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Disentangling The Separate And Intersecting Pathways Of Carbon And Nitrogen Response To Overlapping Drivers

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DISENTANGLING THE SEPARATE AND INTERSECTING PATHWAYS OF CARBON AND NITROGEN RESPONSE TO OVERLAPPING DRIVERS

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ABSTRACT

Anthropogenic activities have drastically altered atmospheric composition — leading to unprecedented disturbances that might push ecosystems across thresholds where important ecosystem services, such as clean water and healthy soils are at risk. Such disturbances include increased heavy precipitation, rain on snow events, and longer-term shifts in rain composition and precipitation amount. Catchment response to such perturbations is widely variable, indicating that specific catchment characteristics may govern the resistance and resilience of the system. Forested catchments in the northeastern, U.S. have reported increasing dissolved organic carbon (DOC) concentrations in streams, and links to shifts in drivers—such as precipitation chemistry, season, and event hydrology—have been proposed. While DOC response to overlapping disturbances is well-studied, changes in dissolved nitrogen (N) species and shifts in stoichiometry have not been investigated as thoroughly, presenting an important knowledge gap. My objective was to investigate the connection between superimposed disturbances, catchment dynamics, and differential stream response of carbon (C) and N in acid impacted soils. I used Sleepers River Research Watershed (SRRW) as a testbed because it has experienced significant shifts in precipitation dynamics and acid deposition, and long-term stream discharge and chemistry records are available. To investigate the connection between overlapping disturbances, catchment soil dynamics, and differential stream response, we combined analyses of these records to with newly collected data from soil core experiments.

I used Seasonal Kendall tests to quantify C and N trends in long-term datasets and compared results to processes in soil core experiments. To investigate how shifts in solution chemistry impact the liberation of C and N, I simulated hydrologic flushing events on soils from SRRW using flushing treatments of varied pH and ionic strength—which represent acid-deposition and reduced-acid deposition conditions. I found significant seasonal variability in both concentration-discharge behavior and soil effluent, indicating that seasonal hydrologic conditions and biological activity are principal drivers of C and N mobility and liberation at catchment scale. DOC and the dissolved organic fraction of N (DON) were coupled by season and landscape position, whereas inorganic N (DIN) was largely decoupled. Changes in soil solution were significant for all species during the winter, highlighting the importance of snowpack for processing and mobilizing materials. This research highlights the complex, coupled, and intersecting pathways of C and N which influence catchment response to disturbance. With these results, I investigated the relevance with respect to ecosystem resistance and resilience, and their significance to the possible trajectory of these disturbances in the future. I conclude that specific catchment characteristics at SRRW such as naturally buffered soils, may make the watershed more resistant to climate extremes.

CITATIONS

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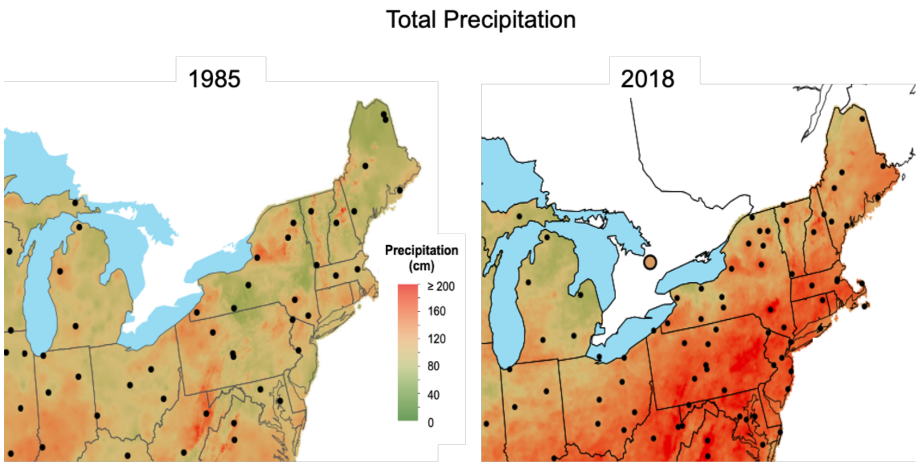
CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1. Disturbances in the Anthropocene

The Anthropocene is characterized by accelerated environmental change (Karl and Trenberth, 2003; Webster et al., 2016), with disturbances that threaten our ecosystems and well-being (Westley et al., 2013; Angeler and Allen, 2016; Webster et al., 2016). Depending on the magnitude of disturbance, ecosystems can reach a critical threshold by which ecosystem services such as clean water and healthy soils are at risk (Diaz and Rosenberg, 2008; Allen et al., 2018). Ecologists have investigated the connection between disturbances and ecosystem response using the concepts of resistance and resilience. In a resistant system, a prolonged or punctuated disturbance may result in little change, while a resilient system might change but will eventually revert to its original state (Diaz and Rosenberg, 2008; Angeler and Allen, 2016; Allen et al., 2018; Falkenmark et al., 2019). Anthropogenic emissions to the atmosphere cause such disturbances—such as acid rain and climate change— both with complex effects that have large regional variation (Seneviratne et al., 2012; IPCC, 2014).

In the northeastern U.S., precipitation has increased in both persistence and intensity over decades, and accounts for the greatest increase in extreme events (upper 10% of rainy days) in the country (IPCC, 2014; Guilbert et al., 2015; Figure 1). In a similar timeframe, the region has also experienced prolonged disturbance from dramatic shifts in the chemical composition of precipitation. First, due to acid deposition through much of the 20th century (Rice and Herman, 2012), then through its reversal after the passage of the Clean Air Act in 1990 (Futter et al., 2014). Following the implementation of the amendments, the region has experienced decreased deposition of anthropogenic acids and their dissociation products (e.g. NO_3^- and H^+; IPCC, 2014; Figure 2).

Figure 1. *Total precipitation (cm) in the northeastern United States from 1985 to 2018 (modified from National Atmospheric Deposition Program (2022).*

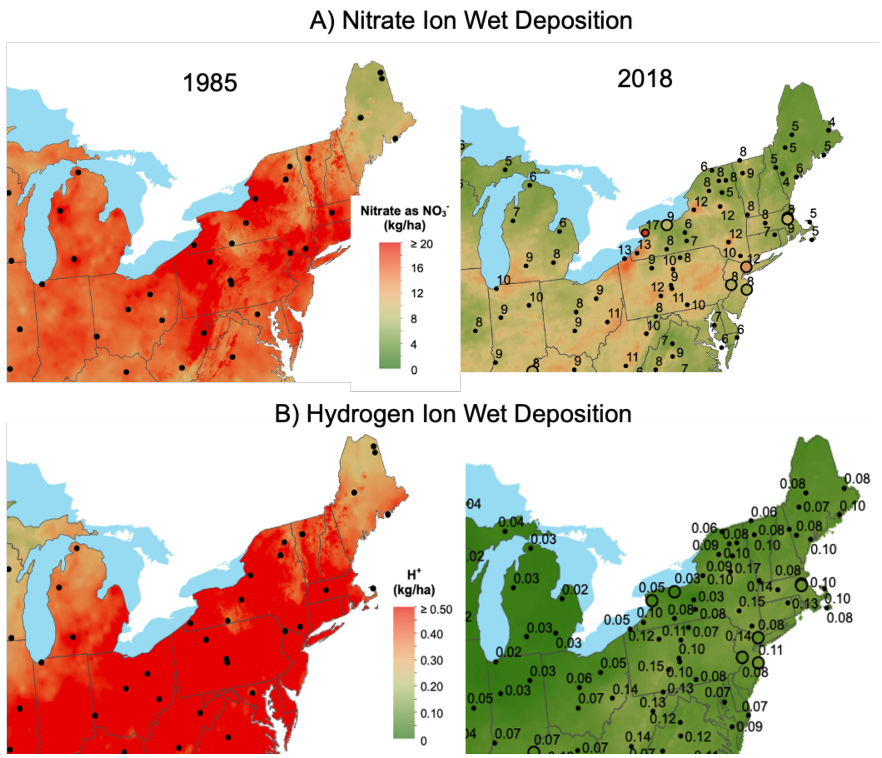


1.2. Impacts on Water Quality

Shifts in precipitation chemistry and increasing heavy precipitation events are impacting the composition of stream water—including carbon (C) and nitrogen (N) forms. These impacts are significant, as stream waters play a large role in the global C cycle, and their contributions to atmospheric CO_2 have been studied extensively (Raymond et al., 2013; Regnier et al., 2013; Aufdenkampe et al., 2016; Marx et al., 2017). Streams and rivers move significant amounts of dissolved organic carbon (DOC)— a labile form of C that is readily processed. As a result, streams are often supersaturated with CO_2, and high concentrations can flux more greenhouse gas back to the atmosphere. Indeed, approximately 82% of streams have twice the concentration of CO_2 compared to atmospheric levels (Regnier et al., 2013). Additionally, high levels of DOC can cause water browning and hazardous disinfection by-products during water treatment (Singer, 1994).

DOC is also a strong complexing agent, which can increase the mobility of toxic metals (Schiff et al., 1990).

Figure 2. *A) Nitrate ion wet deposition (eq/ha) and B) Hydrogen ion wet deposition (kg/ha) from 1985 to 2018 in the northeastern United States (modified from National Atmospheric Deposition Program (2022).*



Aquatic systems are equally important for N dynamics. Denitrification in rivers is a major pathway of N_2O—contributing to approximately 3% of global emissions (Ciais et al., 2013; Maavara et al., 2019). N is a key limiting nutrient in terrestrial and aquatic environments and consists of both dissolved inorganic (DIN) and organic (DON) forms. Rivers are highly efficient in transforming and transporting N, and excessive concentrations has been linked to eutrophication, decreased functional performance in aquatic organisms, and overall losses to biodiversity (Brezonik, 1973; Carpenter et al., 1998; Smith, 2003; Dodds et al., 2004; Gomez Isaza et al., 2020). Additionally, high levels of nitrate is considered a dangerous contaminant in natural waters (Freeze and Cherry, 1979; Allred, 2007), especially in drinking water—causing serious health conditions in humans, such as cancer and methemoglobinemia (blue baby syndrome; Ward et al., 2018).

While the total amounts of C and N species significantly impact water quality, their relative proportions are equally significant for aquatic productivity (Redfield, 1958; Fenn et al., 1998). Generally, ratios that are close to those found in aquatic organisms (i.e. the Redfield ratios C:N:P = 106:16:1) are observed to foster aquatic productivity most (Berner and Berner, 2012). C:N stoichiometry offers information on the energy and nutrient balance within an ecosystem and is greatly impacted by solute inputs, disturbance dynamics, and seasonal hydrologic events (Kincaid et al., 2020).

1.3. Catchment Dynamics and Sources of C and N

Headwater streams are important in the context of C and nutrient dynamics, as smaller streams have been shown to disproportionally account for large fluxes (Dodds et al., 2004; Raymond et al., 2013; Marx et al., 2017). Catchment soils have a significant impact on the composition of these smaller streams, and soil organic matter (SOM) is an important source for DOC and DON (Plante and Parton, 2007; Sposito, 2008).

DOC consists of many reactive forms including humic, fulvic, and hydrophilic-acids that reside within colloids (Schiff et al., 1990). The processes controlling DOC retention and release in soils are largely driven by soil sorption capacity to organo-mineral aggregates (Vandenbruwane et al., 2007; Cincotta et al., 2019; Wen et al., 2020). DON is mostly found in proteins, amino acids, and other soluble organic compounds (Brezonik, 1973). While DON and DOC are governed by similar mechanisms in soils, DON tends to be less retained by mineral phases (Vandenbruwane et al., 2007).

Inorganic forms of N include nitrate, nitrite, and ammonium. As the primary source of plant N uptake, nitrate and ammonium are extremely mobile in soils (Brezonik, 1973; Allred, 2007). Electrostatic interactions are dominant processes controlling nitrate mobility (Allred, 2007); notably, anion adsorption—where positively charged oxide surfaces cause assimilation of nitrate to these sites (Bolt, 1976), and exclusion—which occurs when the negatively charged nitrate anion is repelled from a double diffuse, negatively charged soil surface (Bolt, 1976; Allred, 2007). Overall, the chemical mechanisms that control retention and release of nutrients in soils make DOC, DON, and DIN sensitive to changes in soil solution.

1.4. Spatio-temporal Controls on Solute Production and Transport

C and N mobilization from soil to streams vary across spatio-temporal scales, and are inextricably related to seasonal fluctuations in soil temperature, moisture, and hydrologic conditions (Creed et al., 1996; Pellerin et al., 2012; Wilson et al., 2013; Perdrial et al., 2014, 2018; Webster et al., 2016; Marx et al., 2017; Seybold et al., 2019; Wen et al., 2020). For example, DIN accumulates in soils in absence of flushing events (Kincaid et al., 2020; Rupp et al., 2021). N mineralization is closely linked to soil moisture (Zhang and Wienhold, 2002), and increases linearly with pore water saturation (Zhang and Wienhold, 2002; Allred, 2007). DIN is also strongly linked to plant uptake, which varies seasonally. In the northeastern U.S., stream nitrate concentrations are typically low during peak growing season (summer) when plant N uptake is high, and reach maximum concentrations during the non-growing season (winter) when plant demand is low (Vitousek and Reiners, 1975; Creed et al., 1996; Judd et al., 2007; Goodale et al., 2009; Webster et al., 2016). Although biological mediation is largely considered to be the dominant control on N retention and release (Goodale et al., 2009; Webster et al., 2016), exceptional nitrate surges and crashes have been observed—and other controls such as C:N ratios and bedrock composition have been investigated as possible links (Cristopher et al., 2006; Goodale et al., 2009).

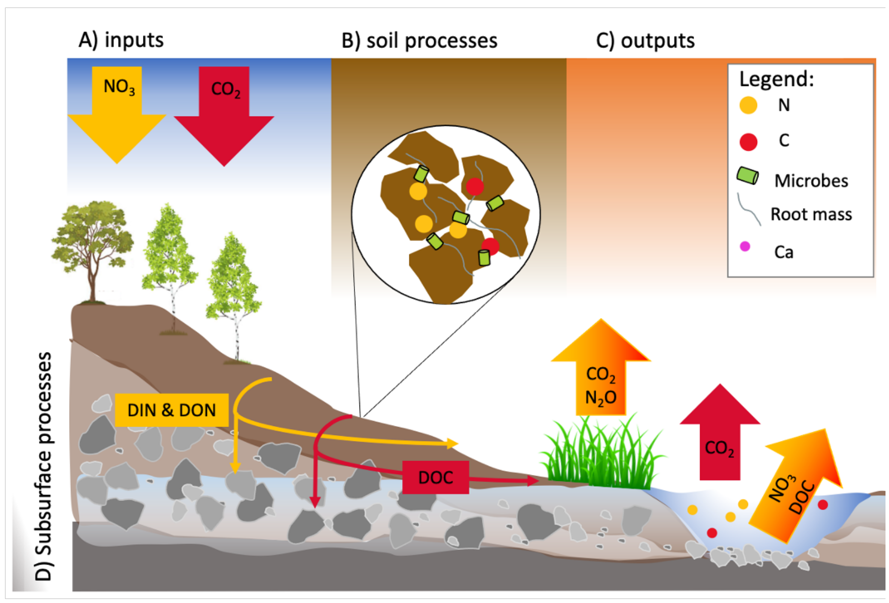
Stream DOC concentrations also have clear seasonal variability—which are closely linked to seasonal changes in flow regimes and hydrology connectivity (Perdrial et al., 2014; Marx et al., 2017; Wen et al., 2020). Temperature dominantly regulates the production of DOC, which increases during warm periods and can lead to accumulation of C until soils are flushed (Gillooly et al., 2001; Wen et al., 2020). Many studies have identified that lateral fluxes of DOC are directly correlated to precipitation events (Perdrial et al., 2014; Marx et al., 2017; Wen et al., 2020)—which hydrologically connect accumulation zones to streams. In seasonally snow-dominated catchments, snowmelt is the most important hydrologic event of the year in terms of both water volume and DOC exports (Brooks et al., 1999; Wilson et al., 2013; Perdrial et al., 2014; Marx et al., 2017). During this time, distant sources of DOC are activated during spring runoff and hydrologically connected to the stream network (Marx et al., 2017). Terrestrial C inputs also largely influence DOC fluxes, and stream C typically increases during fall abscission (Wilson et al., 2013; Marx et al., 2017).

C and N liberation to streams are governed by the overlap of biogeochemical activity and hydrologic connectivity that introduces complex spatial and temporal patterns (Figure 3). The concept of ecosystem control points (Bernhardt et al., 2017) is useful to clarify the interaction between biogeochemistry and hydrology in time and space. For example, permanent control points are those that are consistently hydrologically connected to streams, and have suitable environmental conditions for a continuous supply of DOC or nutrients (e.g. riparian zones; Bernhardt et al., 2017). Riparian zones important areas for N transformation—especially denitrification, because they are often water-logged and have organic rich soils. These zones have an especially strong influence on water and solute inputs to nearby surface waters (Bernhardt et al., 2017; Kincaid et al., 2020). Export control points can also foster biogeochemical productivity, but exports are largely event driven. DOC and nutrient exports are more variable because these localities often lack hydrologic connectivity. For example, planar hillslopes tend to accumulate DOC when they are not hydrologically connected to streams and are well aerated (Wen et al., 2020).

1.5. Research and Objectives

While DOC response to overlapping disturbances is well-studied, changes in dissolved N species and shifts in stoichiometry have not been investigated as thoroughly, presenting an important knowledge gap. My objective was to investigate the connection between superimposed disturbances, catchment dynamics, and differential stream response of C and N in acid impacted soils. I used Sleepers River Research Watershed (SRRW) as a testbed because it has experienced significant shifts in precipitation dynamics and acid deposition and long-term records are available. To investigate the connection between overlapping disturbances, catchment soil dynamics, and differential stream response, I combined analyses of these records to with newly collected data from soil core experiments (Chapter 2). With these results, I investigated the relevance with respect to ecosystem resistance and resilience, and their significance to the possible trajectory of these disturbances in the future (Chapter 3).

Figure 3. *Schematic representation of C and N dynamics in a catchment from A) atmospheric input as deposition/uptake, B) connection to soil processes, and C) outputs as gaseous, dissolved, and particulate forms.*



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CHAPTER 2: DISENTANGLING THE SEPARATE AND INTERSECTING PATHWAYS OF CARBON AND NITROGEN RESPONSE TO OVERLAPPING DRIVERS

Abstract

Reduced acid deposition and increased precipitation impacts stream solutes including dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved inorganic nitrogen (DIN), in complex ways that make predictions of future water quality difficult. To disentangle the separate and intersecting pathways of solute sources and dynamics on streams, we investigated regional disturbances and catchment specific soil processes using a combined “pattern and process” approach using Sleepers River Research Watershed (SRRW) as a testbed. For pattern investigation, we used concentration-discharge (C-Q) relationships and Seasonal Kendall tests on long-term, flow adjusted data to investigate discharge controls and additional drivers separately. To investigate how shifts in solution chemistry impact the liberation of solutes, we flushed intact soil cores with solutions that simulate increased and decreased acid deposition. Our results indicate that DOC and DON often co-varied in long-term data and experiments, and that especially winter soils produced high solute concentrations in effluent. These results were consistent with C-Q relationships during spring snowmelt where especially organic solutes show a linear correlation with Q. Highest concentrations were found in the solution simulating present day conditions of decreased acid deposition, which is in agreement with the general increasing trend in stream DOC over decades. In contrast, reduced acid deposition leads to reduced DIN in streams, but our results indicate that soil processes additionally might exacerbate this trend because highest DIN release was found in solutions representing past conditions of acid deposition. Together, these results point to a pattern of continued increases in stream DOC and decreases in stream DIN—overall driving increasing C:N ratios. Changes in solute stoichiometry have important effects on aquatic productivity, and therefore play a critical role in predicting future conditions.

2.1. Introduction

Both carbon (C) and nitrogen (N) species pose potential threats to the quality of natural waters and are carefully monitored globally (Carpenter et al., 1998; Smith, 2003). The dissolved fraction of organic carbon (DOC) in streams and rivers plays an important role in the global C cycle (Schlesinger and Melack, 1981;Aufdenkampe et al., 2011;Perdrial et al., 2014). Elevated DOC concentraions can lead to water browning and can form hazardous disinfection by-products during water treatment (Singer, 1994). High levels of nitrates in drinking water have been linked to serious health conditions such as cancer, methemoglobinemia (blue baby syndrome), and decreased functional performance in aquatic organisms (Ward et al., 2018; Gomez et al., 2020). Nitrogen is a limiting nutrient in terrestrial ecosystems and as a result, N accumulation can led to eutrophication with significant ecosystem effects (Fenn et al., 1998). While the total amounts of C and N species impact water quality significantly, their relative proportions are equally important for aquatic productivity (Fenn et al., 1998). Ratios that are close to those found in aquatic organisms (i.e., the Redfield ratios C:N:P = 106:16:1) are observed to foster aquatic productivity most (Berner and Berner, 2012). C:N stoichiometry offers information on the energy and nutrient balance within an ecosystem and is greatly impacted by solute inputs, disturbance dynamics, and seasonal hydrologic events (Kincaid et al., 2020).

Hydrology is a dominant driver of C and nutrient export at the catchment scale (Raymond and Saiers, 2010; Wilson et al., 2013; Perdrial et al., 2014; Seybold et al., 2019; Wen et al., 2020), and regional changes in precipitation chemistry and patterns are relevant for total and relative C and N concentrations. In the northeastern U.S., climate change is leading to increases in heavy precipitation (Hayhoe, 2007; Galford et al., 2014; IPCC, 2014), and many discharge (Q) dependent constituents are changing as a result. For most catchments, DOC increases with discharge as soil flushing is an important process for DOC mobilization (Perdrial et al., 2014; Shanley et al., 2022). Many northeastern headwater catchments are snow dominated— and snowmelt is a particularly important time for DOC export, as soils have been accumulating labile C under the snowpack before being flushed out (Brooks et al., 1999). For N species, climate related patterns are complex because sources and processes of N liberation vary. Recent research has especially emphasized the importance of rain on snow events, which account for a significant fraction of N export (Seybold et al., 2019).

In the northeastern U.S. especially, increases in heavy precipitation is superimposed by another disturbance— shifts in atmospheric deposition. Since the implementation of the 1990 Clean Air Act Amendments, deposition of anthropogenic acids and their dissociation products (e.g. NO_3^- and H^+) have decreased, leading to decreases in nitrate in streams (Fenn et al., 1998; Aber et al., 1989; Meixner and Bales, 2003; Lawrence et al., 2020). While C species are not involved in this deposition, this shift has also impacted DOC in streams (Monteith et al., 2007; Hazlett et al., 2020; Lawrence et al., 2020; Adler et al., 2021; Lepistö et al., 2021). Some studies have established links to C mobilization from soils, and showed that soil aggregates can become destabilized in low charge density environments and release DOC as a result (Cincotta et al., 2019; Adler et al., 2021; Bristol, 2021). Because soil organic matter (SOM) is a common source for both C and N species, a connection to N release is likely. These processes, however, have yet to be investigated for N species.

Irrespective of these prolonged and regional disturbances, seasonal dynamics, and spatial variability (i.e., landscape position) have strong effects on C and N dynamics and solute release into streams. For example, some landscape positions such as planar hillslopes might accumulate materials until they are hydrologically connected— while locations such as riparian zones exhibit near continuous connectivity to the stream (Bernhardt et al., 2017). Thus, varied hydrologic connectivity of different landscape position leads to significant variability in C and N export. These dynamics also overlap with biogeochemical controls because microbial processing is regulated by soil temperature, moisture, and oxygen availability (Wen et al., 2020).

While DOC is well-studied, changes in dissolved N species and shifts in stoichiometry in response to overlapping disturbances have not been investigated as thoroughly, presenting an important knowledge gap. Our objective is therefore to investigate the connection between regional disturbances, catchment dynamics and differential stream response and to disentangle the separate and intersecting pathways of C and N response. We used Sleepers River Research Watershed (SRRW) as our testbed as this watershed has experienced overlapping disturbances since 1990, including increasing pH and Q, and has nearly continuous long-term data recording these changes.

We use a "pattern and process" approach to test hypotheses on the seasonal pathways and possible long-term contribution of soil to patterns in concentration-discharge (C-Q). We combine statistical analyses on long-term data to identify general patterns in long-term trends and C-Q relationships (Adler et al., 2021), and soil core experiments that simulate the process of soil flushing with solutions representing increased and decreased acid deposition.

Specifically, we hypothesized that organic species (DOC and DON) covary across seasons and will respond similarly to the different treatment solutions because these species share a common source (SOM). Furthermore, we hypothesized that DIN is independent of the organic species—being mostly impacted by seasonal variations in N production and demand, but unaffected by different treatment solutions. We bring findings from both approaches and investigate insights and limitations in the context of continued shifts in precipitation amount and composition.

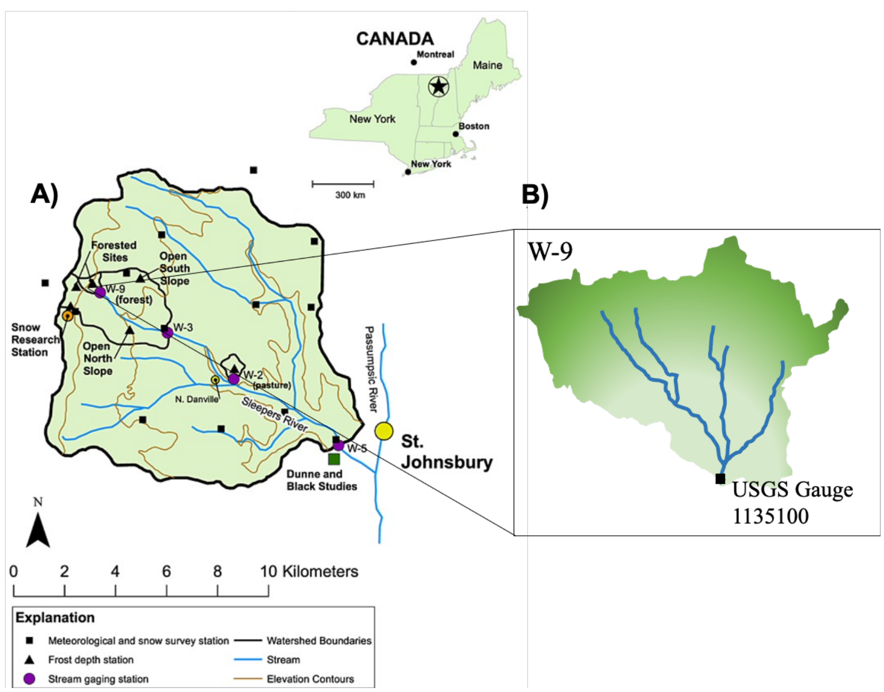
2.2. Methods and Materials

2.2.1 Study Area

SRRW is located in northeastern Vermont and is comprised of nested catchments varying from forested to agricultural landcover. SRRW has received significant amounts of acid deposition in past decades (Shanley, 2000; IPCC, 2014). Hydrologic and biogeochemical databases date back to 1959 and represent one of the longest continuous climate records in the region (Shanley, 2000). Watershed 9 (W-9) consists of 40.5 ha of northern hardwood forest and was used as a testbed to study the connection between precipitation chemistry and surface water composition (Figure 4).

The bedrock geology of the area is dominantly quartz-mica phyllite with interbedded calcareous granulite. The presence of calcite in the parent material distinguishes SRRW from many other northeastern catchments in that the ground and stream water are buffered, and deeper soils are not calcium depleted (Armfield et al., 2019). The bedrock is overlain by 1-4 meters of basal till emplaced from previous glaciation (Shanley et al., 2004). Dominant soil types include Inceptisols and Spodosols on hillslopes, and Histosols in riparian zones (Shanley et al., 2004). Vegetative cover in W-9 consists of sugar maple, beech, yellow birch, and white ash trees (Shanley, 2000). SRRW is located in a humid, temperate region where annual temperatures range from -30 to +30°C (Shanley, 2000; Pellerin et al., 2012). W-9 is a seasonally snow-covered catchment and 20-30% of yearly precipitation accumulates as snow (Pellerin et al., 2012). Water yields are dominated by spring snowmelt and event-driven overland flow therefore, streamflow and solute concentration have distinctive seasonal patterns (Shanley, 2000; Pellerin et al., 2012; Armfield et al., 2019; Shanley et al., 2022).

Figure 4. *Location of field site in the northeastern US. A) Nested catchments in the Sleepers River Research Watershed, B) Forested headwater catchment and study site (W-9) (modified from Shanley et al., 2002).*



2.2.2 Field Sampling and Experimental Design

To capture the seasonal variations in hydrologic drivers and nutrient dynamics, we collected soil cores during the fall, winter, spring, and summer (Table 1). To investigate how landscape position impacts solute release across seasons, soil cores were sampled from both hillslopes and riparian zones. During each of the sampling campaigns, we collected 27 cores— of which 13 were taken from hillslopes and 14 from riparian zones.

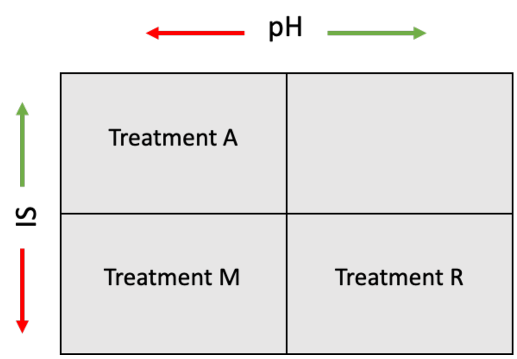
Table 1. *Sampling date, location, landscape position and cores collected at Sleepers River Research Watershed W-9.*

Sampling Date	Location (Decimal Degrees)	Landscape Position	Number of Cores
2020-11-06	44.493920, -72.159630	Hillslope	14
2020-11-06	44.493450, -72.160010	Riparian	13
2021-03-12	44.292943, -72.093544	Hillslope	14
2021-03-12	44.292985, -72.093725	Riparian	13
2021-05-31	44.292834, -72.093585	Hillslope	14
2021-05-31	44.494952, -72.093742	Riparian	13
2021-07-22	44.292914, -72.093556	Hillslope	13
2021-07-22	44.292956, -72.093747	Riparian	14

Before collecting cores, we removed leaf litter and forest debris from the soil surface. This was particularly important for fall soils that were covered by a layer of fresh leaf litter. Winter soils were covered by ~120 cm of snow that was removed before sampling. Our experiments focused on the interaction of event waters and shallow soil layers, therefore only the top 10 cm of soil (O and A horizons) was collected by hammering 2 in diameter PVC pipes into the soil. Cores were carefully removed to maintain the structural integrity of the sample, sealed with parafilm and tape, transported to the laboratory, and stored at 4°C until experimentation within 24 hours of collection.

We designed soil core experiments to test the effects of hydrologic flushing events and shifts in solution chemistry on soil DOC, DIN, and DON release. Treatment "A" (=acidification) simulated conditions during the onset of acidification—having high ionic strength ($3*10^{-2}$ M) from $CaCl_2$, and low pH (=3 adjusted with HCl). Treatment "R" (=recovery) simulated reduced acid deposition—having low ionic strength ($<10^{-5}$ M) and a pH of 5. The third solution (Treatment "M" = mixed) had a low pH (comparable to Treatment A) and low ionic strength (comparable to Treatment R), to allow for testing the influence of pH and ionic strength as individual variables (Figure 5).

Figure 5. *Treatment variables: pH versus ionic strength (IS). pH increases from horizontally (left to right). IS increases vertically (bottom to top).*



For flushing experiments, we followed the procedure outlined in Cincotta et al., (2019) and Adler et al., (2021), in which soil cores were positioned vertically and stop valves placed through the PVC caps to control interaction time between the solutions and the soil. Each flushing consisted of the addition of 120 ml of solution to the top of the core, followed by 5 minutes of interaction time. Gravitationally drained effluent was collected for 4 min into precleaned bottles. Effluent of each flushing was collected individually and filtered through a 0.45-µm polyethersulfone filter, into combusted glass vials within 24 hrs of experiments A schematic of soil core setup is provided in supplementary materials. This process was performed twice, to capture solute release during the onset of an hydrological event, as previous studies have indicated significant decreased solute release thereafter (Adler et al., 2021; Bristol, 2021).

2.2.3 Sample and Data Analyses

Soil effluent was analyzed for DOC and Total Dissolved Nitrogen (TDN) using a Shimadzu Carbon Analyzer (Shimadzu, Colombia, MD, USA). Anions, including nitrate and nitrite, were measured using a Thermo Scientific Dionex Aquion Ion Chromatography System (Thermo Fisher Scientific, USA), and reported as N (e.g., Nitrate-N). pH was measured using a benchtop pH probe and meter to confirm and acceptable range. DON was calculated by subtracting DIN (i.e., nitrate and nitrite) from TDN. To compare results between soil cores, effluent was normalized to the amount of liquid and solid and reported in mg/kg of soil.

All statistical analysis was performed using RStudio Version 1.3.1093. Kruskal-Wallis tests were performed on data from non-normal distributions. Statistical significance for difference in means for treatment and landscape position was determined using an alpha (α) threshold of 0.05 obtained from a chi-square statistic (χ^2).

2.2.4 Long-Term Trend Analysis: Flow-Adjusted Data and Seasonal Mann-Kendall Tests

To investigate stream response to long-term shifts in atmospheric drivers we used two main approaches on datasets from SRRW W-9, USGS Gauge 1135100 (Matt et al., 2021). The first approach investigated how stream solute concentrations vary with variations in Q. For this we used instantaneous raw DOC, DIN, and DON concentrations (mg/L) with corresponding discharge measurements from the closest time stamp as the sampling time and plotted these by season.

Our second approach removed the typically dominant Q control on soil derived stream water solutes. For this we log-transformed DOC, DON, and DIN concentrations and Q, and extracted residuals from a Locally Weighted Scatterplot Smoothing (LOWESS) regression using a smoothing pattern coefficient (f=0.67; Locally weighted scatterplots are available in supplementary materials). Final flow adjusted concentrations (DOC_{FA}, DIN_{FA}, DON_{FA}) were obtained from reordering the LOWESS residuals according to corresponding date/time stamp.

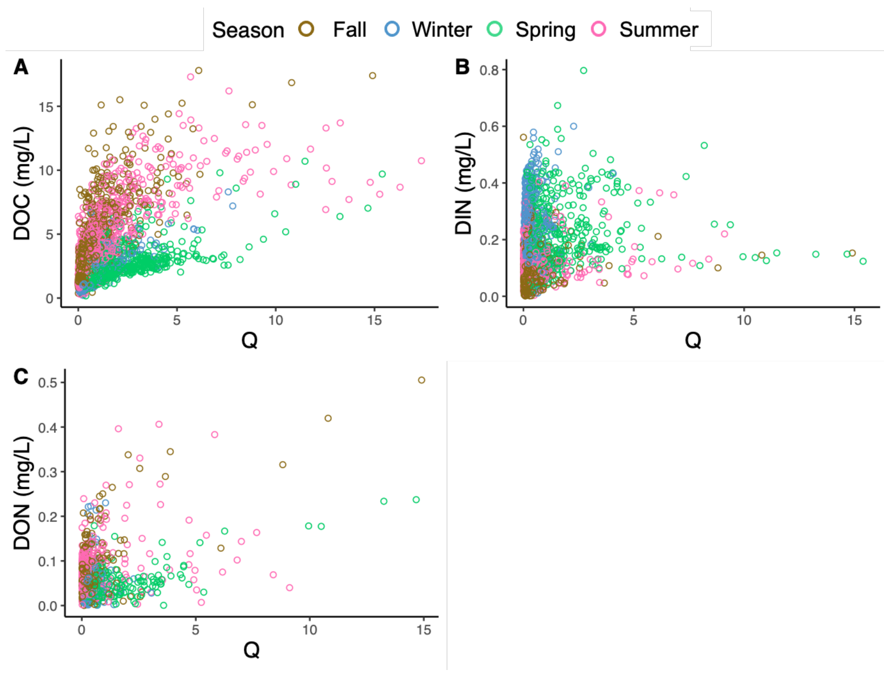
To correct for seasonal dependance, we performed monotonic trend analysis for time series— or Mann-Kendall statistical tests, to detect upward (positive) or downward (negative) trends in flow-adjusted data, independent of seasonal influence (Hirsch and Slack, 1984). Positive and negative trends were identified by the normalized test statistic, Kendall's tau ($\tau = \pm 1$), where positive trends have a tau-value of >0.05 and negative trends of <0.05, with a statistically significant alpha threshold of 0.05. Finally, we applied a Pettitt test to identify change points (trend shifts) in continuous time series data that otherwise could be missed from monotonic trend analysis (Pettitt, 1979).

2.3. Results

2.3.1 Long-Term Stream Chemistry: C-Q Relationships

Stream solute concentrations at SRRW varied seasonally for all investigated species. The concentrations of organic forms (DOC and DON) showed similar behavior for some seasons. Both solutes had variable concentrations in fall and summer and increased linearly with discharge during spring (snowmelt) (Figure 6a & c). For DON, the highest concentrations were found in fall and summer—typically at lower flow. For DOC, these seasons yielded high concentrations across flow regimes. DIN concentrations in contrast did not exhibit systematic changes with discharge but were generally low in fall, and variable in all other seasons irrespective of flow—low in winter and highly variable in spring and summer (Figure 6b).

Figure 6. *Seasonal concentration-discharge (C-Q) behavior for A) DOC (mg/L), B) DIN, and C) DON. Seasons are represented by color: fall (brown), winter (blue), spring (green), summer (pink).*

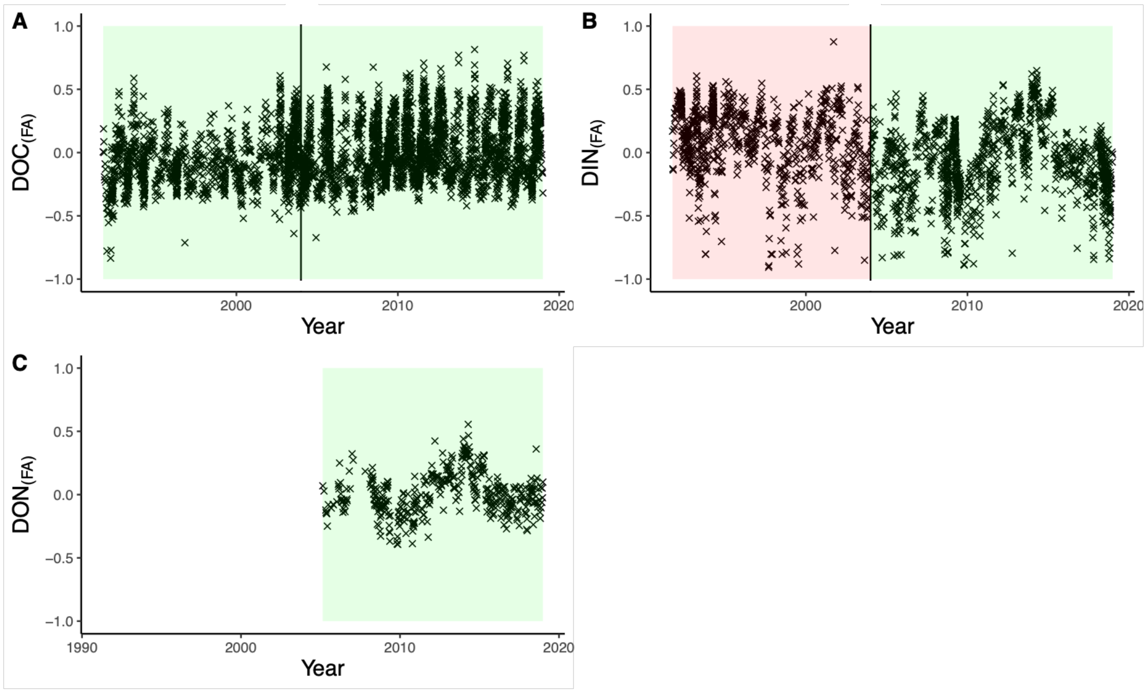


2.3.2 Long-Term Stream Chemistry: Flow-Adjusted Trends

The flow adjusted concentrations of DOC_{FA}, DIN_{FA}, and DON_{FA} showed significant but contrasting trends. DOC_{FA} generally increased between 1991-2018 (τ=0.116, Figure 7a), but no single season drove this increase— as seasonally independent DOC_{FA} trends were insignificant (see supplementary materials for faceted seasonal results). Pettitt change point detection analysis showed that a trend shift occurred in the mid-2000s where before (1991-2004), DOC_{FA} had increased more strongly than thereafter (τ=0.144 vs. 0.08, Figure 7a).

On the contrary, DIN_{FA} generally decreased between 1991-2018 (τ=-0.185, Figure 7b) and significant decreases were observed across all seasons (supplementary materials). Similar to DOC_{FA}, Pettitt change point detection analysis showed a trend shift in the mid-2000s. DIN_{FA} signals were more variable after 2004 and showed a marked drop in concentrations around 2010, followed by a progressive until 2015, after which concentrations decreased again (Figure 7b). Seasonal Kendall tests show the decrease before 2004 to be significant (τ=-0.154). DON data for SRRW is not available prior to 2005 and we could not analyze the longer-term trends. However, DON_{FA} showed a similar fluctuating pattern like DIN_{FA}, where concentrations increase from 2005-2007, sharply decreased between 2007 and 2010, followed by a progressive increase until about 2014, after which concentrations decrease again. The peak in DON_{FA} concentrations was observed in all seasons individually (graph provided in supplementary materials).

Figure 7. *Long-term trends in flow-adjusted A) DOC concentrations, B) DIN concentrations, and C) DON concentrations. Trends are divided prior to 2004 and after 2004. Statistically significant (α ≤ 0.05) positive trends are shaded in green, and significant negative trends in red.*

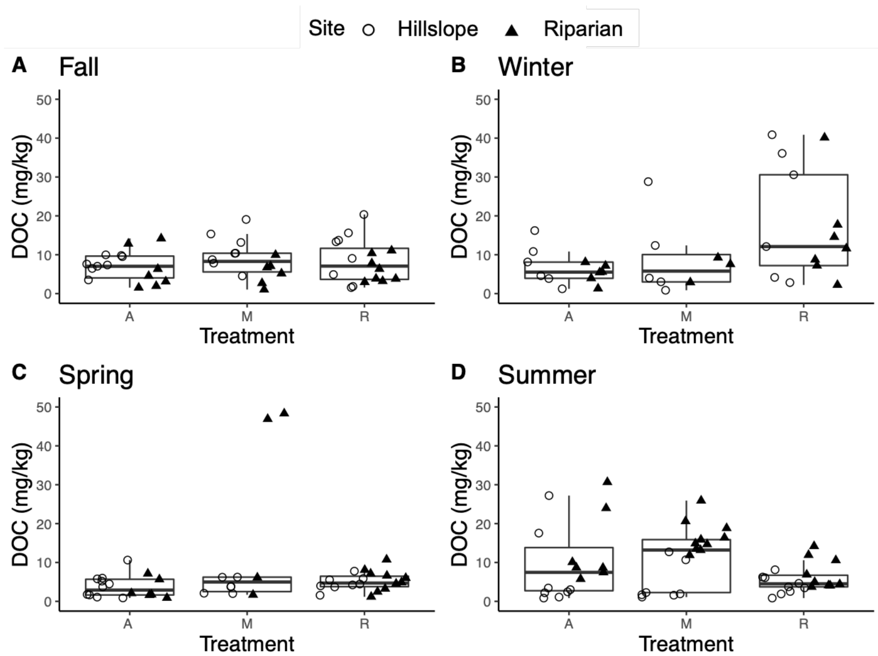


2.3.3 Soil Core Experiments: DOC, DIN, and DON Release by Season, Treatment, and Landscape Position

DOC leachate concentrations varied most significantly by season, but the effect of treatment was only significant for winter samples. Leachate from fall soils were low across treatments (between 1-17 mg/kg, Figure 8a) while DOC concentrations in winter soil had highest mean concentrations from Treatment R for both hillslopes (21.3 mg/kg) and riparian zones (11.6 mg/kg). Pair-wise comparisons of treatments showed the difference in means was statistically significant for Treatments A-M (Dunn, p=0.03) and A-R (Dunn, p=0.008; see supplementary materials).

Spring samples had the lowest concentrations ranging from 0.9-10 mg/kg and treatment did not have a significant effect. Leachate from summer soils did not vary significantly by treatment however, concentrations were generally high—ranging from 0.8-27 mg/kg (Figure 8c). Irrespective of treatment, the highest DOC concentrations were found in leachate from hillslope samples in the fall and winter — and riparian zone samples in the summer.

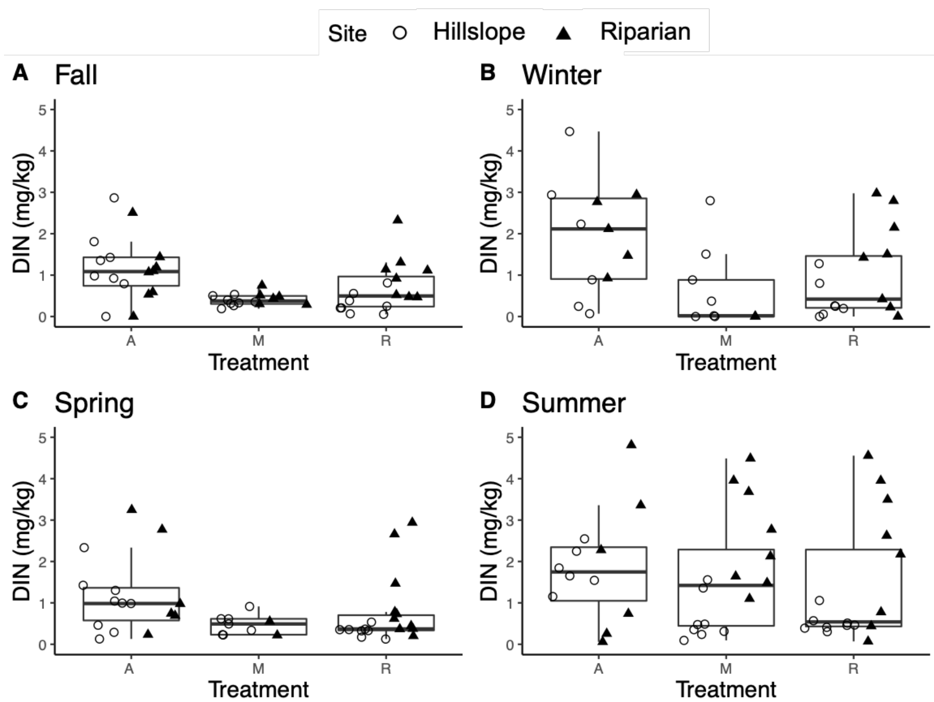
Figure 8. *DOC concentrations from seasonal soil core leaching experiments for A) Fall, B) Winter, C) Spring, D) Summer. Open circles represent samples collected from hillslope positions and triangles represent samples from riparian zones.*



DIN concentrations in leachate varied significantly by season and in some cases by treatment. For example, concentrations in fall soil leachates were generally low (between 0-2.9 mg/kg) with the highest means from Treatment A (1.09 mg/kg, Figure 9a). Pair-wise comparisons of treatments showed statistically significant differences in means between Treatments A-M (Dunn, p= 9.194e-07) and A-R (Dunn, p= 1.256e-04; see supplementary materials). Concentrations from winter soils were generally high (up to 4.5

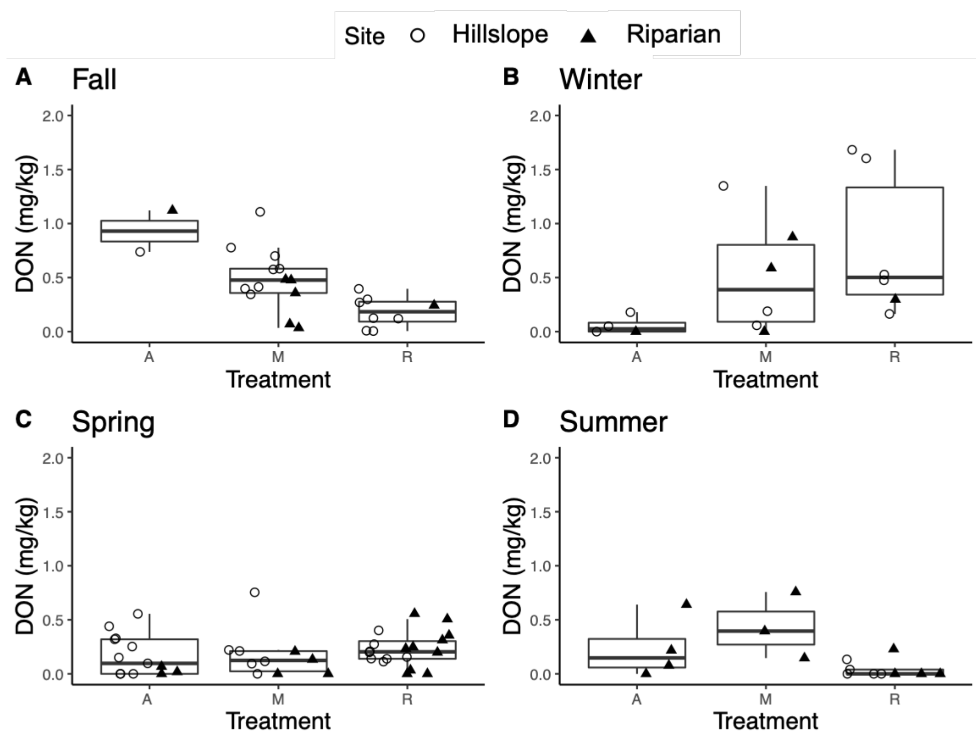
mg/kg), especially for Treatment A in both hillslopes (mean=1.6 mg/kg) and riparian zones (mean=2.1 mg/kg). Mean concentrations from Treatment R were lower, ranging from 0.2 mg/kg for hillslopes to 1.5 mg/kg in riparian zones. Spring samples had the lowest concentrations (with maxima of 2.33 mg/kg) and did not vary significantly by treatment. Leachate from summer samples had highest concentration in soils from riparian zones (up to 4.8 mg/kg) but treatment had no effect.

Figure 9. *DIN concentrations from seasonal soil core leaching experiments for A) Fall, B) Winter, C) Spring, D) Summer. Open circles represent samples collected from hillslope positions and triangles represent samples from riparian zones.*



DON varied most significantly by season and treatment (Figure 10). For leachate from fall samples, the highest means were observed from Treatment A (0.93 mg/kg) compared to other treatments (0.48 mg/kg for M and 0.18 mg/kg for R). Pair-wise comparisons of treatments showed significant difference in means between Treatments A-M (Dunn, $p<0.001$), A-R (Dunn, 4.317e-03), and M-R (Dunn, $p<0.001$; see supplementary materials). Like DOC and DIN, DON concentrations in leachate from winter soils (especially hillslopes) were high (up to 1.68 mg/kg) and varied significantly by treatment. Pair-wise comparisons of showed significant difference in means between Treatments A-M (Dunn, p<0.001) and A-R (Dunn, p= 0.0269; see supplementary materials). Spring samples leachate yielded low concentrations (maximum of 0.51 mg/kg) and did not have a differential response to treatment. Leachate from summer samples, especially riparian zone soils, were generally higher (up to 0.76 mg/kg). The highest means were observed from Treatment M (0.40 mg/kg), which was significantly different to Treatment R (Dunn, p= 0.002).

Figure 10. *DON concentrations from seasonal soil core leaching experiments for A) Fall, B) Winter, C) Spring, D) Summer. Open circles represent samples collected from hillslope positions and triangles represent samples from riparian zones.*



2.4. Discussion

Overlapping disturbances such as reduced acid deposition and increased precipitation impact stream water solute patterns in complex ways (Freeman et al., 2001; Worrall and Burt, 2006; De Wit et al., 2007; Monteith et al., 2007; Eimers et al., 2008; Hruška et al., 2009; Adler et al., 2021; Lepistö et al., 2021), making predictions of water quality in light of continued changes difficult. Our overarching objective was therefore to investigate the connection between regional disturbances, catchment dynamics, and differential stream response, to disentangle the separate and intersecting pathways of C and N response.

2.4.1 Patterns in Stream Water: Do C and N Respond Differentially to Various Drivers?

To identify general patterns in long-term trends and C-Q relationships, we first investigated the discharge control on DOC and N-species in long-tern datasets and found large variability in C-Q patterns for all investigated solutes with pronounced seasonal differences (Figure 6). High flow values were mostly found in spring and summer that are consistent with events (storms in summer and snowmelt in spring). Such events are particularly important for soil flushing that mobilizes significant amounts of DOC and other soil-derived solutes to the streams (Boyer et al., 1997). By water volume, snowmelt is a significant event that— despite the extensive Q related mobilization of solutes—can produce generally lower solute concentrations than shorter lived events in other seasons (Pellerin et al., 2012; Winnick et al., 2015). Indeed, DOC and DON solute concentrations showed a linear correlation with flow during this time, consistent with a common, soil-derived source and concentrations were relatively low due to the dilution effect of the significant water volume. In summer, DOC concentrations systematically increased with Q, and were typically higher but more varied. This is in agreement with predictions that DOC is likely to increase as the result of longer growing seasons (Shanley et al., 2022).

DIN concentrations in contrast, were highest in winter and spring (Figure 6b and c), a signal that is consistent with previous studies in the area that found stream nitrate elevated as a result of rain on snow events and early snowmelt (Pellerin et al., 2012; Casson et al., 2014; Viglietti et al., 2014; Seybold et al., 2019; Kincaid et al., 2020). However, DIN concentrations did not vary systematically with Q, and in contrast to the organic solutes, soil flushing might not the dominant control. Instead, a combination of lack of biological demand, accumulation and retention contribute to these high loads. Because these events are responsible for up to 90% of nitrate exports during the winter (Casson et al., 2014), these types of events need to be considered carefully with respect to future patterns in stream N, as rain on snow events are projected to become more abundant with winter climate change (Jeong and Sushama, 2018).

To assess the presence or significance of drivers—other than the often-dominant discharge control on steam solutes, we also investigated temporal trends in flow-adjusted data. Our findings of increasing DOC_{FA} (Figure 7a) over several decades are in agreement with previous work that identified a significant positive trend for DOC at SRRW that has been attributed to reduced acid deposition (Cincotta et al., 2019; Adler et al., 2021; Bristol, 2021) (DON_{FA} is unfortunately not available for this time period). However, this increase is not driven significantly by any specific season (supplementary), which indicates that a number of processes likely contribute to this pattern. Contrary to the increase in DOC_{FA}, DIN_{FA} data showed a general, significant decrease over past decades (Figure 7b), which is consistent with decreases in atmospheric nitrate deposition and resulting surface water levels across other watersheds in the northeast (Eshleman et al., 2013; Sabo et al., 2016; Winter et al., 2021), and is driven by decreases in all seasons (supplementary materials).

The large fluctuations for DIN_{FA} and DON_{FA} after the mid-2000s, are superimposed onto the general decrease of N in streams and point to additional dynamics independent of shifts in deposition. While the exact cause of these fluctuations is unclear, the abnormal to moderate drought in late 2009 and 2010, followed by an exceptionally wet year in 2013-2014 across New England might have contributed (USDM and NOAA (2014); see supplementary materials). Periods of drought reduce soil microbial activity and plant uptake (Rupp et al., 2021) and lead to N accumulation that is available for flushing thereafter (McClain et al., 2003; Rupp et al., 2021). Indeed, a recent study found that dry periods followed by heavy rainfall can disrupt the water-solute balance in soils, and lead to exceptionally high N concentrations in streams (Rupp et al., 2021).

Even though the flow-adjustment method removes the Q control on DOC and N species, this does not mean that observed changes are not related to shifts in precipitation amounts. For example, increased precipitation can cause increased soil moisture to the extent that carbon is not respired due to anoxic conditions (Wen et al., 2020), whereas N forms can be mineralized. In this case DOC can accumulate despite otherwise favorable conditions for aerobic respiration (e.g., warm summer temperatures) and nitrate would be reduced to gaseous forms (Huang and Hall, 2017). Indeed, summer DOC concentrations at high flow are elevated, but nitrate concentrations, albeit more variable— are high as well. Therefore, more work is necessary to disentangle these various controls (Figure 6).

2.4.2 The Role of Soil Derived C and N: indications of co-variations in pathways

To test our hypotheses on the pathways of DOC, DON, and DIN from soil flushing and shifts in precipitation chemistry, we conducted soil core experiments with solutions representing high and low acid deposition. These experiments allowed us to simulate general conditions of past acidification, with high ionic strength and low pH, as well as current (or future) conditions with higher pH and lower ionic strength. Because availability of solutes for mobilization is a function of seasonal dynamics of production, removal, and catchment connectivity (Bernhardt et al., 2017), we conducted these experiments across seasons and landscape positions.

Specifically, we hypothesized that DOC and DON covary across seasons and are similarly impacted by treatments because they share SOM as a common source. Furthermore, we hypothesized that DIN is mostly impacted by seasonal variations in production and demand, but unaffected by treatment. We consider the results of these experiments are most applicable when the conditions we simulate (i.e. intense hydrological events) also occur in the natural setting. Spring snowmelt is the most important hydrological event in this seasonally snow-dominated system (Brooks et al., 1999; Wilson et al., 2013; Perdrial et al., 2014; Marx et al., 2017). However, maybe counterintuitively, spring soils are not ideal to test the effect of snowmelt on solute mobilization as these soils have already been flushed during snowmelt on site. This effect is visible in the low concentrations of all investigated solutes (Figure 8c-10c), generally independent of treatment solution.

Winter soils however, represent the conditions right before snowmelt and is an ideal time for investigating solute release. During snowmelt, the entire catchment typically becomes hydrologically connected to the stream (Pellerin et al., 2012), hence results from both landscape positions (hillslopes and riparian zones) are relevant. For both organic species (DOC and DON) and landscape positions, high amounts of solutes were released into low charge density Treatment R (for DON additionally into Treatment M, Figure 8 and 10), which is consistent with results of a previous study that found high organic solute mobilization from winter soil experiments (Bristol, 2021). Related studies using batch and soil core experiments found that soils at SRRW treated with the low charge density solution released more DOC and had after treatment, smaller aggregates than those treated with a high charge density solution (Cincotta et al., 2019; Adler et al., 2021; Bristol, 2021). These results indicate soil aggregate breakup as one reason for increased DOC release. DON is equally a constituent of soil aggregates (Wilson et al., 2013), and this result might point to aggregate breakup as a common, soil-derived source. Together, these observations agree with our hypothesis. However, DON might also respond to additional dynamics that are decoupled from DOC. For example, we found variable DON concentrations by treatment in fall soil leachate whereas DOC concentrations did not vary. Generally, fall soils are strongly impacted by leaf litter (Goodale et al., 2009; Wilson et al., 2013) and despite the fact that we removed the litter layers, labile materials might have been present from the fresh litter layer. However, sample size for DON was generally too small, especially to confirm the high concentrations in Treatment A, and more work is necessary to clarify the contribution of DON in this case (Figure 10).

Also, as hypothesized, DIN concentrations in effluent were strongly impacted by seasons and were generally low in spring and fall and high in summer and winter. Even though we did not actively simulate the variety of biogeochemical and hydrological processes across seasons, the conditions of sampled soils are a result of these combined processes prior to sampling, thus, we interpret our results in this context. For example, rising temperatures makes summer is a biogeochemically active time. Riparian zones especially remain wet and offer ideal conditions for biogeochemical cycling (Bernhardt et al., 2017). The high DIN and DOC release from riparian soils indicates that biogeochemical cycling was very active, but that neither aerobic organic matter respiration nor anaerobic nitrate reduction dominated—which would have resulted in low concentrations of either species.

Other than hypothesized, DIN soils responded strongly to treatments and released most nitrate in acidification solution in most seasons but especially from winter soils (Figure 9b). Aggregate breakup, such as for the organic species, is not likely because these become unstable in low charge density solutions (i.e. Treatment R rather than Treatment A as observed; Cincotta et al., 2019) Anion exchange however, might play a role. The introduction of anions with higher affinity for soil exchange sites (e.g. sulfate, phosphate, or in our case, chloride; Allred, 2007), readily liberates nitrate into solution leading to increased concentrations— and is a process fast enough to be captured in our relatively short (minutes) experiment duration. These results are interesting in the context of reduced acid deposition, as, broadly speaking, "A" treatments simulate conditions of the past, where precipitation and soil pH were lower and charge density was higher. At this time, streams were impacted by significant amounts of DIN from the atmosphere (Seneviratne et al., 2012), but our results suggest that soil chemical conditions might additionally have contributed to releasing DIN—which would have exacerbated high N concentrations in streams. Another option might be that our experiments simply mobilized legacies of nitrate that have accumulated from past deposition (or simply over winter) that are released when ions with higher affinity for soil exchange sites are added to the system. Either way, this process is worthwhile to be further considered in the context of N dynamics in the context of multiple overlapping drivers in future investigations.

2.4.3 The Connection Between Long-Term Data and Experimental Results: opportunities and limitations

Our long-term data assessment offers insights into general annual and seasonal patterns, but the attribution of specific processes can be difficult. Our experiments offer insights on specific processes, however, they do not allow for the direct extrapolation to large scale dynamics or long-term patterns. However, both approaches investigate the combined effect of hydrological processes and shifts of solution composition, and we observe some connections.

For example, our experiments on winter soils simulates snowmelt, which is the most important hydrological event in these systems (Brooks et al., 1999; Wilson et al., 2013; Perdrial et al., 2014; Marx et al., 2017). Winter soils leachate was particularly concentrated with respect to DOC, which is significant when considering that this material is typically transported to streams. Indeed, many studies show that consistent snowpack over winter enhances DOC exports during spring snowmelt (Brooks et al., 1999; Winnick et al., 2015; Qiao et al., 2016) because soils are insulated and, in the absence of hydrologic events, accumulate DOC (Groffman et al., 2001). The fact that conditions of low acid deposition (Treatment R) led to highest liberation of DOC and DON from soils indicates that soil processes might have contributed to the long-term increase of stream DOC for decades (unfortunately we do not have access to long-term DON data). However, the fact that trend analyses by season does not indicate spring (or any other season) as main driver for the observed increase in DOC (supplementary) indicates that reduced acid deposition contributes across seasons.

Our experimental results on DIN from winter soils specifically show high (but variable) concentrations in our effluent, which is consistent with the high but variable concentrations in the stream (Figure 6b). Furthermore, our experiments showed lower nitrate release from Treatment R vs. Treatment A, which agrees with generally decreasing nitrate in the streams over decades. In our case, anion exchange might have played a role, which means that at a larger scale, this could have amplified the already high stream nitrate from atmospheric deposition. However, we want to emphasize that atmospheric deposition is only one driver for catchment N cycling (Sabo et al., 2016; Lawrence et al., 2020) and that our experiments do not capture many aspects of the conditions during peak acid deposition (e.g. the more complex precipitation composition). In this context, it is important to consider limitations of this study. For example, although SRRW provides a nearly continuous record of stream chemistry data since 1990, but these data still have gaps. TDN data was not available prior to 2005, hence DON concentrations could not be calculated during early time periods. For our experiments, it is important to note that we only have 4 seasons of data, and our results are not representative on an entire season but rather a snapshot in time. Higher frequency sampling could help to identify season specific signals within soils.

The overlapping drivers of reduced acid deposition and potential climatic impacts lead to complex pattern that effect C and N species differentially and is visible both in the long-term data as well as our experiments. The increase in DOC over decades, coupled with the synchronous decrease in nitrate has led to a progressive increase in C:N ratios at SRRW.

CHAPTER 3: CONCLUSION

Our investigation emphasizes that disentangling C and N in response to specific regional drivers (shifts soil solution and/or hydrology) is complex. Specifically, shifts in pH and ionic strength on C and N mobility are interdependent on spatial dynamics (landscape position) and temporal patterns (seasonality and hydrology). Thus, signals of reduced acid deposition may be superimposed by increases in hydrologic events. In our study, soil signals were greatly influenced by seasonal dynamics, and winter was the best season to measure soil response to solution chemistry because materials had been accumulating in the absence of flushing events. Long-term flow-adjusted data showed that stream DOC and DON concentrations were coupled by season and/or discharge—which point to a similar soil derived source. Indeed, our soil core experiments supported this, where high pH, low IS preferentially released both species in the winter. On the contrary, DIN C-Q relationships were generally opposed to DOC and DON; specifically, stream DIN was lowest in the fall while DOC and DON had high concentrations. Additionally, DIN concentrations in the spring showed high concentrations at low flow, a pattern not observed with the organic counterparts. This finding points to limited stores of soil-derived inorganic N—as DIN concentrations peak before peak spring runoff.

These catchment specific studies can provide insight on the coupled and intersecting pathways of C and N that influence C:N ratios—and long-term data show temporal changes. It is unlikely that recovery from acidification will indefinitely cause increases in DOC exports however, with additional precipitation drivers in the northeastern U.S.—DOC concentrations may not return to pre-disturbance levels in this watershed.

Furthermore, DIN_{FA} and DON_{FA} concentrations showed oscillating patterns we believe correspond to wet-dry extremes. Vermont's Climate Assessment (2021) predicts a continuation of already observed rising temperature and rainfall, especially during the winter months. With disproportionate nitrate exports linked to winter events, surges, and crashes of DIN similar to what we observed at SRRW in 2014, and subsequent punctuated drops in C:N ratios may become more frequent. Periodic surges in N could led to more retention in soils and subsequent cascading effects to downstream ecosystems (eutrophication). This also is concerning for DOC, as concentrations are largely dependent on discharge, therefore the persistence of DOC draining from forested watersheds will likely continue. Rapid changes in stoichiometry presents an important concern for aquatic communities and water quality in the future. Ecosystem resistance to these changes will likely depend on individual catchment characteristics that govern soil processes. Indeed, there are many factors influencing solute stoichiometry not discussed in this study, such as phosphorous (P). As P is closely linked to weathering, further research is needed to investigate the effects of heavy precipitation events on C:N:P stoichiometry.

The interdependency of drivers can produce large variability of biogeochemical response across scales thus, ecosystem resistance and resilience are difficult to quantify. However, soil mechanisms for liberation could provide insights for comparative studies. Our soil core experiments highlighted the significance of ionic strength (specifically total amount of anions in solution) on nitrate mobility. In the context of resistance, soils with high anion exchange capacities may be less resilient to precipitation extremes compared to soils with low anion exchange capacities. This means that SRRW may be more resilient to climate extremes as it is naturally buffered, and soils are generally low in clay content. Combining long-term data with simulation experiments can help illustrate conditions in the past and future and to provide a framework for forest management strategies. There are however limitations to these types of studies which open the door to further research opportunities.

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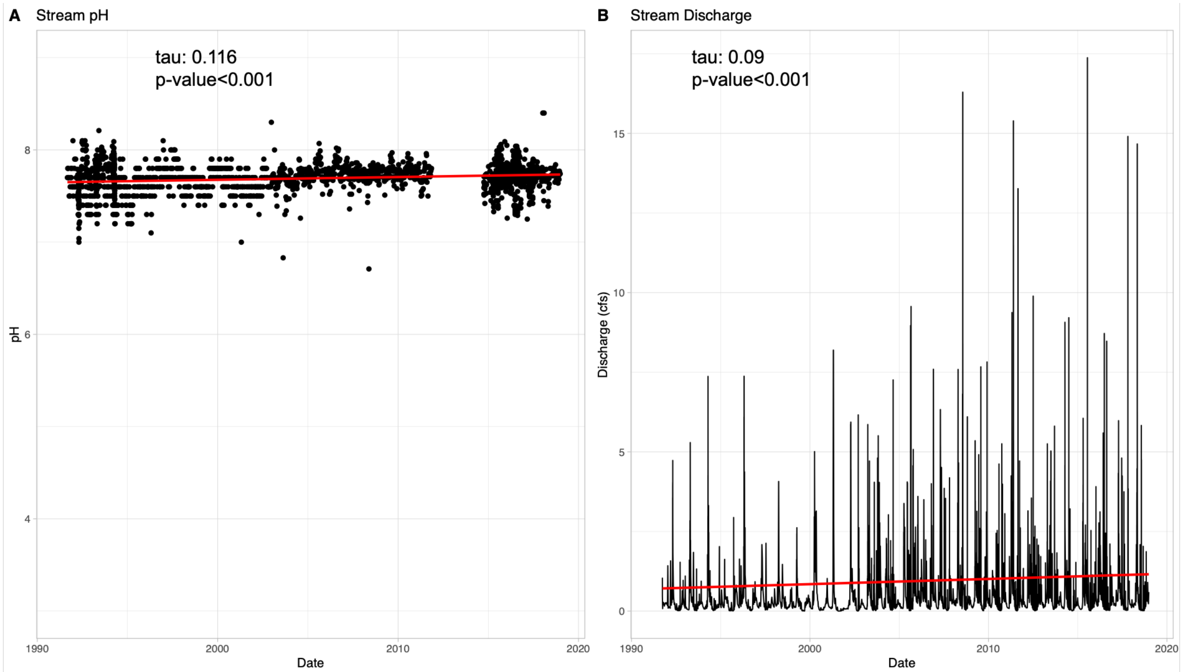
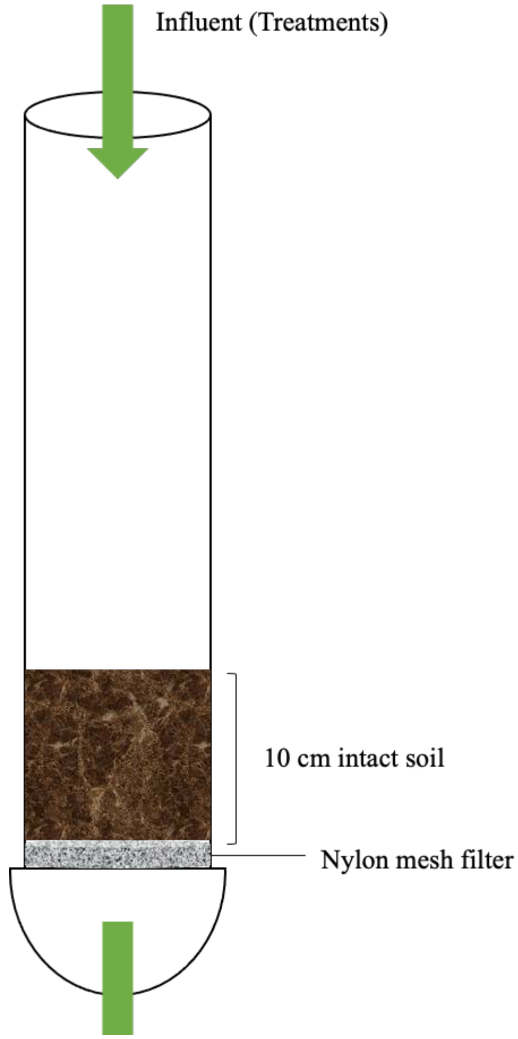
SUPPLEMENTARY MATERIALS

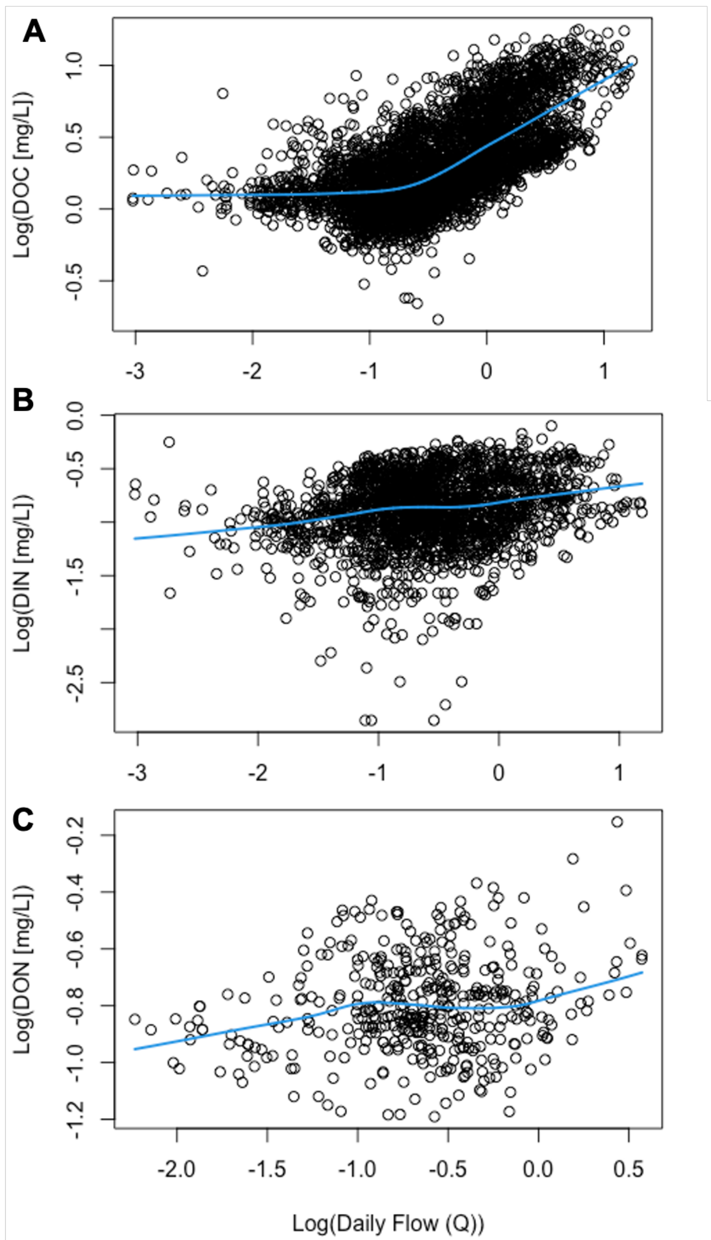
Supplementary 1. *A) Long-term stream pH at SRRW W-9. B) Long-term discharge at SRRW W-9.*



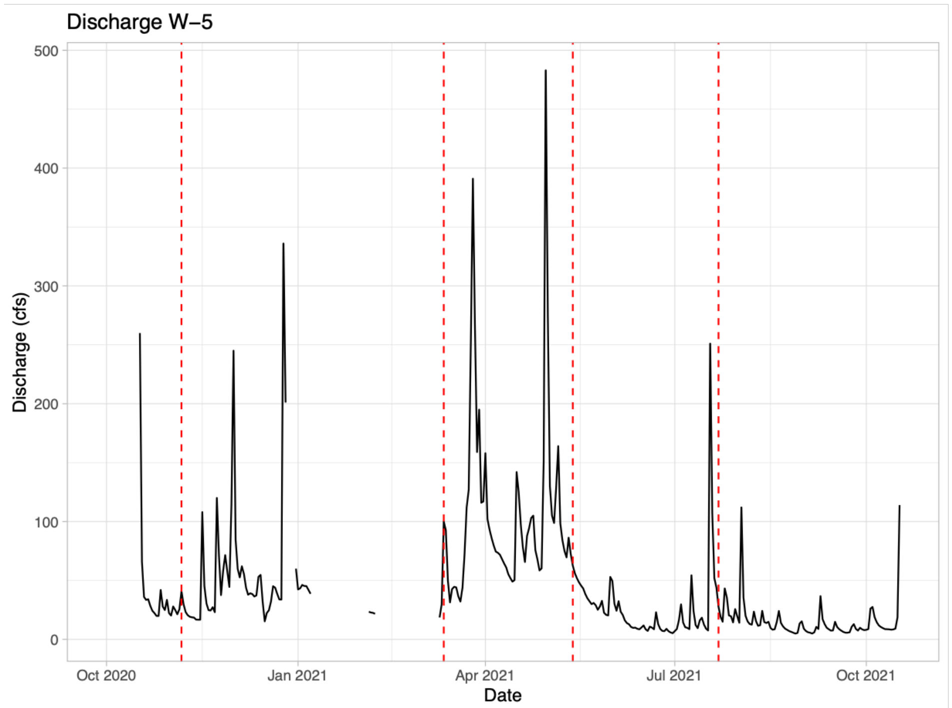
Supplementary 2. *Schematic of soil core experimental setup.*



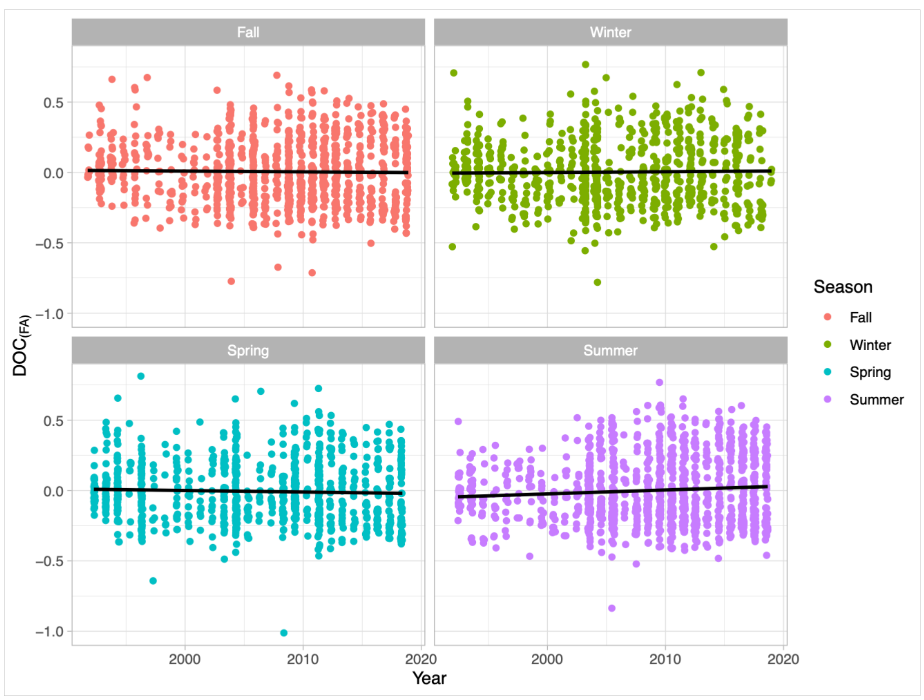
Supplementary 3. *Long-term stream water time series for A) DOC, B) DIN, and C) DON. Data are derived from log-transformed DOC (mg/L) concentrations and discharge (Q) (ft3/s), lines are generated from LOWESS fit (log-DOC ~log-Q) with a smoothing span of 67%.*



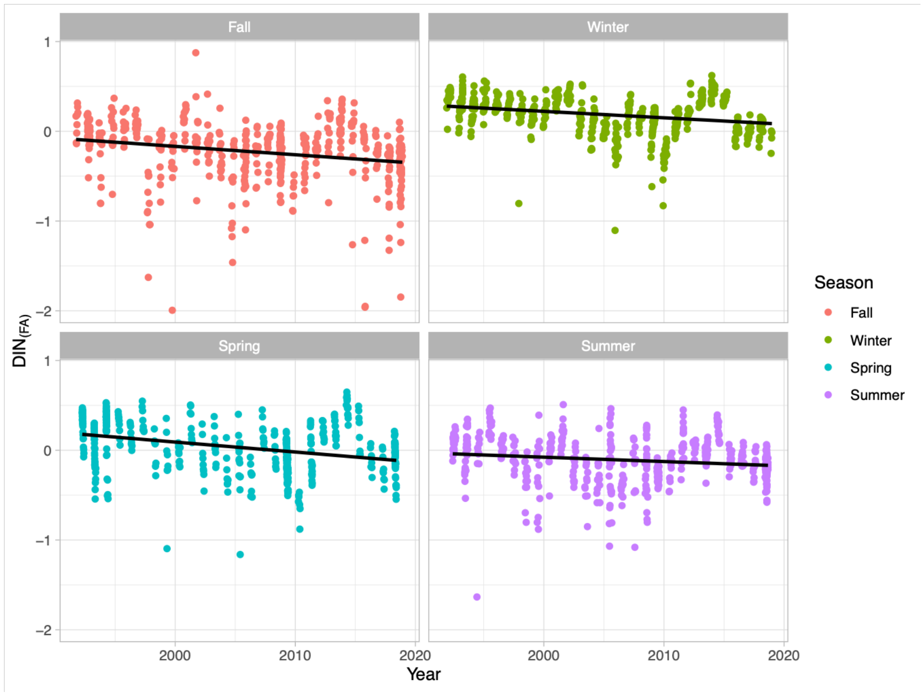
Supplementary 4. *Daily discharge data for Sleepers River Research Watershed (W-5). W-5 encompasses W-9 and has slightly larger discharge and a delayed response however, it provides flow information for antecedent conditions to sampling campaigns. Sampling dates are shown by the dotted red lines.*



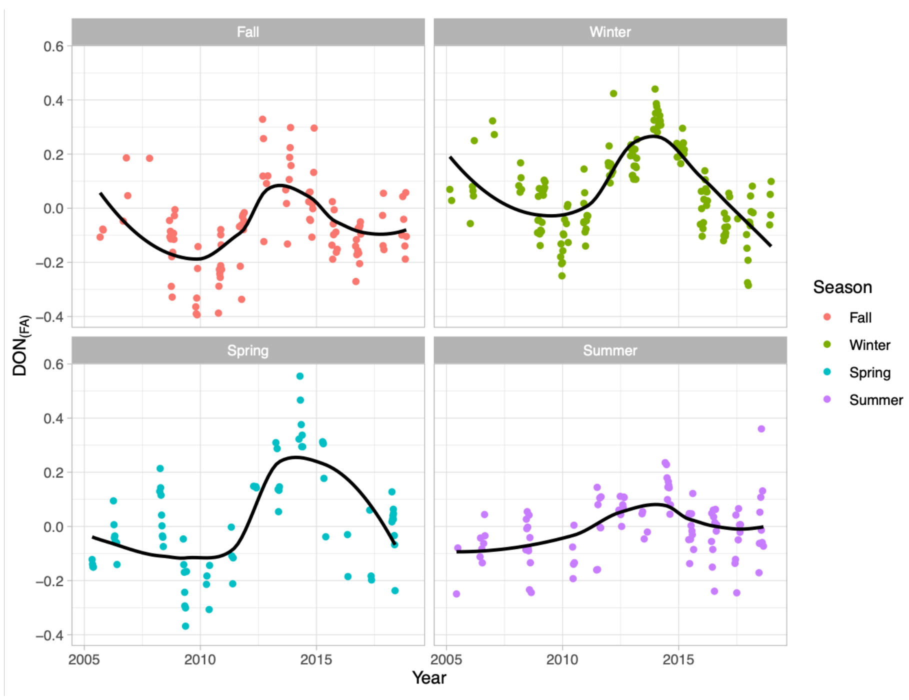
Supplementary 5. Long-term *DOC_{FA} concentrations faceted by season for SRRW W-9.*



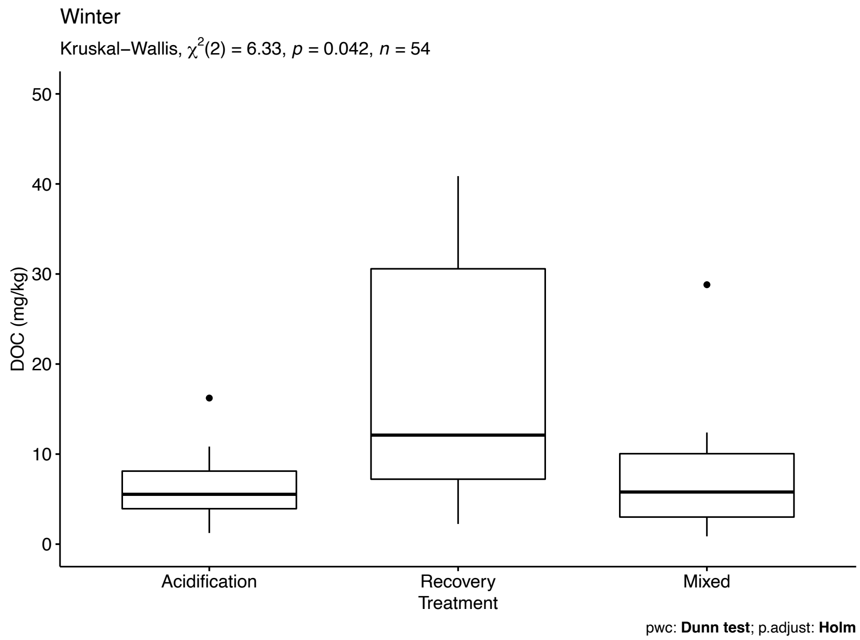
Supplementary 6. *Long-term DIN$_{FA}$ concentrations faceted by season for SRRW W-9.*



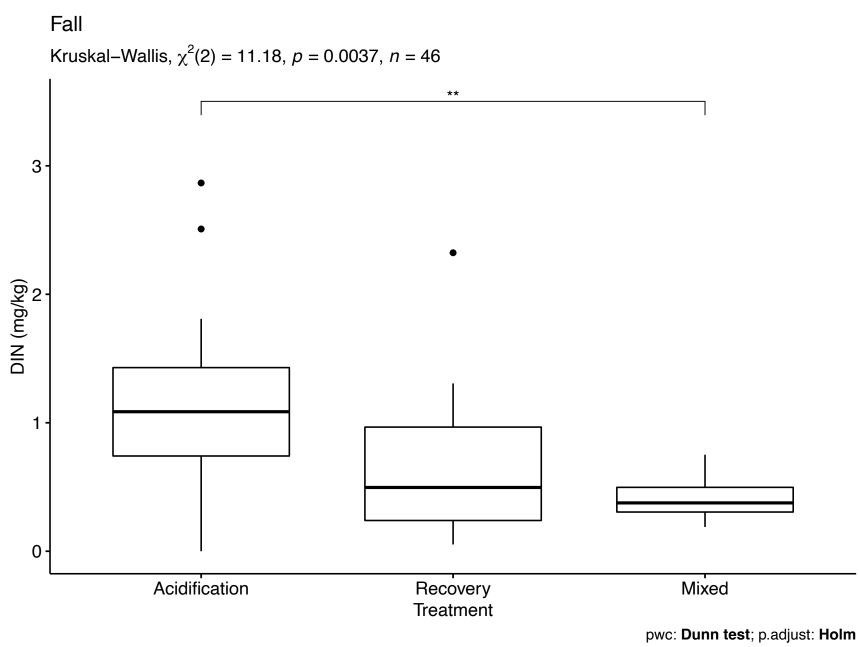
Supplementary 7. *Long-term DON$_{FA}$ concentrations faceted by season for SRRW W-9.*



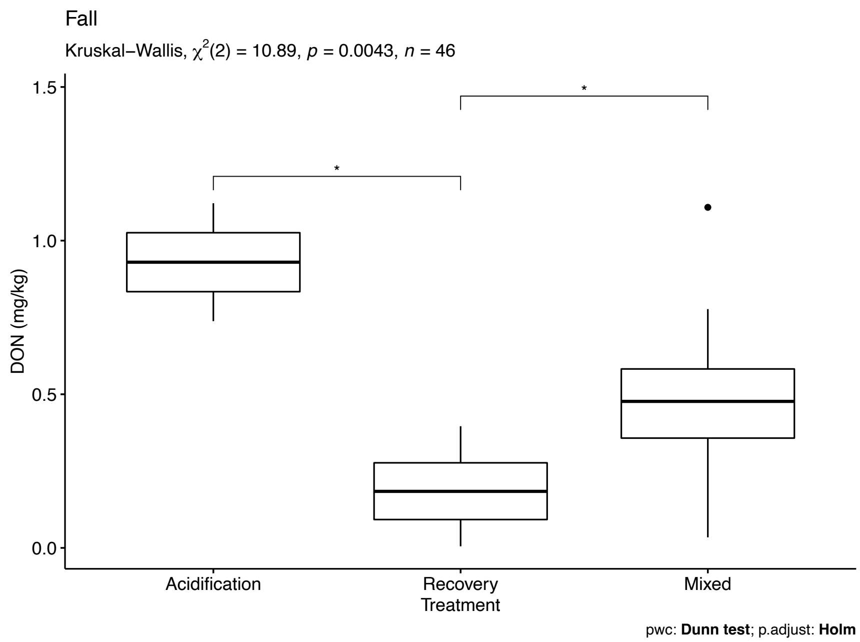
Supplementary 8. *Results of Kruskal-Wallis post-hoc Dunn test for winter DOC concentrations by treatment.*



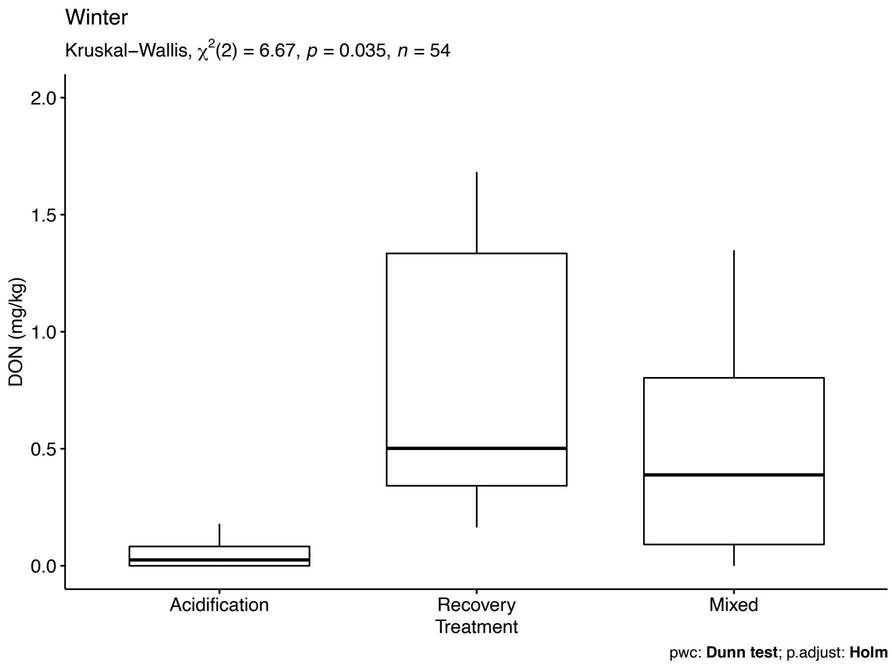
Supplementary 9. *Results of Kruskal-Wallis post-hoc Dunn test for fall DIN concentrations by treatment. The asterisk (*) notes when pair of factor levels is <0.05.*



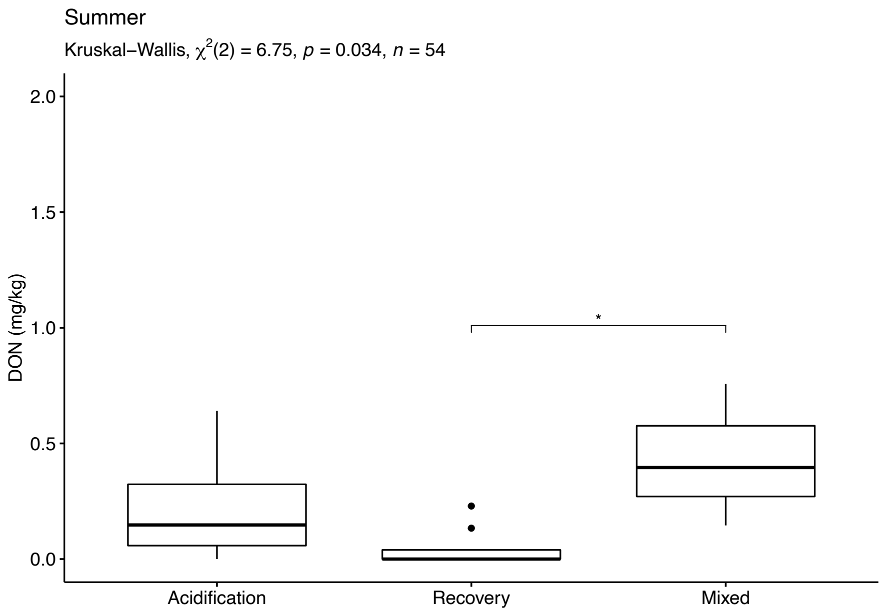
Supplementary 10. *Results of Kruskal-Wallis post-hoc Dunn test for fall DON concentrations by treatment. The asterisk (*) notes when pair of factor levels is <0.05.*



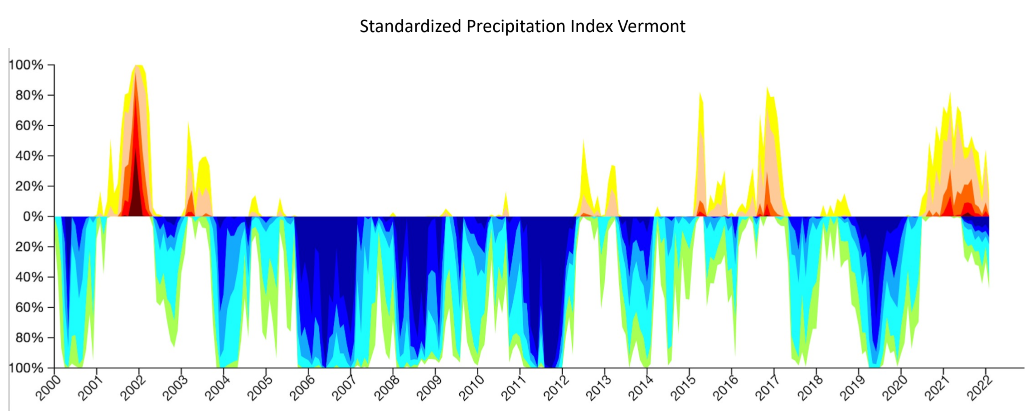
Supplementary 11. *Results of Kruskal-Wallis post-hoc Dunn test for winter DON concentrations by treatment.*



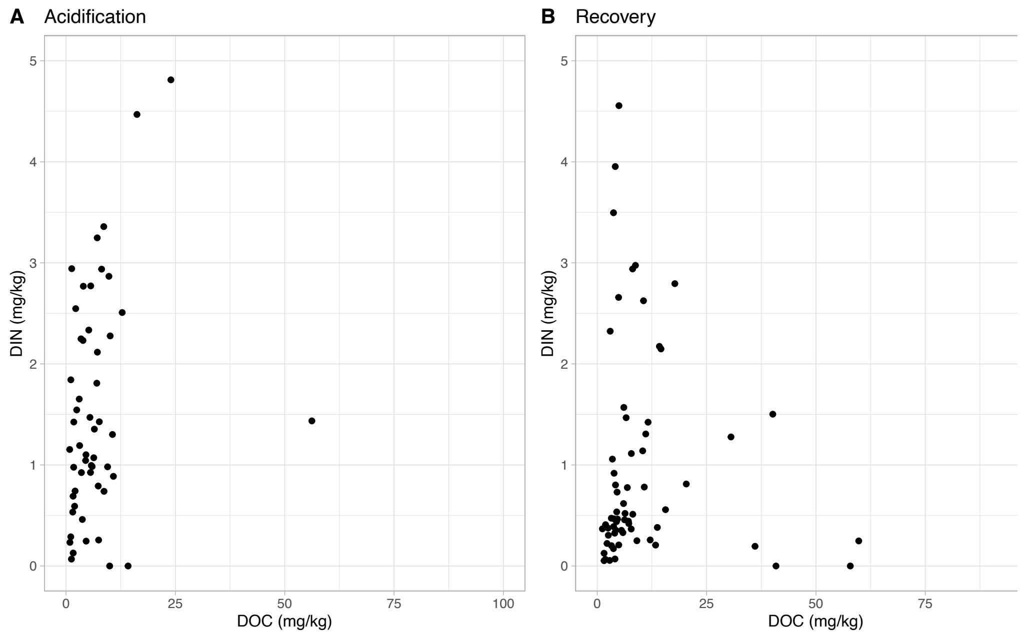
Supplementary 12. *Results of Kruskal-Wallis post-hoc Dunn test for summer DON concentrations by treatment.*



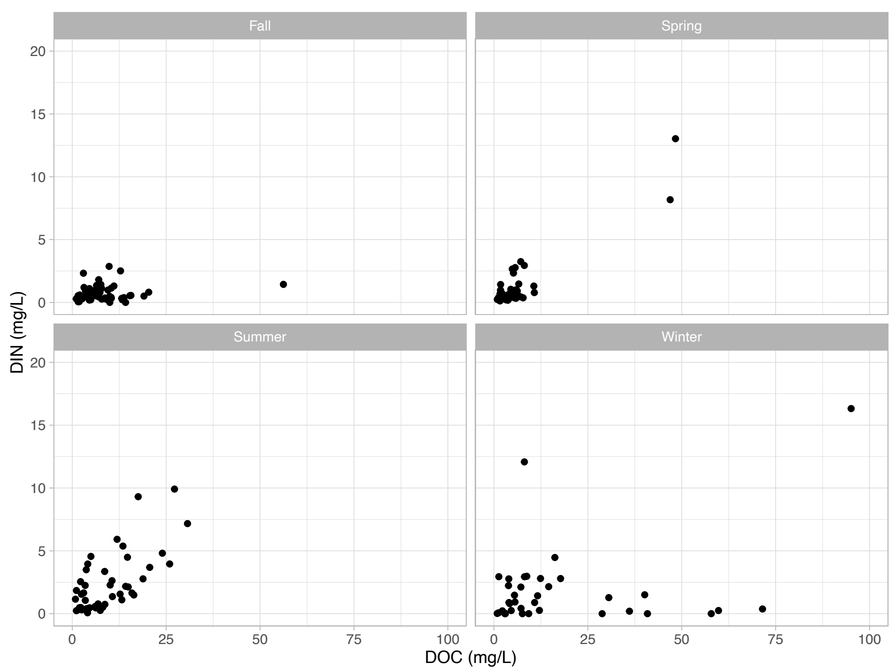
Supplementary 13. *Standardized Precipitation Index for Vermont (2000-2022). Image provided by the NOAA/ESRL Physical Sciences Laboratory, Boulder Colorado from their web site at* https://www.psd.noaa.gov/. *NCEI Climate Division Dataset from Vose, et. al., (2014).*



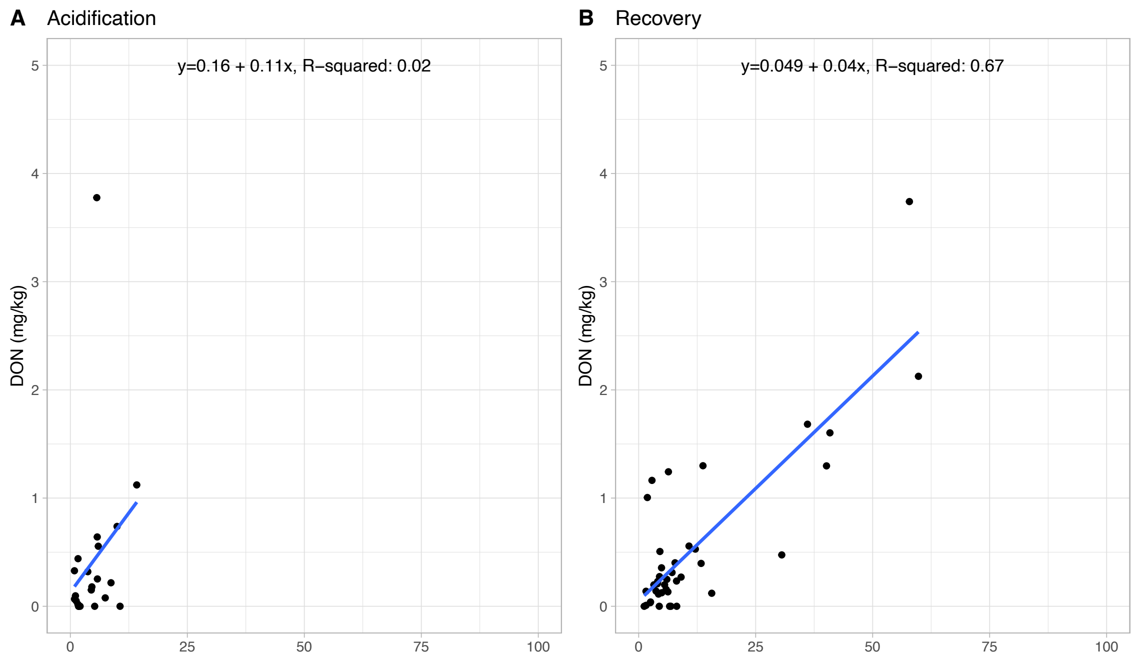
Supplementary 14. *DOC vs. DIN concentrations from experiment effluent after A) Acidification (Treatment A) and B) Recovery (Treatment R).*



Supplementary 15. *DOC vs. DIN concentrations from experiment effluent faceted by season.*



Supplementary 16. *DOC vs. DON concentrations from experiment effluent after A) Acidification (Treatment A) and B) Recovery (Treatment R). Data are fitted with a linear regression model. Slope is compared to Redfield ratios (C:N=0.15).*



Supplementary 17. *DOC vs. DON concentrations from experiment effluent faceted by season.*