Increasing frequency and intensity of summer storms at our study site could contribute to such a change, although analysis of storm recession curves does not suggest any change in flow paths over the period of record (Green and Bernhardt unpublished). Second, the DOC yield of these soil units that contribute to stream flow only under high flow conditions might be increasing faster than (or decreasing slower than) the DOC yield of soil units that regularly contribute to stream flow. Decreases in soil ionic strength and increases in pH could produce this pattern if they progressed faster in the rarely-contributing O horizon than in lower soil horizons, but we see no evidence for this pattern in our data (Figure S1, Figure S2). Alternatively, inputs to or losses from the soil organic matter pool, or soil frost effects on the availability of organic matter for export, might be changing differently in rarely-contributing soil units than in regularly contributing ones (Tiwari et al. 2018, Huntington and Shanley 2022).

The inter-watershed patterns that we observed in the intercept and slope of the DOC concentration-discharge relationship (Figure 3) were broadly consistent with previous literature. An analysis of over 1000 first- through tenth-order streams across the conterminous United States identified steepness, wetland cover, mean annual precipitation, and deciduous forest cover as the most important controls on the intercept of the log-log relationship between discharge and DOC flux (i.e. concentration multiplied by discharge; Zarnetske et al. 2018). The one watershed in our study for which the intercept of the concentration-discharge relationship was substantially higher than the others, Watershed 9, also has substantially lower steepness, higher wetland cover, and substantially lower deciduous forest cover than all the other watersheds (Cawley et al. 2014). For each of these three predictors, the difference between Watershed 9 and the other watersheds is consistent with a higher predicted intercept in the model of Zarnetske et al. (2018). Inter-watershed differences in the slope of the concentration-discharge relationship among our study watersheds were not as pronounced as differences in the intercept, but

Watershed 8, and to some extent Watershed 9, did have a markedly higher slope than the other watersheds, perhaps due to their high evergreen forest cover (90% and 96%, respectively). Evergreen forest cover was one of the strongest predictors of the slope of the DOC flux-discharge relationship in the analysis of Zarnetske et al. (2018). Those authors saw that watersheds which exceeded 50% evergreen cover tended to have positive flux-discharge slopes and attributed this pattern to the effects of evergreen forest cover on DOC production. Our conceptual model suggests a slight modification to that interpretation, emphasizing that it is not just the production of DOC that matters, but the differential production (and respiration and mobility) of DOC in soil units that are rarely or regularly connected to the hydrologic network (Figure 1). Positive, "transport-limited" concentration-discharge relationships arise not from increases in organic matter inputs to soils per se, but rather because those inputs are concentrated in soil units, like the O horizon, which become connected to the hydrologic network only under water-rich conditions that also lead to high stream discharge. Furthermore, while watersheds with <50% evergreen cover or <20% wetland cover tend to show "source-limited" negative relationships between DOC flux and discharge (Zarnetske et al. 2018), our results in Watersheds 1 through 6, all of which have ≤19% evergreen cover and 0% wetland cover, emphasize that "transport limitation" does occur under such conditions. In our watersheds this may be in part because organic, shallow-to-bedrock soils in the upper reaches of the watershed quickly saturate during precipitation events and deliver DOC to channel heads without substantial interactions with mineral soil in which DOC might be immobilized (Gannon et al. 2015, LoRusso et al. 2021). A corollary point is that so-called "source-limited", negative concentration-discharge relationships may not necessarily arise from an actual limitation of DOC sources; even if carbon sources are abundant on the landscape, a negative concentration-discharge relationship can occur if adding water to the landscape does not change which soil units are hydrologically connected in such a way as to increase the mean DOC yield of all contributing areas.

Exports of DOC from watersheds to surface waters have changed substantially over the past several decades and are likely to continue to change in complex ways for decades to come. Between 1976 and 1980, DOC export from the Bear Brook watershed, which is mostly comprised of Watersheds 5 and 6, ranged from 17 to 24 kg C ha^{-1} y^{-1} (McDowell and Likens 1988). Since 2005, however, export from Watershed 6 has exceeded 24 kg C ha^{-1} y^{-1} in half of all years, and the mean export from Watersheds 5 and 6 was 21 and 25 kg ha^{-1} y^{-1}, respectively (Figure 7). This apparent long-term increase in DOC export arises both from an increase in precipitation and runoff (Green et al. 2021) and from an increase in the average amount of DOC that the watersheds yield at any level of runoff, driven largely by changes in soil ionic strength (Figure 4). More generally, future long-term trends in the average stream DOC concentration at a given discharge may vary from one watershed to the next, despite identical changes in atmospheric deposition, climate, and other drivers, due to differences in soil properties or history of acidification. In watersheds like those at Hubbard Brook, where previous acid deposition has stripped available nutrient cations from the soil and greatly reduced soil ionic strength, DOC solubility and stream DOC concentrations may decline from their current elevated levels only very gradually over many years, despite substantial reduction in acid deposition and recovery of soil pH, as soil ionic strength is very gradually replenished by the slow process of mineral weathering (Lawrence and Roy 2021). Watersheds that experienced smaller changes in soil ionic strength, due to better initial buffering or lower acid deposition, should see more rapid recovery from any small increases in DOC solubility and stream concentration. Both acid-sensitive and acid-resistant watersheds are also experiencing ongoing climate change, which may impact DOC exports via the intercept or slope of the DOC concentration-discharge relationship or via changes in discharge itself. Our analysis suggests that these climate effects may manifest first via the effects of hydrologic intensification on average flowpaths (and thus the slope of the concentration-discharge relationship) and total discharge, but ultimately changes in precipitation and temperature may also influence both the slope and intercept of the concentration-discharge relationship via effects on primary production, respiration, and the size and nature of soil organic matter pools. Building a mechanistic and predictive understanding of these complex dynamics remains an important challenge for future research.

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Data availability statement

All of the data used in this paper are available in public repositories with DOIs, which are cited throughout the manuscript and code. All code to access those data and reproduce the analyses and figures is available at https://github.com/ctsolomon/HB-DOC (doi: 10.5281/zenodo.15882497)

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Table 1. Summary of the model describing the relationship between DOC concentration and stream discharge (Equation 2, fit by restricted maximum likelihood to log-transformed concentration and discharge). Point estimates ± 1 SE are shown for the fixed effects, followed by the standard deviations of any random effects. The model was fit to 10,759 observations of DOC concentration across 30 water years, 9 watersheds, and 182 water year by watershed combinations.

Model component		Estimate
Intercept	β_0	0.825 ± 0.165
Water year	σ_j	0.086
Watershed	σ_k	0.493
Water year : Watershed	σ_{jk}	0.061
Slope	β_1	0.127 ± 0.013
Water year	σ_j	0.016
Watershed	σ_k	0.039
Water year : Watershed	σ_{jk}	0.019
Seasonal cycle	β_2	0.249 ± 0.003
	β_3	0.032 ± 0.003
$\sigma_{residual}$		0.182
marginal R^2=0.145, conditional R^2=0.905		

Figure 1

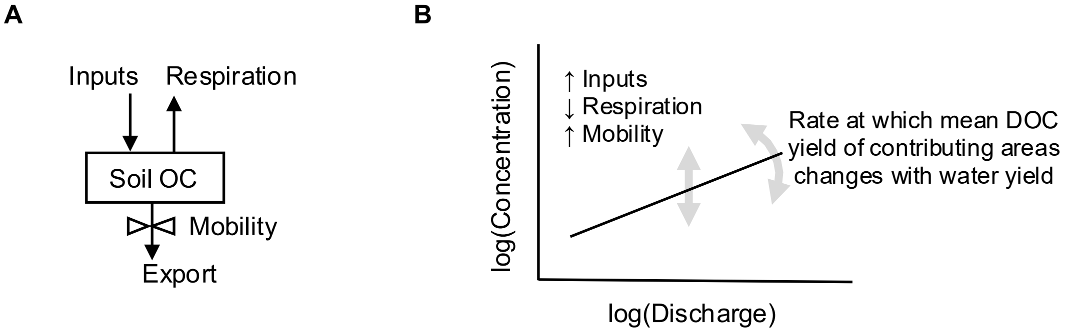

Figure 1. (A) DOC exports from watersheds depend mechanistically on inputs to, respiratory losses from, and thus the size of the soil organic matter pool; on chemical reactions that control organic matter mobility; and on hydrologic flows and flowpaths (see e.g. Kalbitz et al. 2000, Futter et al. 2007, Clark et al. 2010). (B) Differences in these mechanisms across space or time are manifested in the concentration-discharge relationship. The intercept of the log-log concentration-discharge relationship shifts upwards in response to greater inputs, lower respiratory losses, or higher DOM mobility across all contributing areas. The slope pivots upwards if there is an increase in the rate at which the mean DOC yield of all contributing areas increases with water yield from the landscape; this could occur due to differential changes in the DOC yield of frequently- and rarely-connected contributing areas, or due to changes in average flow paths.

Figure 2

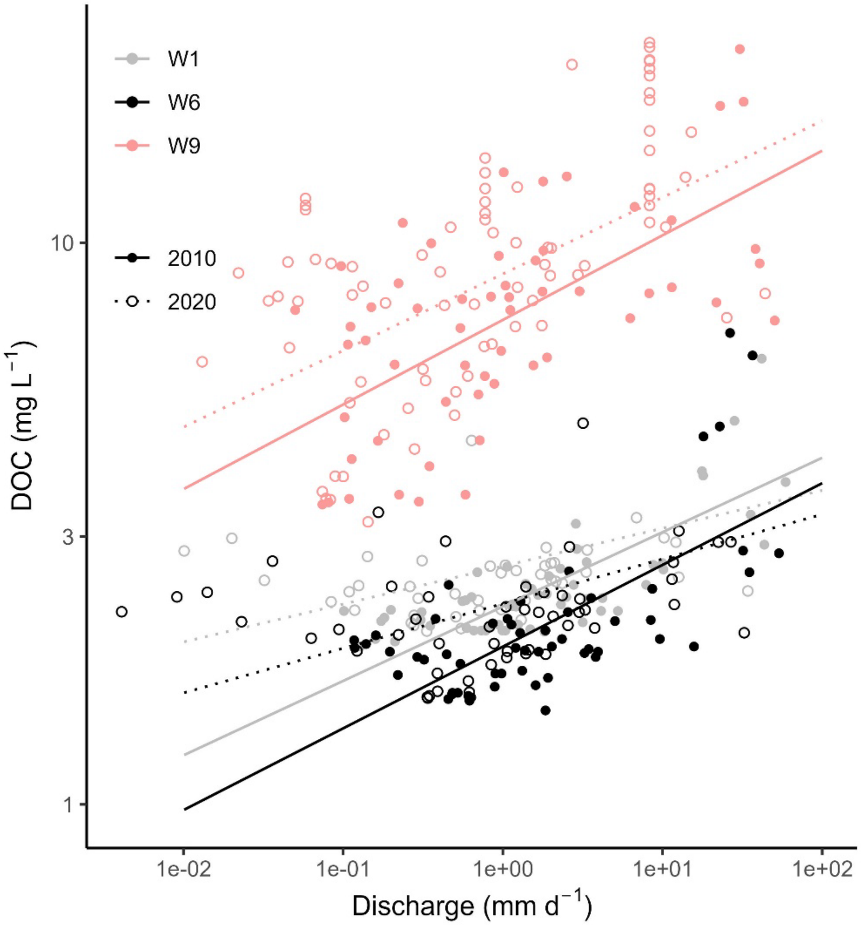

Figure 2. Data and model fits for three watersheds in two water years, to illustrate the full data set and model (which include 9 watersheds, 30 water years, and 182 water year by watershed combinations). For each watershed-year combination, the line gives the model fit at the midpoint of the seasonal cycle; additional variation parallel to the fitted line is accounted for by the seasonal cycle, which is not shown here. Filled points and solid lines indicate data and fits for 2010; hollow points and dotted lines indicate data and fits for 2020; and colors indicate different watersheds.

Figure 3

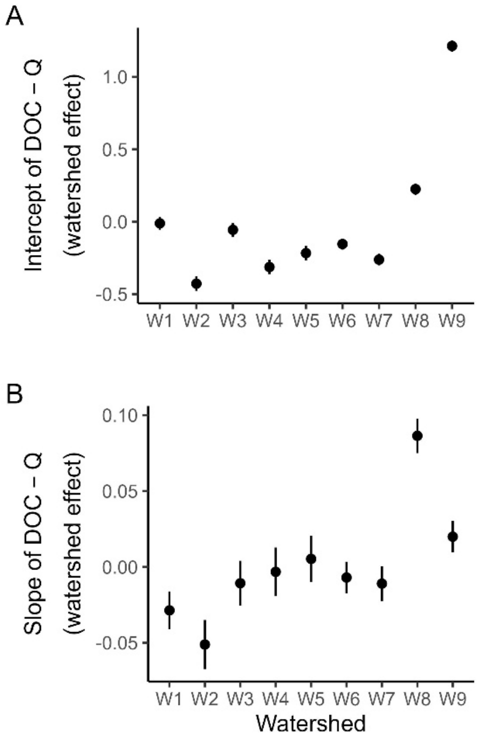

Figure 3. Differences among watersheds in the relationship between DOC concentration and stream discharge. Points are the estimated watershed effects, for the average water year and at the midpoint of the seasonal cycle, on the intercept (A) and slope (B) of the concentration-discharge relationship (see Fig. 4 for estimated water year effects, and Fig. S3 for the full coefficient estimates including watershed, water year, and interaction effects). Error bars indicate 95% confidence intervals; note that in panel A the confidence intervals are narrow and largely hidden by the points.

Figure 4

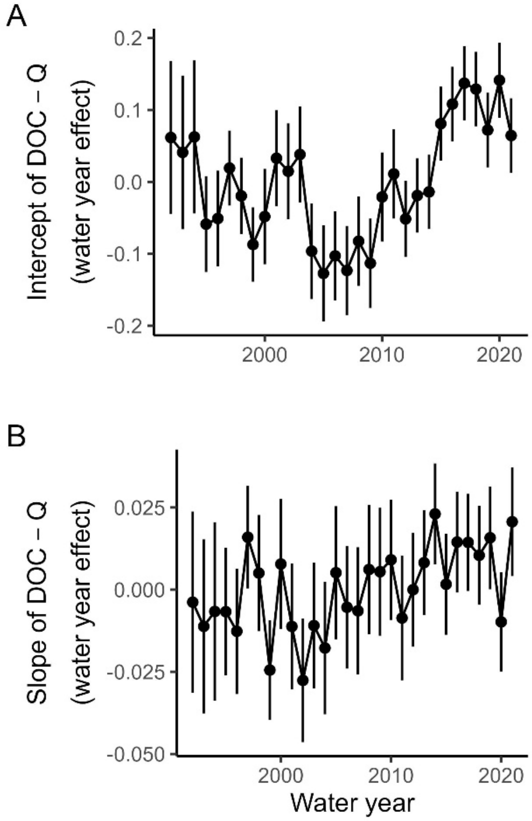

Figure 4. Differences among years in the relationship between DOC concentration and stream discharge. Points are the estimated year effects, for the average watershed and at the midpoint of the seasonal cycle, on the intercept (A) and slope (B) of the concentration-discharge relationship (see Fig. 3 for estimated watershed effects, and Fig. S3 for the full coefficient estimates including watershed, water year, and interaction effects). Error bars indicate 95% confidence intervals.

Figure 5

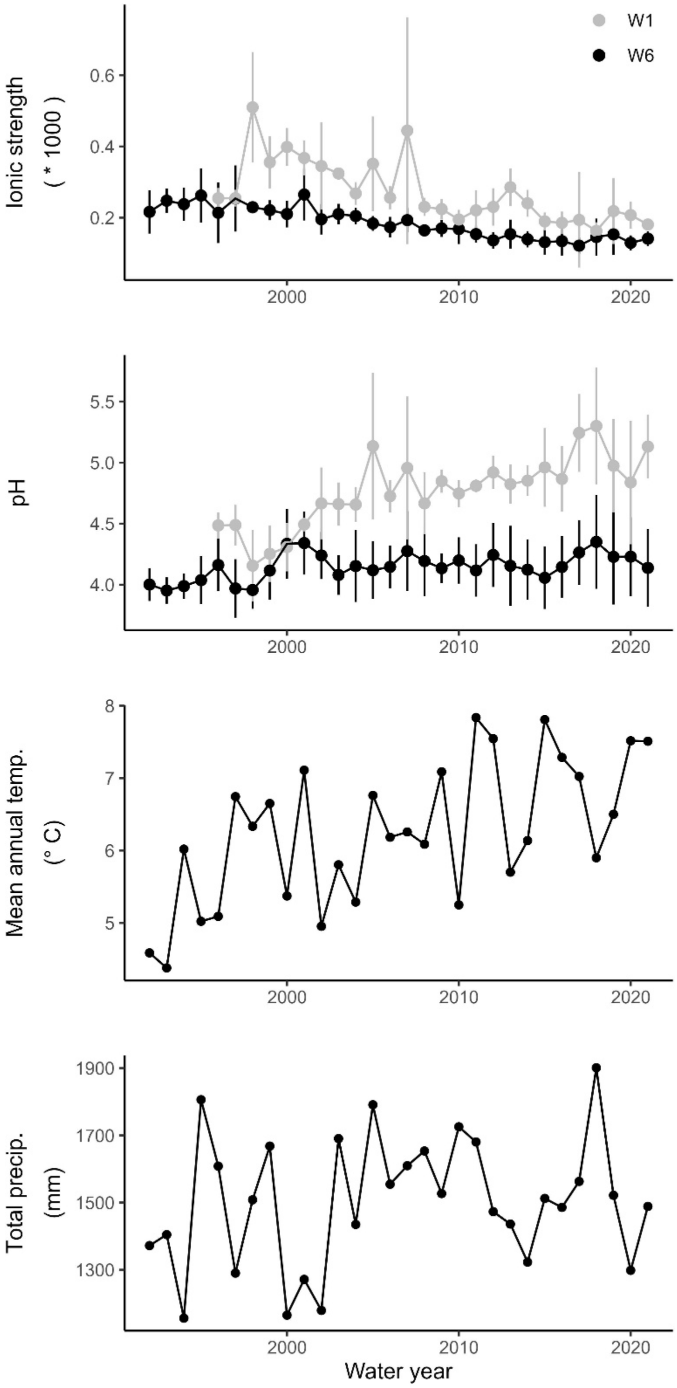

Figure 5. Soil solution ionic strength, soil solution pH, mean annual temperature, and total annual
795 precipitation in the study watersheds. Soil solution data are shown for watersheds 1 and 6. Error bars
indicate ± 1 SD.

Figure 6

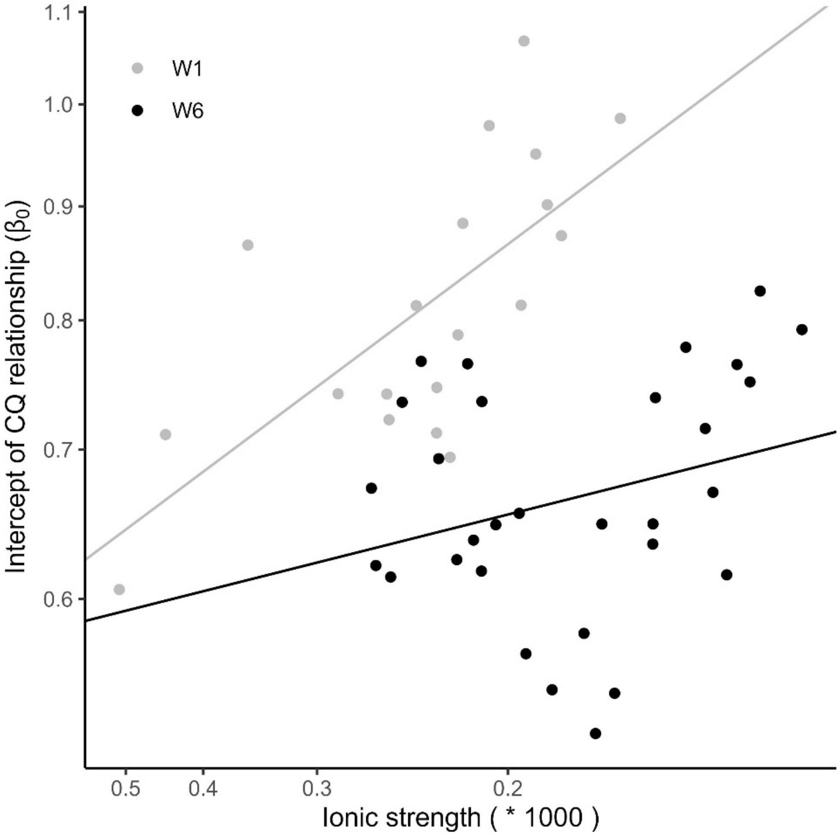

Figure 6. In Watersheds 1 and 6, variation among watersheds and water years in the intercept of the DOC concentration-discharge relationship (β_0; y-axis) is related to the ionic strength of the soil solution (x-axis). Lines show fits from the model with the highest ability to predict variation in β_0 (Model 1 in Table S1). Note that ionic strength is plotted on an inverse square root scale, in keeping with the theoretically expected relationship between organic matter solubility and ionic strength (Debye and Hückel 1923, Monteith et al. 2023); thus low values of ionic strength are at the right of the figure.

Figure 7

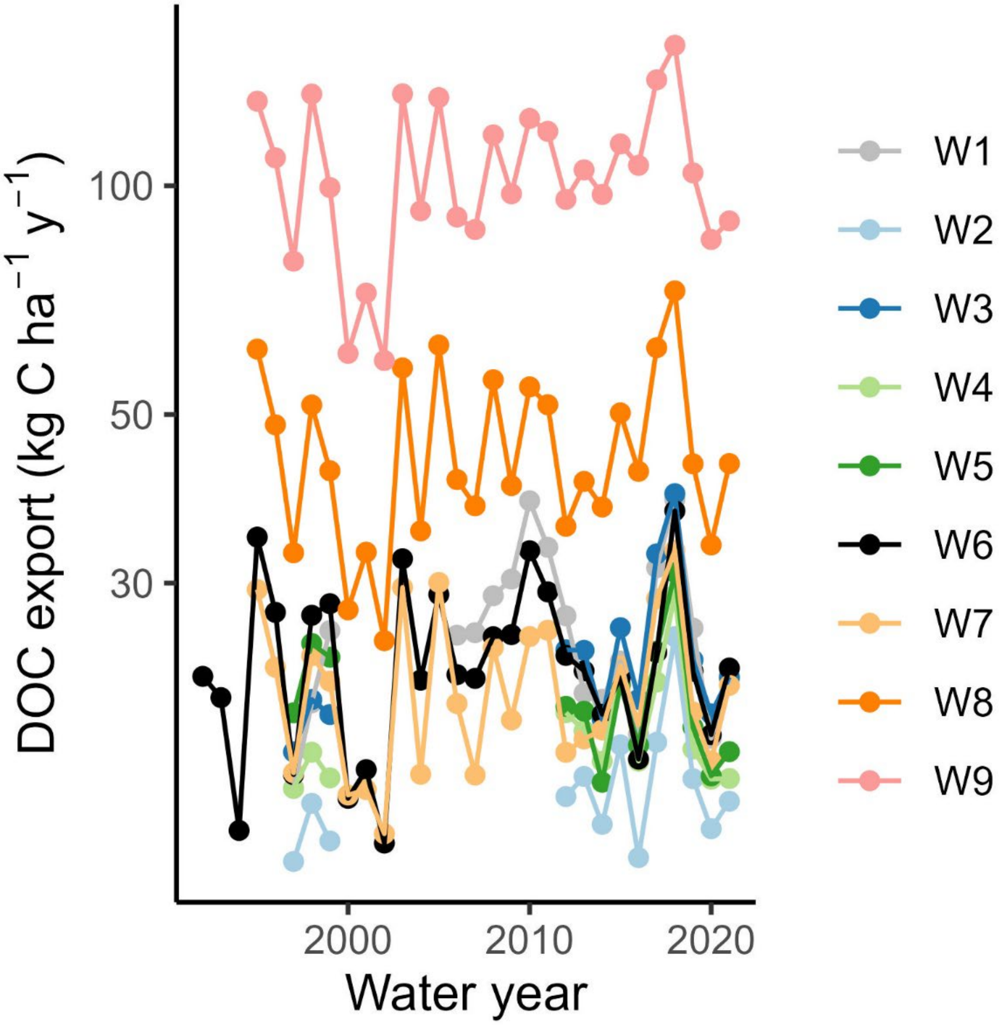

Figure 7. Export of dissolved organic carbon from each watershed in each water year.

Supplementary material

Table S1. Summary of models explaining variation in the intercept of the DOC concentration-discharge relationship (β_0) among watersheds and water years. The model with the best predictive ability appears at the top, and alternative models within 4 AICc units of that best model appear below that, ranked by ΔAICc. Coefficient estimates (with standard errors) are given for each term included in each model. In addition to an overall intercept, candidate predictor variables included an intercept term describing the offset of Watershed 6 from Watershed 1, the inverse square root of soil solution ionic strength, soil solution pH, total annual precipitation, mean annual temperature, and interaction terms allowing the ionic strength, pH, precipitation, and temperature effects to vary by watershed. All of the continuous predictors were Z-transformed prior to fitting, and soil ionic strength was multiplied by 1000 prior to inverse square root transformation. Models were fit to estimates of β_0, weighted by the inverse of their variances, from Watersheds 1 and 6 only, where soil solution chemistry data were available.

Model rank	ΔAICc	intercept	watershed	ionic strength	ionic strength : watershed	pH	pH : watershed	precipitation	precipitation : watershed	temperature	temperature : watershed	R^2
1	0.00	1.06 (0.17)	-1.67 (0.23)	0.81 (0.19)	-0.56 (0.25)							0.56
2	0.94	0.38 (0.31)	-1.46 (0.56)	0.38 (0.14)		0.50 (0.24)	-1.01 (0.48)					0.58
3	1.93	1.07 (0.17)	-1.68 (0.23)	0.83 (0.20)	-0.57 (0.25)			-0.08 (0.11)				0.57
4	2.33	0.90 (0.36)	-1.41 (0.58)	0.72 (0.26)	-0.50 (0.28)	0.13 (0.25)						0.56
5	2.45	0.36 (0.31)	-1.43 (0.56)	0.39 (0.14)		0.54 (0.24)	-1.04 (0.48)	-0.11 (0.11)				0.59
6	2.60	1.06 (0.18)	-1.68 (0.26)	0.81 (0.20)	-0.56 (0.26)					-0.01 (0.12)		0.56
7	2.79	0.93 (0.17)	-1.66 (0.24)	0.46 (0.13)								0.51
8	2.83	0.61 (0.41)	-1.59 (0.58)	0.58 (0.27)	-0.28 (0.32)	0.35 (0.30)	-0.78 (0.55)					0.58
9	3.04	0.55 (0.31)	-0.97 (0.53)	0.35 (0.15)		0.33 (0.23)						0.53
10	3.39	1.04 (0.18)	-1.66 (0.23)	0.78 (0.20)	-0.51 (0.26)			0.10 (0.21)	-0.26 (0.24)			0.58
11	3.59	0.41 (0.33)	-1.50 (0.59)	0.40 (0.16)		0.50 (0.24)	-1.01 (0.49)			-0.03 (0.12)		0.58

Table S2. Summary of models explaining variation in the slope of the DOC concentration-discharge relationship (β_1) among watersheds and water years. The model with the best predictive ability appears at the top, and alternative models within 4 AICc units of that best model appear below that, ranked by ΔAICc. Coefficient estimates (with standard errors) are given for each term included in each model. In addition to an overall intercept, candidate predictor variables included an intercept term describing the offset of Watershed 6 from Watershed 1, the inverse square root of soil solution ionic strength, soil solution pH, total annual precipitation, mean annual temperature, and interaction terms allowing the ionic strength, pH, precipitation, and temperature effects to vary by watershed. All of the continuous predictors were Z-transformed prior to fitting, and soil ionic strength was multiplied by 1000 prior to inverse square root transformation. Models were fit to estimates of β_1, weighted by the inverse of their variances, from Watersheds 1 and 6 only, where soil solution chemistry data were available.

Model rank	ΔAICc	intercept	watershed	ionic strength	ionic strength : watershed	pH	pH : watershed	precipitation	precipitation : watershed	temperature	temperature : watershed	R^2
1	0.00	-0.55 (0.21)	0.90 (0.27)									0.19
2	1.13	-0.84 (0.34)	1.40 (0.53)			0.28 (0.25)						0.21
3	1.57	-0.56 (0.21)	0.89 (0.27)					0.12 (0.14)				0.20
4	1.87	-0.51 (0.22)	0.79 (0.31)	0.11 (0.17)								0.20
5	2.29	-0.53 (0.22)	0.88 (0.28)							-0.04 (0.14)		0.19
6	2.97	-0.42 (0.24)	0.77 (0.29)							-0.34 (0.27)	0.41 (0.32)	0.22
7	3.13	-0.80 (0.34)	1.33 (0.54)			0.24 (0.26)		0.10 (0.15)				0.22
8	3.41	-0.89 (0.36)	1.27 (0.61)			0.33 (0.28)	-0.29 (0.66)					0.21
9	3.43	-0.83 (0.34)	1.39 (0.54)			0.29 (0.26)				-0.06 (0.14)		0.21
10	3.59	-0.80 (0.41)	1.33 (0.71)	0.03 (0.20)		0.25 (0.30)						0.21
11	3.73	-0.52 (0.22)	0.81 (0.32)	0.09 (0.17)				0.11 (0.15)				0.21
12	3.84	-0.74 (0.34)	1.33 (0.53)			0.32 (0.26)				-0.39 (0.27)	0.45 (0.32)	0.24
13	3.87	-0.45 (0.24)	0.69 (0.35)	0.17 (0.19)						-0.11 (0.16)		0.20
14	3.88	-0.46 (0.24)	0.79 (0.32)	0.26 (0.27)	-0.23 (0.34)							0.20
15	4.00	-0.54 (0.22)	0.88 (0.28)					0.12 (0.14)		-0.03 (0.14)		0.20

Figure S1

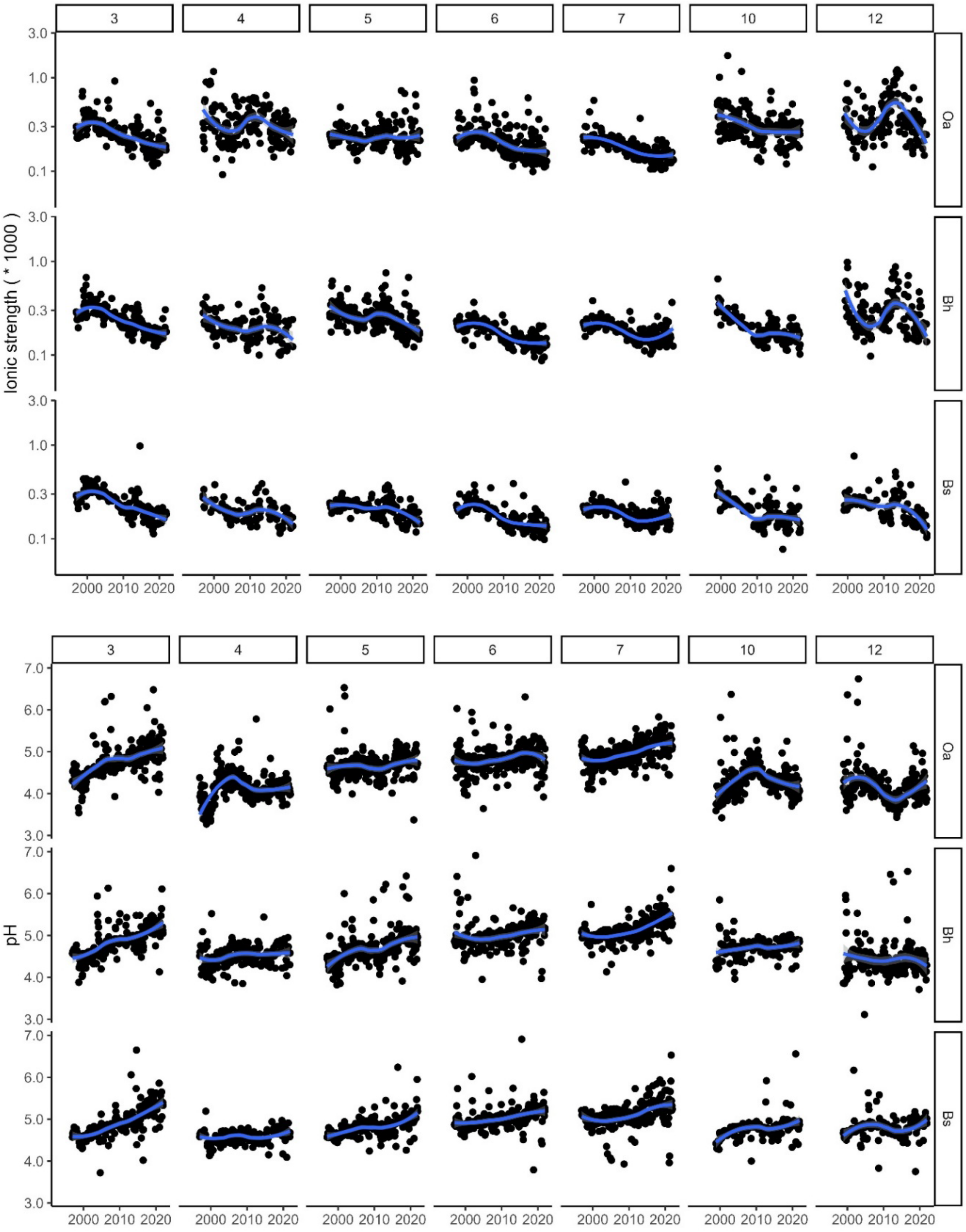

Figure S1. Ionic strength (top) and pH (bottom) of the soil solution in Watershed 1. Each panel displays data for a particular location (columns, numbered 3 through 12) and soil horizon (rows). Note that the y-axis limits exclude a few outlying observations.

Figure S2

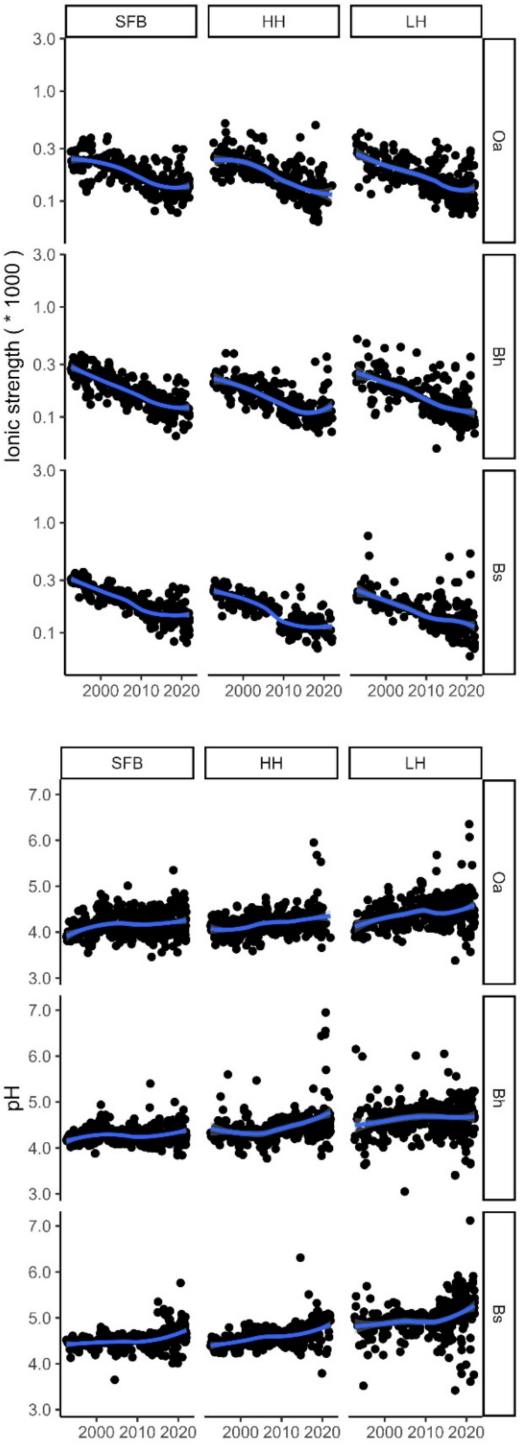

Figure S2. Ionic strength (top) and pH (bottom) of the soil solution in Watershed 6. Each panel displays data for a particular location (columns, SFB=spruce-fir-birch zone, HH=high hardwood zone, LH=low hardwood zone) and soil horizon (rows). Note that the y-axis limits exclude one outlying observation.

Figure S3

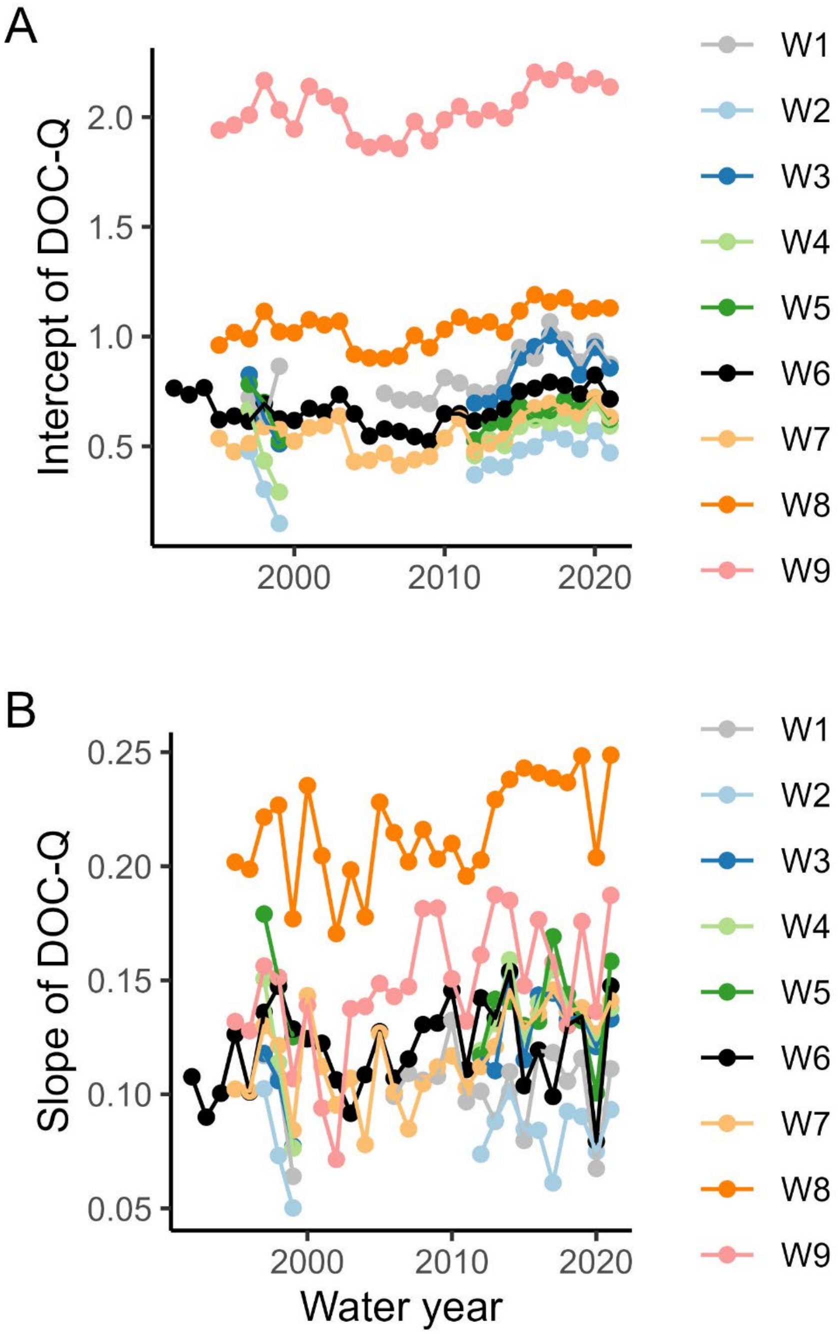

Figure S3. Estimated intercept (A) and slope (B) of the $\log_e$-$\log_e$ relationship between DOC concentration (mg L^{-1}) and stream discharge (mm d^{-1}) for each watershed by water year combination, at the midpoint of the seasonal cycle. These estimates include watershed effects (Figure 3), water year effects (Figure 4), and watershed by water year interaction effects.

855 Figure S4

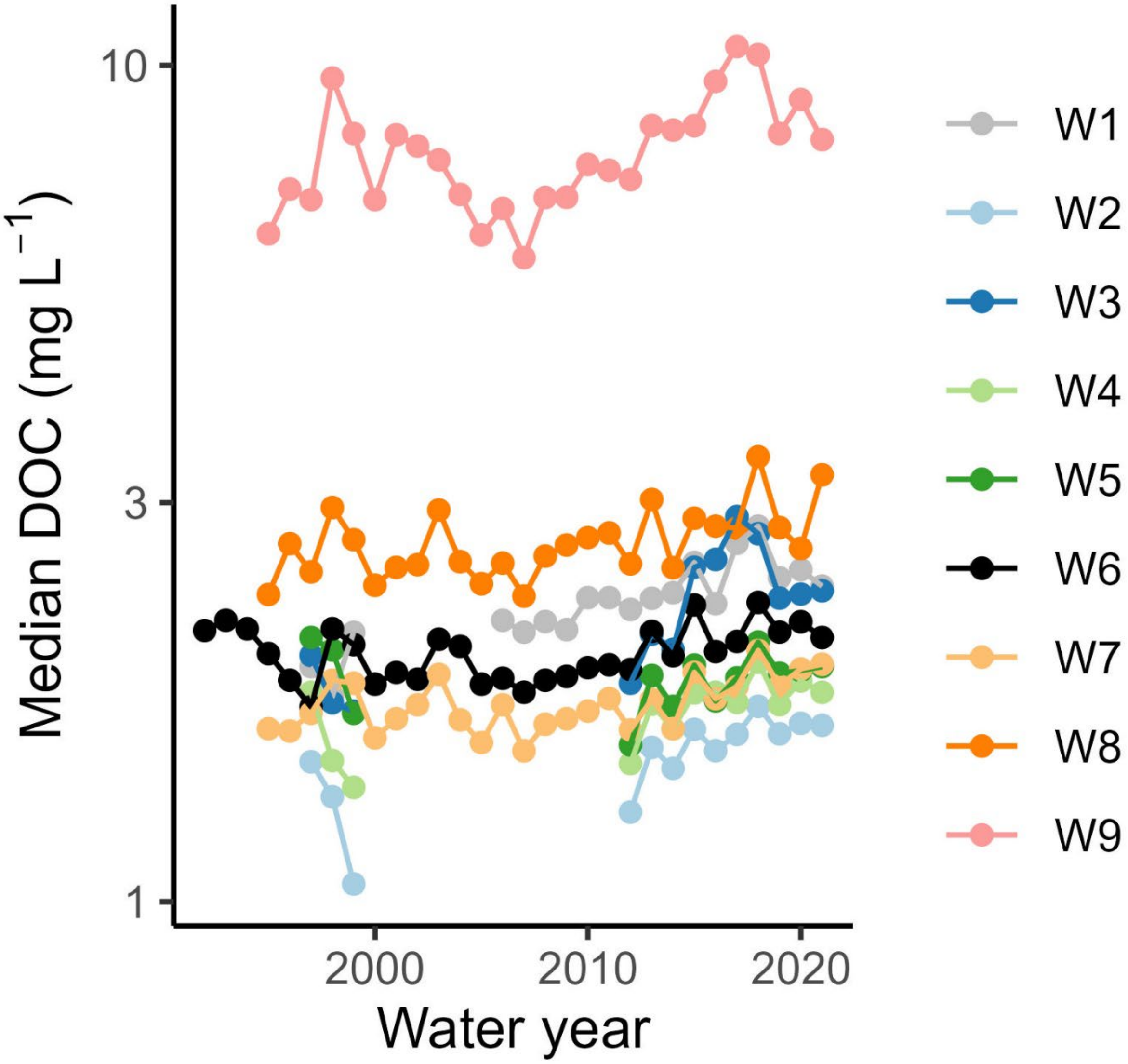

Figure S4. Median DOC concentration for each watershed in each water year (excluding 10 watershed-years for which fewer than 26 observations of DOC concentration were available).

Figure S5

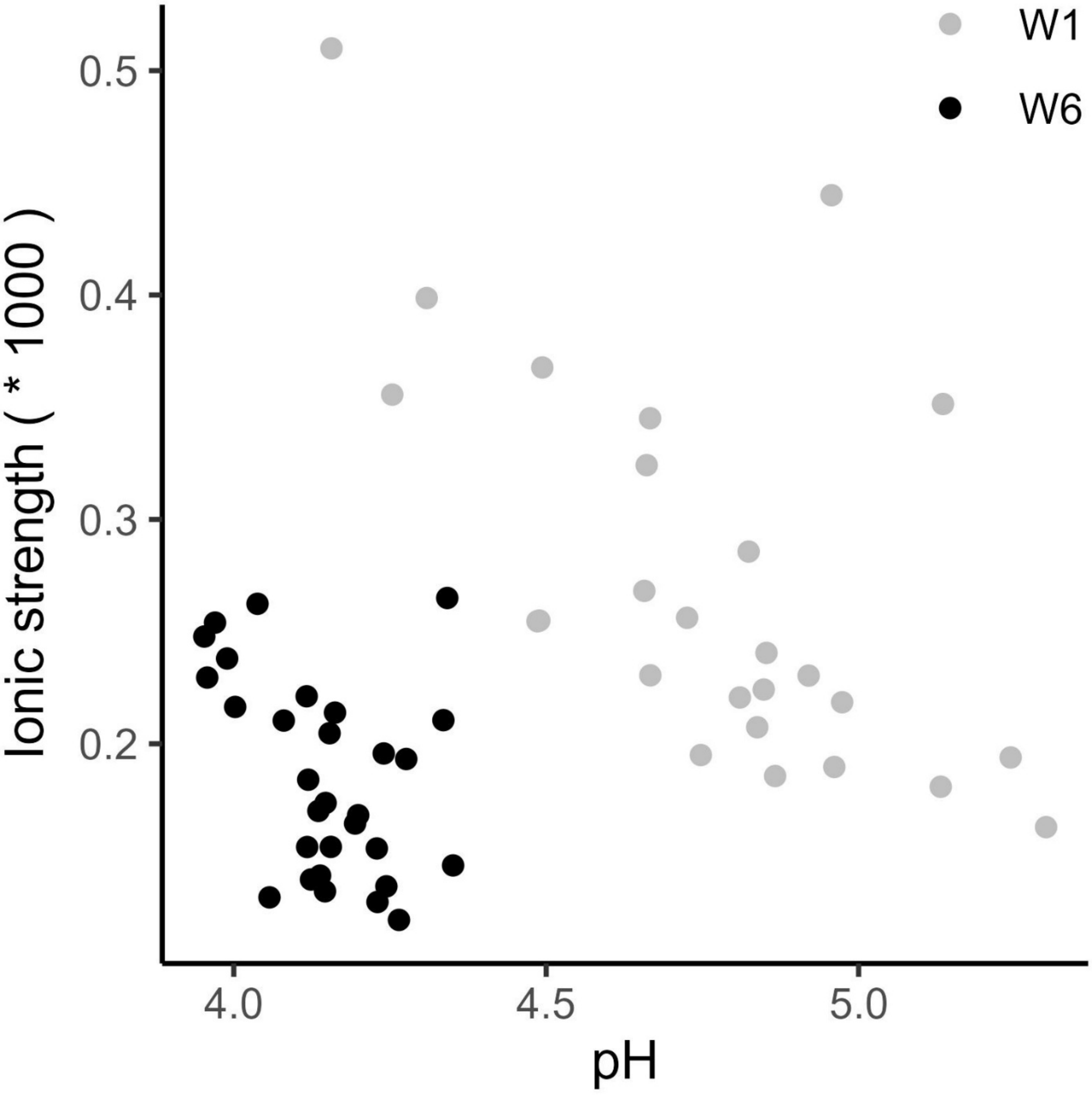

Figure S5. Ionic strength and pH of the soil solution in Watersheds 1 and 6 over the course of the study period. Each point represents an annual mean. In Watershed 1 the ionic strength declines at a fairly constant rate relative to the increase in pH – that is, all the points cluster around a single line with negative slope. In Watershed 6 there seems to be a breakpoint in this relationship around 2005, after which ionic strength declines and then levels out without substantial increases in pH.