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Assessing The Impact Of Changes In Acid Deposition On Dissolved Organic Carbon Mobilization From Two Forested Headwater Catchments: A Combined Lab And Field Study

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ASSESSING THE IMPACT OF CHANGES IN ACID DEPOSITION ON DISSOLVED
ORGANIC CARBON MOBILIZATION FROM TWO FORESTED HEADWATER
CATCHMENTS: A COMBINED LAB AND FIELD STUDY

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ABSTRACT

Over the past few decades, dissolved organic carbon (DOC) concentrations in headwater streams in the northern hemisphere changed. Because these changes in DOC coincided with decreased acid deposition, a potential link was proposed early on. More recent research indicated that catchment attributes, especially soil characteristics and the presence of Ca-bearing minerals, play an important role in modulating DOC release from watersheds, but further research is necessary.

To investigate the role of catchment characteristics on DOC dynamics, I use several watersheds in the Northeastern United States with similar attributes and well-constrained differences. Sleepers River Research Watershed (SRRW) has naturally occurring Calcium (Ca) bearing minerals versus Hubbard Brook Experimental Forest (HBEF) which has experimentally added Ca minerals in one watershed. To assess differences in long-term stream DOC trends in response to shifts in acid deposition, I use stream pH and flow-adjusted DOC stream water concentrations and performed Seasonal Kendall tests. I complement these analyses with experiments on soil cores across watersheds at SRRW and HBEF, seasons (SRRW only), and landscape positions.

Despite similar increasing pH trends, SRRW and HBEF have contrasting long-term DOC responses. My results show that all watersheds show a significant increase in DOC, but the timing and magnitude of this increase vary. My soil experiments with simulated acidification and recovery treatments indicate SRRW varies significantly by season, and generally, recovery solutions extract more DOC. In contrast HBEF soils, landscape positions largely influenced DOC export (and aggregate sizes). I also investigate these findings with a conceptual lens of resistance and resilience as these are widely used concepts to evaluate response to disturbances. In this context, I discuss the long-term data for all watersheds and provide ideas for integrating experimental data in the timeline of changes in atmospheric deposition.

ACKNOWLEDGEMENTS

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Chapter 1: **INTRODUCTION**

We live in a time of accelerated environmental change that is often manifested in the form of large-scale disturbances such as climate change and changes in precipitation composition. These changes have fundamental effects on our ecosystems and might threaten life-sustaining ecosystem services such as providing clean water or regulating biogeochemical flows (Bates et al., 2008; Malhi et al., 2020). Ecology uses resistance and resilience concepts to classify ecosystem responses to disturbances, where a resistant system shows little change. In contrast, a resilient system might change but reverts to its original state (Angeler & Allen, 2016). If a system is unable to adapt, ecosystem services are threatened, and the anticipation of such shifts is an important area of research.

A common problem for studies on disturbances is that a response to a disturbance is often governed by very localized processes unique to one specific place and cannot be reconciled with generalized large-scale patterns (Beven, 2000; Levin, 1992; NSF, 2018). A typical example is acidification and reduced acid deposition (or "recovery" from acidification), where regional changes in precipitation composition might interact very differently with specific catchments (Sawicka et al., 2021). While direct upscaling and downscaling might lead to loss of information, an approach investigating larger-scale patterns and site-specific processes in tandem might provide some remedy (Sivapalan, 2006). In such an approach, regional patterns might point to a possible process, while process investigation might offer more insights into a pattern (Adler et al., 2021; Reichstein et al., 2019; Underwood et al., (in prep)).

I apply this concept to investigate dissolved organic matter (DOC) export from forested headwater catchments in the Northeast (NE) United States in response to shifts in acid deposition. For this, I use a combination of long-term pattern analyses and local process observations to provide conceptual insights on two forested catchment locations with similar disturbance histories.

Chapter 2: BACKGROUND AND LITERATURE REVIEW

2.1. DOC changes in streams

DOC transport from small headwater streams represents an important flux in the global carbon (C) cycle, and these systems are thus monitored carefully (Battin et al., 2009; Butman & Raymond, 2011; Cole et al., 2007; Raymond et al., 2008; Smiley & Trofymow, 2017). For many catchments, DOC is mostly flushed from soils during hydrological events; therefore, DOC dynamics are very vulnerable to disturbances related to changes in precipitation amount (Raymond & Saiers, 2010; Zarnetske et al., 2018). However, changes in precipitation composition might also affect DOC dynamics and might overlap with the climatic drivers (Cincotta et al., 2019; De Wit et al., 2007; Evans & Monteith, 2001; Hruska et al., 2009; Monteith et al., 2007).

For example, DOC in many headwater streams was reported to increase since the 1990s (Freeman et al., 2001; Skjelkvåle et al., 2001, 2001; Stoddard et al., 2003) and because many areas were impacted by acidification (**Figure 2-1**), a possible connection between precipitation chemistry and DOC dynamics was proposed (Cincotta et al., 2019; De Wit et al., 2007; Evans & Monteith, 2001; Hruska et al., 2009; Monteith et al., 2007). Since the Industrial Revolution, drastic atmospheric deposition changes have led to significant system acidification, especially the NE in the United States. After the 1990 Clean Air Act, the acidification trend has begun to revert, and many systems experience "recovery," i.e., the return of soil and stream pH to pre-acidification levels (Armfield et al., 2019; Futter et al., 2014; Rice & Herman, 2012). This shift is significant as data from the (*National Atmospheric Deposition Program (NRSP-3)*, 2020) shows that precipitation pH changed from 4.0-4.5 in 1985 to 5.0-5.5 by 2015 (**Figure 2-1**).
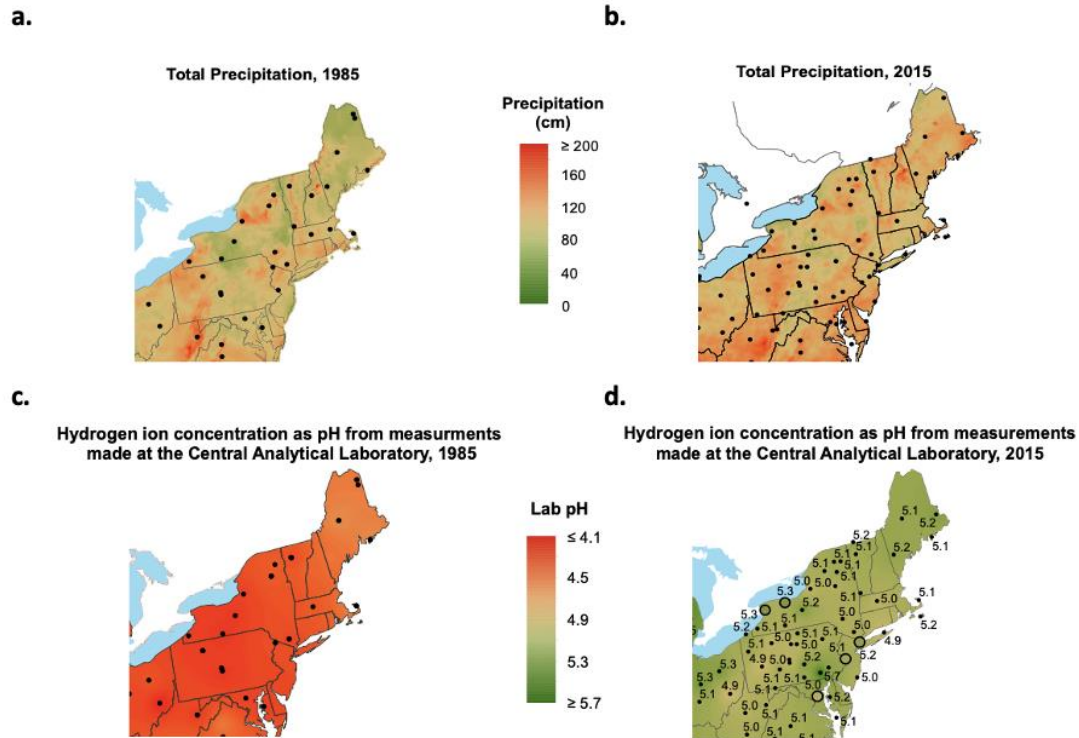
Figure 2-1 Total annual precipitation in cm (a. and b.) and pH concentration (c. and d.) in 1985 versus 2015. Where larger amounts of precipitation are red, and lesser amounts are green. The low pH values are in red, and the higher pH values are in green (adapted from National Atmospheric Deposition Program (NRSP-3), 2020).

However, not all catchments have DOC increases and respond this way. Some catchments have increased in DOC concentrations despite the absence of continued acidification (Oni et al., 2013), while other catchments did not increase DOC exports despite reduced acidification (Löfgren & Zetterberg, 2011). The contrasting responses of stream water DOC were investigated by Clark et al. (2010). They concluded that spatial and temporal variations for various drivers might mask otherwise potentially compatible patterns. Additionally, recent research indicates that catchment attributes might strongly impact the DOC response to shifts in precipitation composition (Adler et al., 2021; Sawicka et al., 2021).

Furthermore, changes in precipitation amount might superimpose the effects of reduced acidification. In particular, results from a long-term, paired catchment study show

the impact of acid deposition reduction and shifts in precipitation amount (SanClements et al., 2018). This study investigated two catchments, where one received continuous acid treatment, whereas the other was allowed to recover from acidification. The recovering catchment exported significantly more DOC, indicating a substantial effect from atmospheric composition changes; however, DOC dynamics in both catchments responded similarly to precipitation events.

Disentangling the processes that lead to increased DOC mobilization in streams is important because these drivers (precipitation amount and composition) evolve towards very different trajectories. To illustrate, shifts due to climate change, such as increased precipitation, could lead to more DOC in streams and potentially more C liberation into the atmosphere, constituting positive feedback (Ritson et al., 2014; Yang et al., 2017). In contrast, precipitation composition is slowly returning towards pre-disturbance levels, and DOC liberation in response to shifts in precipitation composition might be transient. Investigations of DOC due to reduced acid deposition should use techniques that allow the isolation of one of the two effects.

2.2. Soil and catchment processes

DOC is mostly sourced from soil organic matter (SOM); hence soil processes play an important role in DOC liberation (Gmach et al., 2020; Kaiser & Guggenberger, 2007; Saidy et al., 2015) and are also investigated in the context of acid deposition. For example, solution chemistry affects the solubility of organic matter and is more soluble in high pH solutions because of the oxygenation of functional groups (Kleber & Johnson, 2010); this

means that during reduced acid deposition, organic matter might become increasingly soluble (Curtin et al., 2016; Ekström et al., 2011).

Reduced acid deposition also changes the ionic strength (or charge density) of precipitation and soil solution, generating conditions that shift from high to low charge density. Colloidal associations tend to clump up, and aggregates are typically stabilized in high charge density environments (e.g., during acidification); thus, in soils where this process dominates, reduced acid deposition can reverse aggregation and lead to DOC release (Clark et al., 2011; Hruska et al., 2009; Münch et al., 2002). Because SOM is typically stabilized in aggregates (Blanco-Canqui & Lal, 2004; Rasmussen et al., 2005; Six et al., 2000; Totsche et al., 2018), this process can have significant effects on DOC release in some, but not all cases. For instance, recent experiments on aggregate stability report strong effects of solution chemistry on aggregate stability for soils from Sleepers River Research Watershed (SRRW) in Vermont (Adler et al., 2021; Cincotta et al., 2019) but not for soils from Susquehanna Shale Hills Critical Zone Observatory (SSHCZO) in Pennsylvania (Adler et al., 2021).

The sensitivity of aggregates to simulated changes in atmospheric deposition might be related to catchment-specific conditions such as soil elemental composition and mineralogy. Namely, recent research has indicated that soils rich in Calcium (Ca) might be more effective in storing organic matter (Rowley et al., 2018, 2021). Ca – DOC linkages have been investigated in this context (Cincotta et al., 2019). The relative importance, sensitivity to acid deposition, and DOC release might be linked to Ca-bearing minerals and/or their effect on soil chemistry.

2.3. Temporal and spatial variability: seasons and landscape positions

When investigating the connection between acid deposition, catchment soil, and stream response, we need to consider the inherent temporal and spatial variability in DOC dynamics that modulate the general response. Irrespective of prolonged disturbances impacting an entire region, smaller-scale variations in time (i.e., seasons) and space (i.e., landscape position in a catchment) have strong effects on C dynamics and DOC release into streams.

For example, biogeochemical processes vary seasonally and influence the amount of DOC available for transport. In fall, significant amounts of labile C are produced via litterfall and consumed through microbial processes. In seasonally snow-covered areas, winter DOC production and microbial consumption are slowed (Blume et al., 2002), and soil DOC flux is insignificant (Rosa & Debska, 2018). Conversely, warmer soil temperatures allow for more microbial processing in spring and summer, leading to loss of C as CO_2 (Huang et al., 2014). These seasonal dynamics on microbial activity are superimposed by the seasonal water availability for DOC transport. Increased water availability allows for more potential DOC to be flushed during spring snowmelt and storm events.

These processes also vary spatially because landscape position strongly impacts soil DOC production, accumulation, and removal (Bernhardt et al., 2017; Gannon et al., 2015). For instance, convergent areas store large amounts of leaf litter and, if proximal to the stream, are generally highly connected; thus, convergent topography can contribute to DOC continuously via hydrological exports. Dissimilarly, linear convex hillslopes do not provide optimal organic matter production and accumulation (Andrews et al., 2011);

however, because such landscape positions are not always connected to the streams, materials are removed less frequently and can contribute to DOC during hydrological events. Further research also found soil total organic carbon (TOC) content to be one of the most important predictors for DOC production (W. Huang et al., 2013) and can account for a portion of DOC's spatial heterogeneity.

2.4. Response to disturbances: the concept of resistance and resilience

Resilience and resistance are increasingly studied topics in ecology and ecosystem sciences (Jiang et al., 2018; Turner et al., 2019) and lend themselves to investigate a catchment response to disturbances. In the context of acid deposition and DOC, the absence of a stream DOC response to acidification might indicate partial system resistance. In contrast, the capacity to return to pre-acidification levels might demonstrate resilience. Seen with this lens, resistance and resilience might be catchment dependent and might arise from catchment-specific processes, especially soil processes. For example, a recent study on DOC in headwaters streams has attributed variable DOC responses to catchment characteristics such as soil depth and slope, which then modulate the catchment response (DOC export) to reduced acid deposition (Adler et al., 2021). The sensitivity of aggregates to changes in atmospheric deposition might be one control on system resistance and resilience at a very small scale that ultimately influences catchment response and stream DOC. While ecosystem resistance and resilience concepts to disturbances are regularly used in silviculture, water resources functions, geomorphology, and marine ecosystems contexts (DeRose & Long, 2014; Diaz & Rosenberg, 2008; Falkenmark et al., 2019; Rathburn et al., 2018), it has not been applied to acid deposition and DOC specifically. I will evaluate its usefulness as part of my study.

2.5.   My research approach, objectives, and hypotheses

Because recent findings emphasize that catchment specific characteristics might modulate DOC response to shifts in precipitation composition**, my main research objective was to investigate soil and stream water DOC response for watersheds with well-constrained differences in such characteristics.**

I chose SRRW, a well-studied watershed in NE Vermont that contains abundant calcite in the soil-forming parent material. The parent material at the other equally well-studied study site, Hubbard Brook Experimental Forest (HBEF), is calcite-free. Still, one sub-watershed at HBEF received wollastonite (Ca-silicate) treatment as part of a catchment-scale experiment in 1999. Other catchment attributes are very similar, and both SRRW and HBEF experienced a prolonged disturbance in the form of dramatic shifts in the chemical composition of precipitation, making these watersheds ideal candidates for this study.

For long-term data exploration, I investigate the potential role between catchment characteristics and its linkage with increasing stream pH and DOC response. I use flow-adjusted DOC data to remove the discharge (Q) and use Seasonal Kendall tests to control for the season. Flow-adjustments isolate the possible acidification and recovery indicators for in-stream DOC concentrations (Helsel et al., 2020). For experimental investigations, I examine the effect of solution composition on DOC release and soil aggregate stability. For this, I use soil cores from both catchments with differing long-term DOC trends. To test the impact of temporal and spatial variability, I collected soils across seasons (SRRW) and landscape positions (SRRW and HBEF). Finally, I investigate my results through the lens of resistance and resilience to test this concept as a possible framing for DOC response.

With this setup, I test the following hypotheses:

1.) **Long-term stream flow-adjusted DOC trends vary by catchment** and increase when additional Ca-bearing minerals were available to stabilize SOM during acidification or early recovery, thus accumulating stores that can be released during progressing recovery.

2.) **Experimental solution impacts DOC release from soils**: DOC release from soils treated with acidification and recovery solutions varies by catchments; precisely, soils from watersheds with abundant Ca release more DOC into recovery simulations (i.e., low IS, high pH solutions) because C-stabilized aggregates might break up.

3.) **Season impacts DOC release** (superimposing the effect of reduced acid deposition) because of seasonal dynamics in DOC production and removal. Explicitly, I hypothesize that winter and early spring soils accumulate the most labile C and yield the highest DOC in experiments.

4.) **Landscape position impacts DOC release** due to shifts in accumulation versus removal. Specifically, I hypothesize that concave landscape positions have the highest TOC content and yield the highest amounts of DOC across watersheds.

Chapter 3: **MATERIALS AND METHODS**

3.1.   Study sites

3.1.1. Description

To assess catchment response to shifts in acid deposition—in the context of resilience and resistance of ecosystem services—in the NE United States, I selected two forested headwater catchments with extensive records for stream water quality variables: DOC, pH, and Q (**Figure 3-1**). My sites were SRRW, a USGS research site in NE, Vermont (**Figure 3-1a**), and HBEF, a Long-Term Ecological Research site in the White Mountains of New Hampshire (**Figure 3-1b**). Both small forested headwater catchments have a humid continental climate with 1,100 and 1,400-mm precipitation each year (20-30% snow). These watersheds have an average winter temperature of -9 to -10 °C in January and 18 to 20 °C in July (Bailey et al., 2003).

I focused on the SRRW sub-watershed, W-9, which is 0.405-km^2 large and has 155-m of relief (**Figure 3-1c**). The soil till is up to 4.5-m thick, and the main soil types are Spodosols and Inceptisols in the uplands (known as podzols and cambisol outside of United States soil taxonomy) and Histosols in the lowlands (Kendall et al., 1999). SRRW catchment is underlain by calcareous granulite and quartz mica phyllite bedrock, covered by carbonate-containing soils, leading to buffered groundwater and stream water.

The HBEF catchment is 31-km^2, which encompasses several sub-watersheds that are similar in size to SRRW. I focused on HBEF sub-watersheds W-1, which is treated with wollastonite, hereafter referred to as HBEF-T, and untreated control sub-watersheds W-3 (HBEF-HC, hydrologic control) (**Figure 3-1d**), and sub-watershed W-6 (HBEF-BC, biogeochemical control).
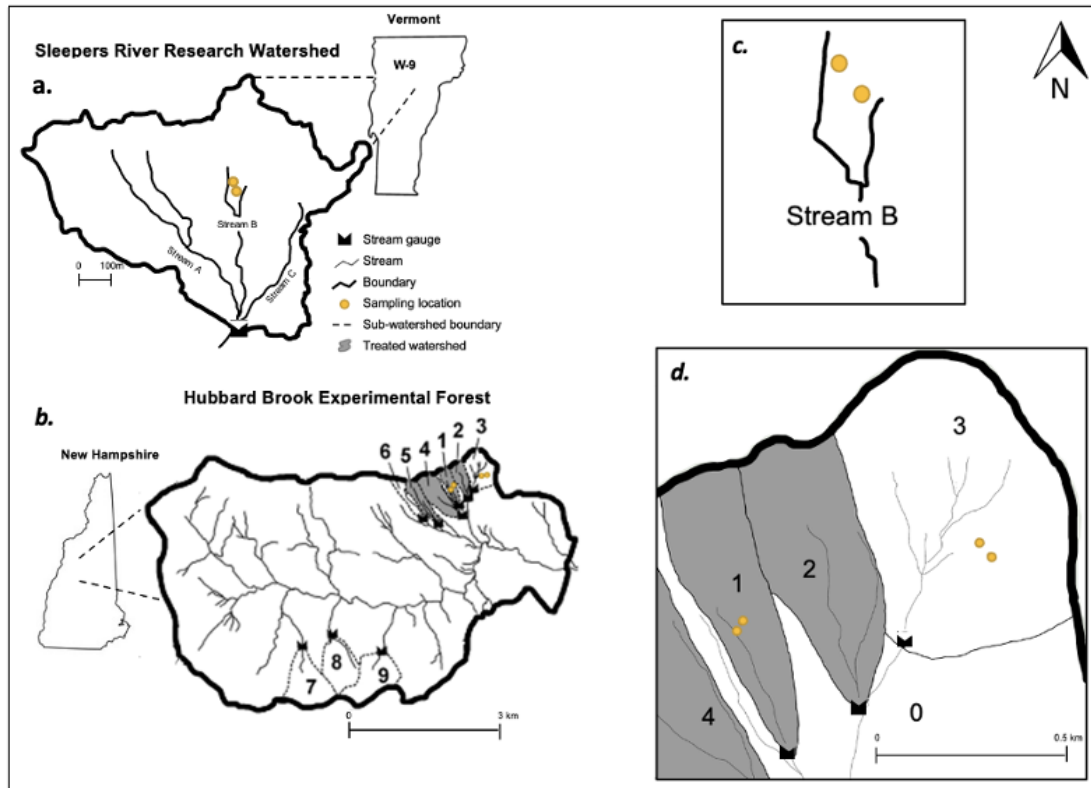
Figure 3-1 a. Sleepers River Research Watershed (SRRW) b. Hubbard Brook Experimental Forest (HBEF) c. SRRW W-9 Catchment (adapted from Sebestyen et al., 2009). d. HBEF W-1 (HBEF-T, treated) and W-3 (HBEF-HC, hydrological control) catchments (adapted from Cawley et al., 2014). Sampling locations are highlighted with yellow circles.

The HBEF has similar overall relief as SRRW. The soil till thickness ranges from 0-m to 50-m at HBEF, but most watersheds are overlain with 2-m of till. At HBEF, there are no residual soils derived from weathered bedrock; instead, the carbonate-free glacial till is the soil parent material (Bailey et al., 2014). The essential difference between SRRW and HBEF is that the till at HBEF does not contain carbonates (**Table 3-1**). The soils are primarily characterized as well-drained Spodosols (Likens, 2013). The watershed is underlain by a complex of metasedimentary and igneous rocks, consisting of quartz mica schist and quartzite interbedded with sulfidic schist and calc-silicate granulite bedrock (Gannon et al., 2015).

Table 3-1 Summary of study area characteristics and data availability. Sleepers River Research Watershed (SRRW) and Hubbard Brook Experimental Forest (HBEF) in HBEF-T (treated), HBEF-HC (hydrological control), and HBEF-BC (biogeochemical control).

Site	Catchment Area (km²)	Catchment Characteristics	Record Length	Source
SRRW	0.405	Carbonates in till	1991-2018	(Matt et al., 2021; Shanley et al., 2021)
HBEF-T	0.118	Ca-Treated (1999)	1991-2019	(Driscoll, 2019; Bernhardt et al., 2020)
HBEF-HC	0.424	Reference	1963-2019*	(Campbell et al., 2019; Bernhardt et al., 2020)
HBEF-BC	0.132	Reference	1982-2019	(Driscoll, 2019; Bernhardt et al., 2020)

DOC data gap from 2000 to 2012

3.2. Long-term data and statistical analyses

3.2.1. Flow-adjustments

I used long-term data to investigate patterns in stream response to shifts in atmospheric deposition. Because I examined the effects of acid deposition changes specifically, I flow-adjusted all solute concentrations to remove the otherwise typical Q control on most constituents (Helsel & Hirsch, 2002; Hirsch & Slack, 1984). For this, I used the instantaneous raw DOC concentrations [mg/L] and the closest discharge value to the time measurement (see **Appendix 1**, **Figure A-1**) Some concentration observations were missing Q date and time stamps at the exact sample time, so the closest comparative date-time stamp for those Q observations is used as an estimate. DOC concentrations were log-transformed, plotted against Q, and regressed using the Locally Weighted Scatterplot Smoothing (LOWESS) algorithm with a smoothing pattern coefficient (f=0.67). The residuals were extracted and reordered from the LOWESS fit based on the date of each observation. These resulting data are termed flow-adjusted DOC (DOC_{FA}) concentrations.

3.2.2. Seasonal Kendall tests

To determine the directionality of long-term DOC_{FA} trends independent of seasonal variability, I used Seasonal Kendall tests. The outcome of the flow-adjustments and the Seasonal Kendall test is the normalized test statistic, Kendall's tau (τ), ranging from -1 to 1. A value greater than $\tau = 0.05$ is considered a positive trend, and a τ value less than -0.05 is regarded as a negative trend, and τ values in between indicate no-trend. Where τ less than ($\pm$) 0.10 is very weak, values between ($\pm$) 0.10 to 0.19 is weak, ($\pm$) 0.20 to 0.29 is moderate, and ($\pm$) 0.30 or above is strong.

3.3.   Field sampling and soil core leaching experiments

To test the effect of changes on solution chemistry on soil DOC release for different watersheds, I collected soil core samples in SRRW, HBEF-T, and HBEF-HC (sampling access to HBEF-BC is restricted). Because of the large variations in soil processes by landscape position, I sampled two differing locations, where the landscape position is expressed in two paired directions, upslope and downslope (vertical slope contour) and across-slope (horizontal slope contour) (). In this case, I sampled linear convex hillslopes (Linear Convex, LV) (**Figure 3-2a**) and concave landscape positions (Concave-Concave, CC) in each watershed (**Figure 3-2b**) (Schoeneberger et al., 2017). To allow comparison between treated and untreated watersheds at HBEF, I focused on soils of the same type (defined as Bh and BhS (Bailey et al., 2019)) with similar soil textures and rock fragments for each landscape position.
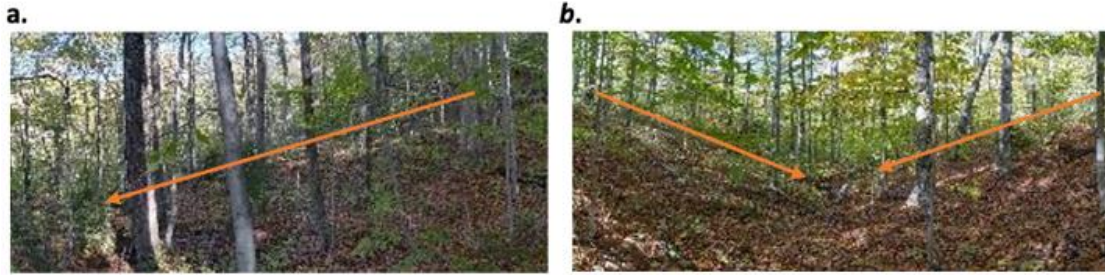
Figure 3-2 a. Linear convex hillslope (LV) and b. concave landscape position (CC) representative landscape positions. Orange arrows show general slope direction. Images are taken at Hubbard Brook Experimental Forest, Watershed 3 (HBEF-HC, hydrological control) on October 10th, 2020.

Before taking cores, I cleared each location for leaf litter and avoided decaying trees, heavily rooted areas, and other excess organic matter sources. I collected soil cores using a 5.1-cm diameter PVC pipe that is beveled at the base. I hammered the cores into the soil until a depth of 10-cm. I then carefully removed them to ensure that the soil core is kept intact, capping the cores for transport and placing them in a cooler. Cores were stored in a 4 °C fridge until experimentation.

The number of cores varied per site varied by availability; a total of 27 cores were available on each collection date (**Table 3-2**). SRRW was sampled several times across seasons; however, HBEF was sampled only once due to COVID-19. I collected samples in a 1-m^2 grid approach (unless there is prohibiting root or rock). I also collected bulk soil for each sample location using a hand shovel from the first 10-cm in several areas in the 1-m^2 grid. I carefully mixed the soil in a Ziploc bag to generate a composite sample representative for each sampling location (i.e., specific watershed and landscape position) for soil characterization, aggregate separation, and batch experiments. Bulk composite samples were stored in a 4 °C fridge until air-dried.

Table 3-2 Sample date, location, and the number of cores collected at Sleepers River Research Watershed (SRRW) and Hubbard Brook Experimental Forest (HBEF) in HBEF-T (treated), HBEF-HC (hydrological control). All samples are collected in two different landscape positions: linear convex hillslope (LV) and concave landscape position (CC).

Site	Collection Date	Landscape Position	Location (Decimal degrees)	Number of Cores
SRRW	02/22/2020	CC	44.493450, -72.160010	13
	03/12/2020	LV	44.493920, -72.159630	10
		CC	44.493450, -72.160010	10
	11/06/2020	LV	44.493920, -72.159630	14
		CC	44.493450, -72.160010	13
HBEF-T	10/10/2020	LV	43.955401, -71.727927	6
		CC	43.955191, -71.728066	7
HBEF-HC	10/10/2020	LV	43.957263, -71.719486	7
		CC	43.957521, -71.719894	6

3.3.1. Experimental approach

I conducted soil leaching experiments, simulating an intense hydrologic event, on all sampled cores within 24-hrs of the sample collection date. I poured 120-mL of solution into the core and allowed it to interact with the soil for 5-mins before being drained gravitationally for 4-mins. I repeated this treatment three more times to simulate repeat flushing events, collected effluent and analyzed each flushing's effluent separately. To investigate the effects of DOC response to the onset of a simulated precipitation event, I examined results from the first two pours. To explore the capacity of the soil to sustain DOC release over repeat events, I investigated all four pours.

I prepared several solutions to investigate the pH and IS effects on DOC liberation in soil cores. High IS and low pH solutions simulated acidification conditions (A) with a pH of 3, and an IS of 3.00×10^{-2}M (from 0.01 M $CaCl_2$). The low IS and high pH solution simulated reduced acid deposition or "recovery "conditions (R) and is double deionized

(nanopure) water with a pH of 5 and has an IS close to zero. Finally, the low IS, and low pH solution simulated mixed conditions (M), which allowed us to evaluate the influence of pH and IS separately, where the pH was the same as the acidification treatment (pH=3) and has the equivalent low IS as the recovery treatment (IS=close to zero) (**Table 3-3**). I adjusted the pH for the lower pH solutions with concentrated HCl until the desired pH was within ± 0.05. I filtered the effluent through a 0.45-μm polyethersulfone filter into combusted glass vials for DOC analyses.

Table 3-3 [IS] versus pH for each treatment type. [IS] increases vertically (bottom to top) while pH increases horizontally (right to left).

[IS] ↑ ↓		Acidification (A)
	Recovery (R)	Mixed (M)
	↑ **pH** ↓	

To investigate shifts in aggregate morphology and size based on treatment, I used composite soil samples from HBEF watersheds and separated the aggregates by air-drying and then sieved between 250-μm and 63-μm (SRRW aggregates are described in (Adler et al., 2021; Cincotta et al., 2019)). Once I separated aggregates, I combined solutions (the same as the soil core experiments) at a 1:5 mostly liquid ratio (by mass). I shook them slowly for nine minutes on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA). The aggregates and solution were then carefully separated by filtering solution using a 0.45-μm polyethersulfone filter. I then prepared the isolated and treated aggregates for SEM analyses.

3.3.2. Laboratory procedures and analytical techniques

The soil core effluent was analyzed using a Shimadzu Carbon Analyzer (Shimadzu, Columbia, MD, USA) to track DOC's mobilization from the leaching soil core experiments. I normalized all resulting effluent concentrations [in mg/L] to the effluent amount [in L] and the dry mass of soil [in kg] to allow for comparisons between cores (**Equation 1**).

$$DOC\left[\frac{mg}{kg}\right] = \frac{\left(DOC\left[\frac{mg}{L}\right]\right) * (Effluent\ Solution\ [L])}{Dry\ soil\ mass\ [kg]} \qquad (\boldsymbol{Equation\ 1})$$

To characterize the TOC in soil, I analyzed dried, sieved (<2-mm), and ball-milled bulk soil samples. Each sample was weighed using a Mettler-Toledo XP26 balance and pressed into 5x9-mm tin capsules (Costech Analytical Technologies, Inc.) I then used an NC2500 combustion-based elemental analyzer (CE Instruments, Milano, Italy) in the Geology Stable Isotope Lab at the University of Vermont. I compared the resulting percent C values (TOC % w/w) to benchmark standards (B2150 for high organic content sediment standard and B2176 for low organic content soil standard) provided by Elemental Microanalysis Limited.

The separated and treated aggregates from the bulk experiments were air-dried and mounted on double-sided C tape on metal stubs and sputter-coated with C before analysis. I analyzed samples with a Zeiss Sigma 300 VP Field-Emission Scanning Electron Microscope (FE-SEM) with *AZtec* Elemental Mapping software in the Microscopy Imaging Center Lab at the University of Vermont. I performed observations with backscattered electron (BSE) SEM mode at 5 keV acceleration voltage to capture electron density differences; I used this mode to identify larger atomic particles (denser, mineral

grains) versus smaller atomic particles (less dense, organic material). I acquired energy-dispersive spectroscopy (EDS) maps for five minutes. To compare HBEF sub-watershed aggregates between landscape positions and treatments, I took secondary electron (SE) images at the same magnification (100x). I took the SE images in variable pressure mode with 30 pascals and 15 keV.

To quantify particle size differences and distributions, I used the image analysis software (ImageJ) and reported values in percent. I converted the 100x magnification images to binary colors, scaled the image's size, and used the "analyze particles" function with a minimum area set at 40 μm^2 and excluded particles that touched the image's edge.

3.3.3. Statistical analyses

I used R Studio Version 1.2.5033 and IMB SPSS Statistics Version 27.0.0.0 for statistical analyses to analyze the effluent data from leaching experiments. I performed Kruskal-Wallis tests to determine significant differences in the DOC released by categorical independent variables such as treatment and landscape position within a watershed. I also used this Kruskal-Wallis test to determine significant differences in DOC released between watersheds. Additionally, a chi-square statistic (χ^2), with a significant alpha (α) threshold of 0.05, determined if there were differences in average DOC exports between treatments, landscape positions, or other watersheds. The post-hoc Dunn test explicitly identified which groups differed from other groups.

Chapter 4: **RESULTS**

4.1.   Long-term stream water trend analysis

4.1.1. Long-term pH trends

Over the observed period ranging from the early 1960s (HBEF-HC), 1980s (HBEF-BC), and 1990s (SRRW and HBEF-T) to the second decade in the new millennium, pH generally increases for all streams (**Figure 4-1**). SRRW pH is highest with a mean of 7.69 pH units and increases moderately over time (τ= 0.238, **Figure 4-1a**). In contrast, pH values for HBEF are generally lower, and all have a strong positive trend where: HBEF-T τ= 0.484, HBEF-HC τ= 0.600, and HBEF-BC τ= 0.382 (**Figure 4-1b-d**). Before 1999, the average pH for HBEF-T, HBEF-HC, and HBEF-BC is 4.90, 5.14, and 4.96 and then increased to 5.30, 5.56, and 5.14 for the remainder of the record, respectively. The well-documented spike in pH for HBEF-T occurred in the late 1990s and early 2000s in response to the applied wollastonite treatment (**Figure 4-1b**).
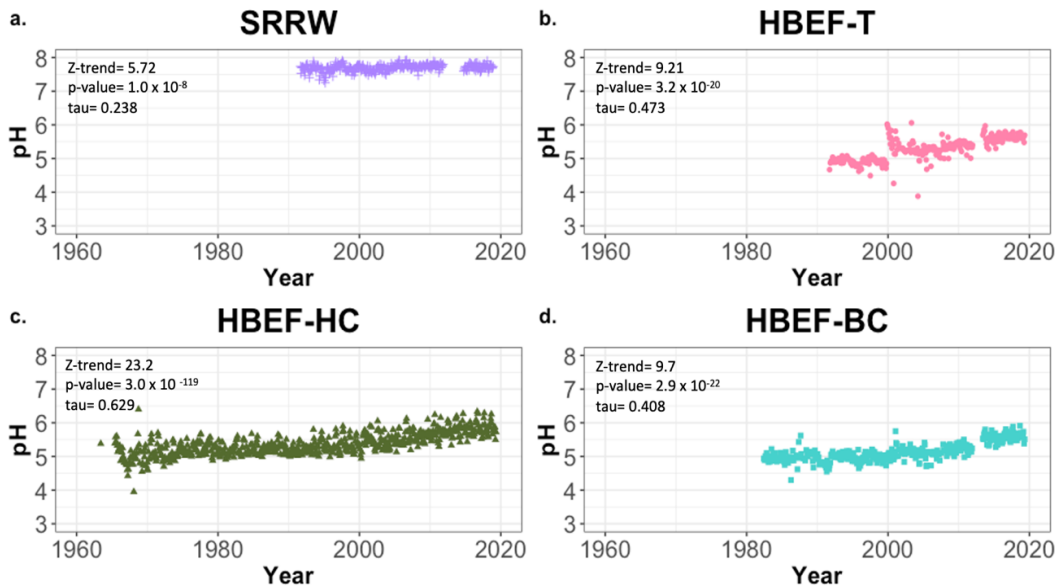
Figure 4-1 Long-term time series for stream water pH values and trends for a. SRRW, b. HBEF-T (treated), c. HBEF-HC (hydrological control), and d. HBEF-BC (biogeochemical control). All statistics are derived from the Seasonal Kendall test.

4.1.2. DOC-discharge relationships and DOC_{FA} trends

DOC concentrations for SRRW are highly variable, ranging from less than 0.6 mg/L in low flows to over 7.6 mg/L at high flows (**Appendix 1, Figure A-1**). The average DOC concentration during base flow is 2.1 mg/L at SRRW. At HBEF, DOC concentrations show a similar range, varying between 0.1 mg/L and 6.4 mg/L (**Appendix 1, Figure A-1**) but show a less systematic increase in DOC concentrations with Q (**Appendix 1, Figure A-2**).

The flow-adjusted stream water DOC concentration (DOC_{FA}) trends vary by catchment (**Figure 4-2**). For SRRW, variability in DOC_{FA} is high but has an increase that is strong and statistically significant ($\tau = 0.299$, **Figure 4-2a**). For the HBEF streams, the DOC_{FA} concentrations are much less variable. There is a strong positive trend for HBEF-T ($\tau = 0.365$, **Figure 4-2b**) and HBEF-HC data has a large gap that precludes a continuous trend analysis; however, a t-test on the average DOC_{FA} concentration for the data before 2000 versus data after 2013 on the residuals reveals a significantly higher means for the later timeframe (-0.064 log(mg/L), i.e., 0.86 mg/L) versus (0.030 log(mg/L), i.e., 1.07 mg/L), respectively t= 4.52, p=3.0 x 10^{-5} (**Figure 4-2c**). In contrast, the HBEF-BC data record is continuous, and the tau statistics indicate a weak but statistically significant increasing trend for DOC_{FA} ($\tau = 0.120$, **Figure 4-2d**).
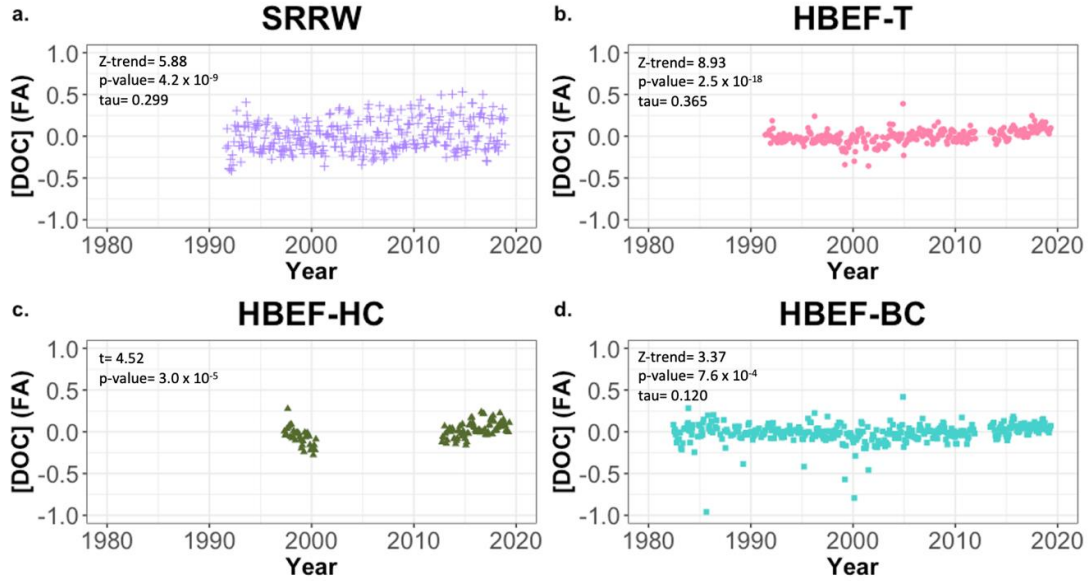
***Figure 4-2** Long-term and flow-adjusted stream water dissolved organic carbon (DOC$_{FA}$ in log[mg/l]) time series for a. SRRW, b. HBEF-T (treated), c. HBEF-HC (hydrological control), and d. HBEF-BC (biogeochemical control). For a., b., and d. statistics are derived from the Seasonal Kendall test and c. from the t-test.*

4.2. Soil analyses and experiments

4.2.1. TOC by watershed

TOC analyses on soils (sampled in fall) vary by landscape position (**Table 4-1**). At SRRW, the top 10-cm of the soil in the CC concave landscape position has a TOC content of ~20% C compared to the LV hillslope position, which exhibited ~5% C (Adler et al., 2021). At HBEF-T, the soil also has a higher TOC content for the CC landscape positions (~17%) than in the LV landscape position (10%, **Table 4-1**). However, at the hydrological control watershed HBEF-HC, soil TOC is ~34% in the CC landscape position and ~40% C in the LV landscape position.

Table 4-1 Total organic carbon in Sleepers River Research Watershed (SRRW) and Hubbard Brook Experimental Forest (HBEF). All samples are collected in two different landscape positions: linear convex hillslope (LV) and concave landscape position (CC).

Site	Landscape Position	Carbon (% w/w)
SRRW*	LV	5
	CC	20
HBEF-T	LV	10
	CC	17
HBEF-HC	LV	40
	CC	34

*from Adler et al., 2021.

4.2.2. Seasonal variability of leachable DOC from SRRW soils

To assess DOC amounts leached from SRRW soil cores during the onset of a hydrological event, I compared the first two simulated flushing events across season, landscape position, and treatment (see box plots for all four flushing's in **Appendix 1, Figure A-4**). In general, DOC amounts varied more strongly by season than by treatment: winter soil cores from the CC landscape position released the highest DOC amounts (in mg of DOC per kg of soil), where mean DOC varied from 18.4 mg/kg for acid treatment (A) to 32.4 mg/kg recovery treatment (R) (**Figure 4-3a**). Because of access issues, data for LV are not available for the winter samplings. Cores from spring snowmelt generally released lower amounts of DOC with means ranging from 8.1 mg/kg (A) to 25.1 mg/kg (R), and variability between replicates is low (**Figure 4-3b**). The fall soil cores released the least amount of DOC with means ranging from 11.3 mg/kg (A) to 9.5mg/kg (R). The exception is one core, where the (A) treatment solution released 56.2 mg/kg of DOC (**Figure 4-3c**).

DOC amounts leached from soil cores did not systematically vary by landscape position (see box plots for all four flushing's in **Appendix 1, Figure A-4**). For example, during spring and fall, the leached DOC is similar for (A) and (R) treatments for CC and LV landscape positions. However, in the case of the mixed solution treatment (M, low pH, low IS) for spring and fall, soil cores from LV landscape positions (open circles) leached significantly more DOC (χ^2=5.8, p=2.0 x 10^{-2} and χ^2=5.4, p=2.0 x 10^{-2}, **Figure 4-3b** and **c**). For a complete report on statistics of means by season, landscape position, and treatment, please see **Appendix 1, Table A-1**.

I also investigated the shift in DOC release from these soils as a function of repeated flushing simulations to test the soil's capacity to sustain DOC supply during subsequent events (**Figure 4-4**). Winter soils released the highest DOC amounts during the second simulated flushing for all solutions (**Figure 4-4a-c**), and leachable DOC decreased progressively for subsequent treatments. Both the (A) and (M) solution treatments generally have low amounts of DOC for the spring snowmelt samples and release gradually less over time (**Figure 4-4d** and **e**). Additionally, spring soils from the LV landscape position released statistically higher amounts of DOC than the CC landscape position for (M) solutions (**Figure 4-4e**). Conversely, the CC landscape positions released the highest amounts of DOC during the first treatment, especially for (R) treatments, with progressive decreases in DOC after (**Figure 4-4f**). Generally, fall soils released low amounts for most treatments and landscape positions, and DOC amounts did not change significantly with repeat treatments (**Figure 4-4g-i**). The exception are cores from the CC landscape position and the (A) solution that released the highest DOC amounts at the beginning of the experiment (**Figure 4-4**).
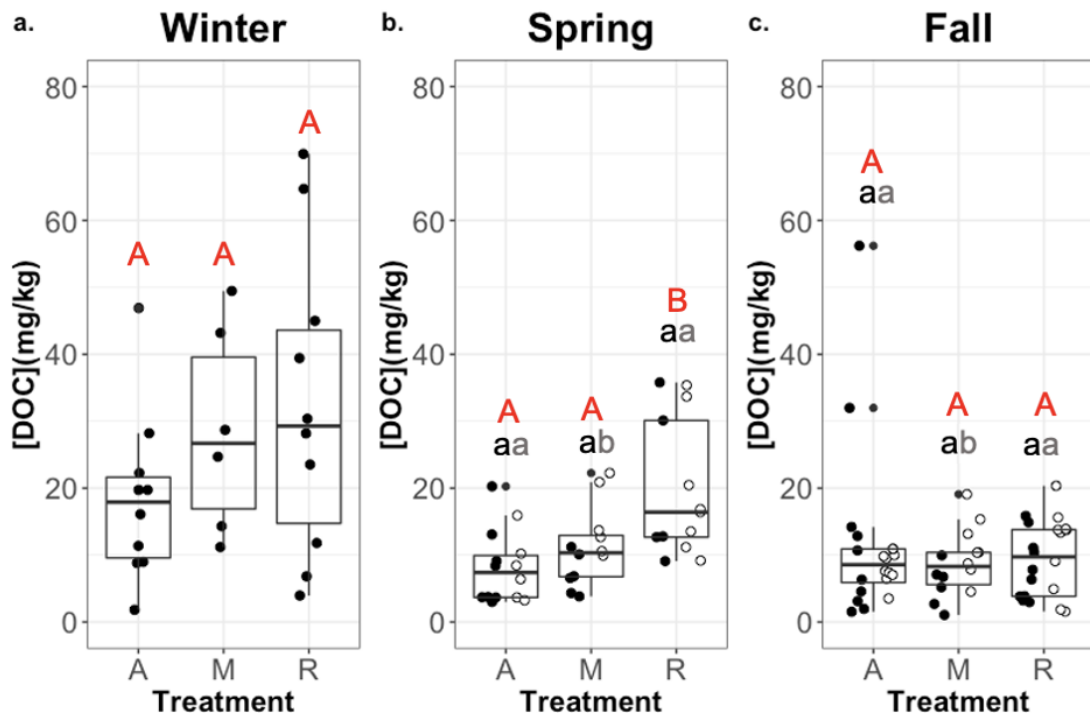
Figure 4-3 Sleepers River Research Watershed seasonal soil core leaching experiments comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) within a watershed for a. Winter, b. Spring, and c. Fall. Filled circles represent concave landscape (CC,) and open circles represent linear convex hillslope (LV). Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by treatment for both landscape positions combined (upper case letter) and for each landscape position separately (lower case letter, CC= black letter, and LV = grey letter).
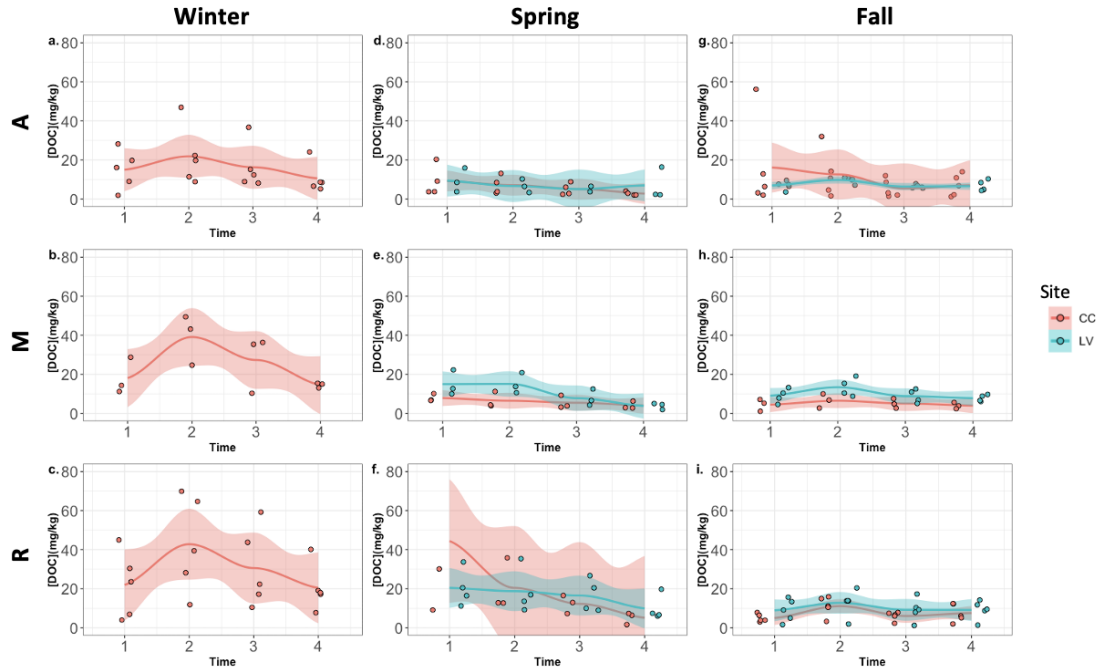
Figure 4-4 Sleepers River Research Watershed seasonal soil core leaching experiments comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) across rows and seasons across columns. Sites represent and concave landscape positions (CC) and linear convex hillslope (LV). Shading represents the 95% confidence interval.

4.2.3. Comparison of leachable DOC between soils from SRRW and HBEF catchments

Because of access restrictions, I could only sample HBEF soils in the fall and restrict my comparison between watersheds to fall soil results. To investigate flushing at the beginning of a hydrological event, I compare DOC amounts of the first two flushing's only (See **Appendix 1, Figure A-5** and **Figure A-6** for boxplots on all four flushing's). Compared to SRRW, DOC amounts in HBEF soil core leachate varied more strongly by landscape position (**Figure 4-5**). While SRRW DOC leachate values were generally low except for a core that released very high amounts into (A) solution (**Figure 4-5a** and **Figure 4-3c**) several HBEF soil cores released high DOC across treatments and showed high variability between field replicates. Here, DOC amounts from HBEF-T soil cores were generally high with means ranging from 20.9 mg/kg (A) to 16.0 mg/kg (R) with high

variability between leaching replicates (**Figure 4-5b**). Compared to all of the fall experiments, the HBEF-HC soil released overall the most DOC with means ranging from 17.8 mg/kg (A) to 22.5 mg/kg (R) (**Figure 4-5c**). On average, at HBEF, more DOC is leached from cores in CC landscape positions than LV landscape positions. The CC locations leached significantly more DOC than LV landscape positions in the case of HBEF-HC treated with (M) and (R) solutions treatment. However, because of the high variability between replicates, the difference in DOC leachate amounts is not significant between watersheds and treatments. For a complete report on statistics of means by watershed, landscape position, and treatment, please see **Appendix 1, Table A-2**.

I also investigated DOC release dynamics as a function of repeated flushing simulations (**Figure 4-6**). SRRW fall soil DOC release is low for most cases, and DOC concentration in leachate did not progressively change with subsequent treatment (**Figure 4-6a-c,** *also see section* **4.2.2**). The HBEF soils released more DOC than SRRW and showed high variability (within CC landscape positions), and DOC amounts did not significantly change with subsequent flushing events (**Figure 4-6d-i**).
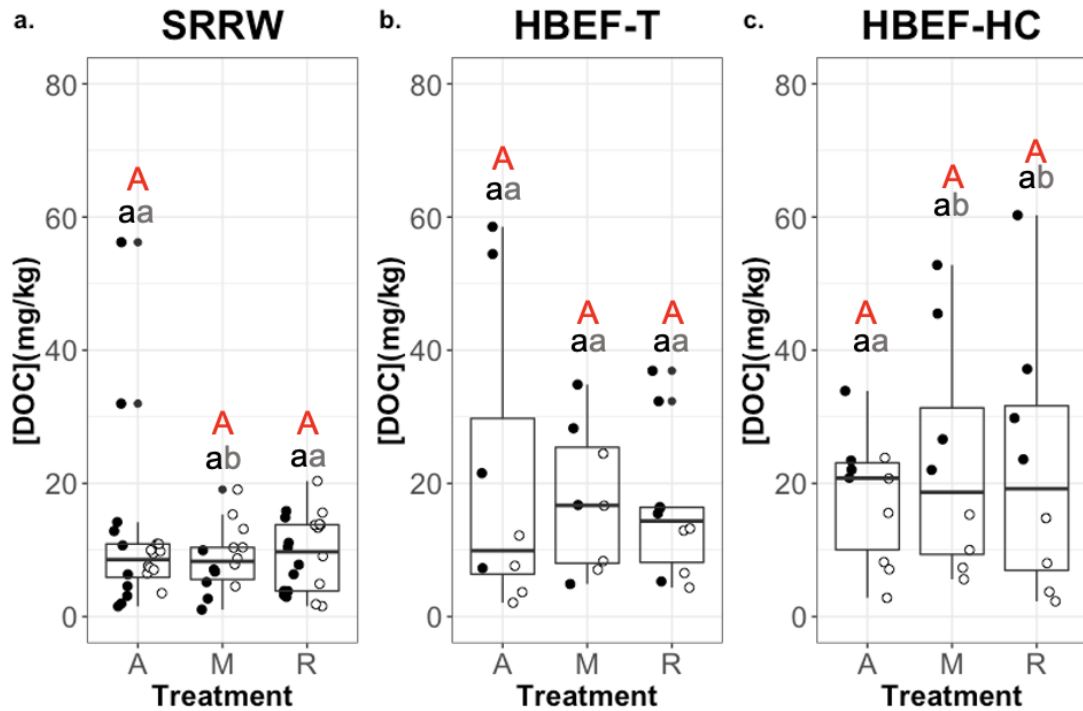
Figure 4-5 Fall 2020 soil core leaching experiments at a. Sleepers River Research Watershed (SRRW), b. Hubbard Brook Experimental Forest, HBEF-T (treated), and c. HBEF-HC (hydrological control) comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) within a watershed. Red capital letters indicate statistically significant ($\alpha \leq 0.05$) differences across landscape positions within a watershed and season. Filled circles represent concave landscape (CC), and open circles represent linear convex hillslope (LV). Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by treatment for both landscape positions combined (upper case letter) and for each landscape position separately (lower case letter, CC= black letter, and LV = grey letter).

Figure 4-6 Fall 2020 soil core leaching experiments comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) across rows and watersheds across columns Sleepers River Research Watershed (SRRW), Hubbard Brook Experimental Forest, HBEF-T (treated), and HBEF-HC (hydrological control). Sites represent and concave landscape positions (CC) and linear convex hillslope (LV). Shading represents the 95% confidence interval.

4.3.   Soil Aggregates under a Scanning Electron Microscope

My SEM analysis of aggregates at HBEF showed differences in aggregate size, composition, and morphology by watershed and landscape position but not by treatment (**Figure 4-7** and **Figure 4-8**). Soil constituents and aggregates in the CC landscape position of the treated watershed HBEF-T were generally small. They contained abundant organic material with only a few minerals (**Figure 4-7a** and **b**). A close-up on a representative aggregate shows compact associations of mostly organic material and fine-grained minerals. In contrast, larger mineral fragments do not appear to be bound to the aggregate (**Figure 4-7c**).

In contrast, soil constituents and aggregates in LV landscape positions were generally larger and containing single mineral particles, root fragments, and aggregates of

up to ~115-µm in diameter (with a max 355-µm diameter) (**Figure 4-7e** and **f**). The minerals within and outside of aggregates were mainly platy (**Figure 4-7e** and **f**), suggesting phyllosilicates, but fragments of angular minerals, likely primary quartz and feldspar, were present as well.

The largest particle sizes were present in samples treated with (R) solutions for each landscape position. However, these differences were not systematic, and treatments did not significantly affect aggregate size (**Figure 4-7d** and **h**). The exception is the LV landscape position, where mid-sized aggregates (area ranging between ~185 and 230-µm) are more abundant after (R) treatment than after (A) treatment (**Figure 4-7e** and **f**).

Aggregates from the untreated control HBEF-HC varied less in size by landscape position. Still, again, CC aggregates were smaller (the area was mostly smaller than 100-µm) than those from LV positions (including several aggregates between 110 and 150-µm, **Figure 4-8d** and **h**). Aggregates from both landscape positions contain organic-rich materials, fine root fragments, and few platy minerals. The close-up on a typical aggregate in this group shows a close association between organic materials and fine-grained minerals (**Figure 4-8c**).

Again, the treatment did not have a significant impact on size distribution for the CC aggregates. However, mid-sized aggregates (~110 to 150-µm) were more abundant after the (A) treatment than the (R) treatment (**Figure 4-8h**) for the LV landscape position.
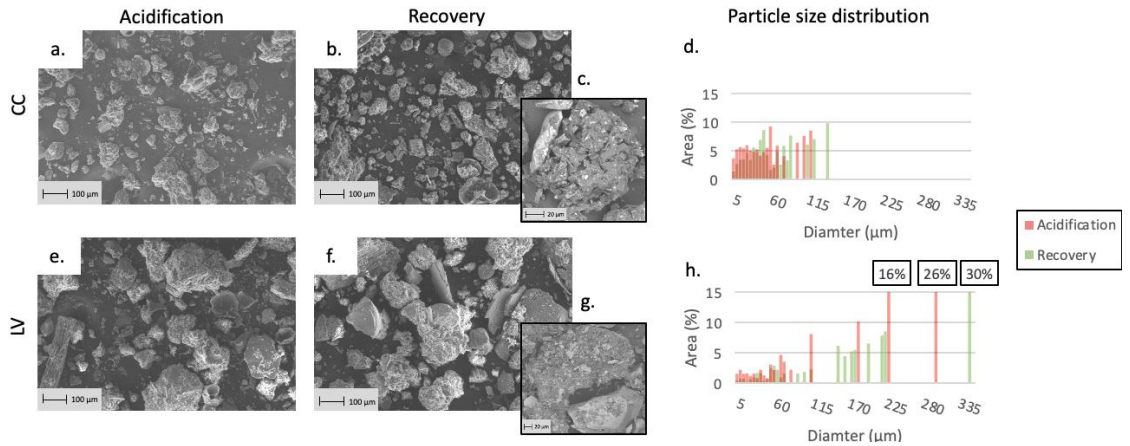
Figure 4-7 Secondary electron scanning electron microscopy (SE-SEM) images of soil aggregates at Hubbard Brook Experimental Forest, HBEF-T (treated) comparing landscape positions: concave landscapes, CC (a. and b.) and linear convex hillslopes, LV (e. and f.) to laboratory treatments acidification (a. and e.) and recovery (b. and f.) solutions. Zoomed-in aggregates are visualized with backscatter electron (BSE-SEM) on recovery solution (c. and g.). Particle size distribution from image analyses for CC (d.) and LV (h.) aggregates expressed in % covered area (i.e., the area that is covered by particles that belong to a given size bin).
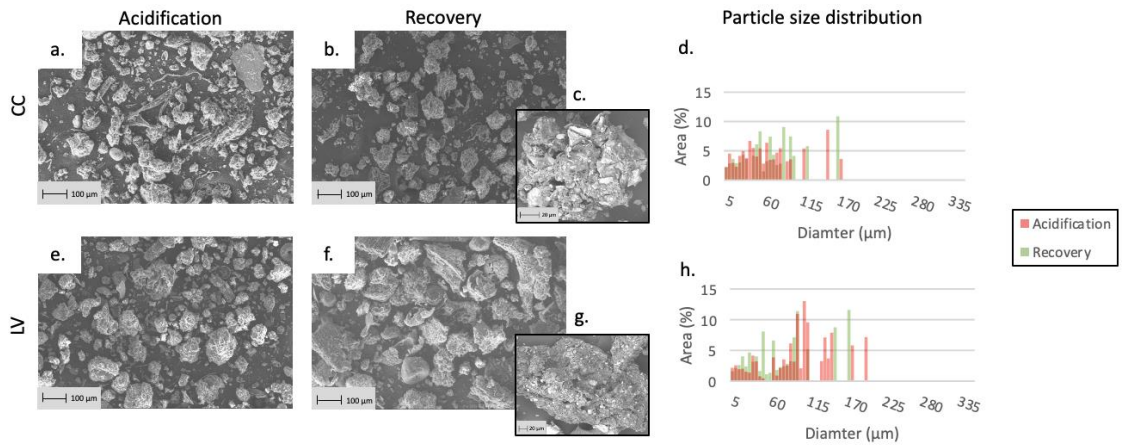
Figure 4-8 Secondary electron scanning electron microscopy (SE-SEM) images of soil aggregates at Hubbard Brook Experimental Forest, HBEF-HC (hydrological control) comparing landscape positions: concave landscapes, CC (a. and b.) and linear convex hillslopes, LV (e. and f.) to laboratory treatments acidification (a. and e.) and recovery (b. and f.) solutions. Zoomed-in aggregates are visualized with backscatter electron (BSE-SEM) on recovery solution (c. and g.). Particle size distribution from image analyses for CC (d.) and LV (h.) aggregates expressed in % covered area (i.e., the area that is covered by particles that belong to a given size bin).

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Chapter 5: **DISCUSSION**

5.1. Reduced acid deposition and stream DOC: insights from long-term datasets

Many areas that experienced decreased acid deposition also showed increases in DOC concentrations and fluxes (Freeman et al., 2001; Skjelkvåle et al., 2001, 2001; Stoddard et al., 2003), and a possible connection between precipitation chemistry and DOC dynamics was proposed early on (Cincotta et al., 2019; De Wit et al., 2007; Evans & Monteith, 2001; Hruska et al., 2009; Monteith et al., 2007). However, recent findings emphasize catchment-specific characteristics that might modulate DOC response to shifts in precipitation composition (Adler et al., 2021; Sawicka et al., 2021). The presence of Ca-bearing minerals especially has been investigated lately, and the accumulation of SOM is attributed to Ca in soils (Kerr & Eimers, 2012; Rowley et al., 2018, 2021). I, therefore, chose to investigate soil and stream water DOC response for two watersheds with similar attributes but distinct differences in the presence of Ca-bearing minerals in soil parent material: the glacial till at SRRW contains the natural, pH-buffering calcite. In contrast, the HBEF watersheds have no naturally occurring pH buffer. However, one location received a one-time addition of wollastonite as part of an experiment, making these ideal watersheds candidates to investigate the effect of select catchment characteristics on DOC release. I hypothesized that the degree of stream response would vary by catchment and that SRRW, with abundant calcite, would release most DOC, followed by the Ca-silicate treated HBEF-T (hypothesis 1).

My long-term data analyses showed that all streams, irrespective of Ca-minerals, show an increase in pH over the past decades (**Figure 4-1**), which is a typical response to decreases in acid deposition and represents a preliminary sign of recovery from

acidification (Cosby et al., 2006; Driscoll et al., 2001; Watmough et al., 2005). Even at SRRW, where the naturally occurring calcite buffers the streams, pH increased slightly over the past decades, signaling reduced acid deposition and/or recovery (**Figure 4-1a**).

Because DOC concentrations are largely discharge controlled, and since this region experiences increases in precipitation due to climate change (Arnone et al., 2011; Campbell et al., 2009; Jentsch et al., 2007; Seneviratne et al., 2012), I flow-adjusted concentrations. Flow-adjustments, therefore, isolate the signals that are attributable to reduced acid deposition (**Figure 4-2** and **Appendix 1**, **Figure A-1**). My data shows that flow-adjusted stream DOC_{FA} concentrations increased in all streams over the past decades. However, the extent of this increase varied by catchment (see **Figure 4-2** and **Appendix 1**, **Figure A-1**). As an example, the calcite containing SRRW shows a strong progressive increase in flow-adjusted stream DOC_{FA} concentrations (despite the weakest change in stream pH), a trend that is well documented for this watershed (e.g., (Adler et al., 2021; Cincotta et al., 2019)). The wollastonite treated HBEF catchment (HBEF-T) shows DOC_{FA} increases, especially after 2010, and the control watersheds also show increased DOC_{FA}. Still, data is sparser (HBEF-HC), and for HBEF-BC trend is weak (**Figure 4-1b-d**). Compared to SRRW, DOC dynamics at HBEF are generally less thoroughly investigated, but DOC was not thought to show significant changes during reduced acid deposition, and the upward trend in flow-adjusted data is a novel finding (Fuss et al., 2015; Palmer et al., 2004). However, the extent and timing of pH versus DOC trends do not jibe well. For example, HBEF-T shows the most significant and consistent increase in pH, while increases in DOC are mostly observable over the recent decade. Either this represents a considerable lag between cause

and effect, threshold dynamics, or another (non-flow related) process that drives DOC in this case.

5.2. Simulation shifts in acid deposition: insights from soil core experiments across watersheds

Because SOM is a primary source for DOC, I investigated these processes. Previous work at SRRW has indicated that low charge density solutions (consistent with reduced acid deposition and/or recovery conditions) remove more DOC from soils compared to high charge density solutions (Adler et al., 2021; Cincotta et al., 2019).

I conducted similar experiments to investigate the effect of acidification versus reduced acid deposition ("recovery") on DOC release from soils with different parent material. I hypothesized that for watersheds with abundant Ca (SRRW and HBEF-T), more DOC would be mobilized into recovery simulations (i.e., low IS, high pH solutions) because C-stabilized aggregates might break up (hypothesis 2). I could only compare fall soils across all catchments because the COVID-19 pandemic made repeat trips to HBEF impossible.

Other than expected, neither SRRW nor HBEF fall soils showed systematic and significant differences in DOC release by treatment solution (**Figure 4-5b** and **c**). In previous studies, SRRW aggregates were investigated. They appeared to be much larger after acidification treatments than those treated with recovery treatments (Adler et al., 2021; Cincotta et al., 2019), attributed to aggregate breakup and ensuing DOC release. I did not repeat SEM analyses for SRRW samples and cannot test a possible link to aggregate size for this location. However, my HBEF soil SEM analyses show no effect of treatment solution on aggregate size (**Figure 4-7** and **Figure 4-8**). These results agree with the lack

of response in DOC concentrations by treatment (**Figure 4-5**) and suggest that, at least for these fall soils, aggregates are not a significant source for DOC for these samples, irrespective of soil Ca dynamics.

5.3.   Catchment soil processes: the importance of temporal and spatial variability

Because seasonal biogeochemical and hydrological processes strongly impact SOM and DOC dynamics, I tested seasonal controls for the soils I had access to during the pandemic (i.e., SRRW). I hypothesized that compared to fall, the winter and early spring soils would accumulate the most labile C that our simulated flushing experiments could extract (hypothesis 3). Indeed, my results show the highest DOC mobilization from winter soil cores (**Figure 4-3**), consistent with my hypothesis.

During winter, such material might only be slowly processing under the snowpack and only removed during intermittent winter melt events or spring thaw (Landsman-Gerjoi et al., 2020). The combined slow processing (minor C losses through biogeochemical processes) and absence of melting might have contributed to the high amounts of DOC available for leaching from these samples. However, contrary to my hypothesis, pre-snowmelt spring soil cores showed the lowest DOC concentrations in leachate, which might be due to a single flushing event antecedent to our sampling where 8.4mm of rain occurred in this watershed (**Appendix 1**, **Figure A-7**). This event might have removed labile C and temporarily emptied stocks even before the main snowmelt had begun.

My results on DOC across seasons also show that response to treatment was utmost dominant for winter and spring soils, where the most DOC was liberated into recovery solutions. This indicates that if aggregates play a role, they might also be controlled by seasonal dynamics and need to be investigated across seasons.

Another critical factor controlling DOC release, independent of treatment, are catchment scale variability in soil characteristics, DOC production, accumulation, and removal by landscape position. Because concave landscape positions are areas of confluence, they lend themselves for accumulation. I hypothesized that CC landscape positions would have the highest TOC concentrations and yield the highest amounts of DOC for all watersheds (hypothesis 4).

Indeed, for HBEF, DOC release was highest for soils from CC landscape positions in most cases (**Figure 4-5b** and **c**). However, there were fewer flushing events before sample collection at SRRW than HBEF for the same season (**Appendix 1**, **Figure A-8**). My SEM data also indicates significant differences in aggregate size by landscape position. For example, in the wollastonite treated HBEF-T, materials from LV landscape positions were substantially larger than CC materials (**Figure 4-7** and **Figure 4-8**), which might result from greater stability against breakup and might suggest aggregates could contribute to DOC. For instance, if aggregates were the primary source for DOC, we would expect that their size is reduced after treatment, as is the case for CC landscapes. However, to test this idea, aggregates sizes before and after treatment would need to be compared, which offers opportunities for further studies.

Other than hypothesized, TOC concentrations did not explain the varied DOC response by landscape position. In particular, CC versus LV landscape positions in the control watershed HBEF-HC had similar TOC concentrations, but the CC soil cores released significantly more DOC (**Table 4-1**). Previous research found that DOC concentrations vary greatly in groundwater from different soil types (Bailey et al., 2014; Gannon et al., 2015), which might decouple DOC supply from local TOC soil content; this

may be due to accumulation environments where organic carbon is immobilized as spodic materials (Bourgault et al., 2015; Gannon et al., 2015).

Lastly, and contrary to my hypothesis, SRRW did not significantly differ in DOC release by landscape position in either season, emphasizing the unpredictability between catchments even in similar settings. The supply and availability of DOC within a catchment are bound to complex and coupled biogeochemical and hydrological processes (Bernhardt et al., 2017; Landsman-Gerjoi et al., 2020; Perdrial et al., 2014, 2018) that generate large variability. Namely, linear convex hillslopes do not typically provide optimal conditions for organic matter production and accumulation and are thus not prone to be significant DOC sources (Andrews et al., 2011). However, because these locations are not always connected to the stream, they might accumulate materials that our experiments liberated. In turn, riparian zones tend to be more connected to the stream and more regularly flushed than hillslopes and might temporarily not be a good DOC source (Wen et al., 2020). Because we had hydrological events antecedent to most of our samplings (**Appendix 1**, **Figure A-7**), the otherwise dominant landscape position control might have been lessened. Either way, my results confirm that investigations of recovery and acidification need to acknowledge the effect of short-term seasonal dynamics and antecedent conditions that superimpose response signals to treatments.

5.4.   Soil and stream DOC dynamics with a resistance and resilience lens: a thought experiment

Changes in acid deposition constitute a prolonged disturbance, and ecologists have investigated ecosystem response to disturbances using resistance and resilience concepts. A prolonged or punctuated disturbance may result in little change in a resistant system,

while a resilient system might change but will eventually revert to its original state (Angeler & Allen, 2016; Diaz & Rosenberg, 2008; Falkenmark et al., 2019). In this context, it is reasonable to assume that the continuously buffered SRRW might have exhibited the highest degrees of resistance to acidification, followed by the treated HBEF-T. It is also appropriate to think that the untreated HBEF-HC should have shown the lowest degrees of resistance.

However, when investigating acid deposition in this context, the big challenge is that even long-term datasets do not fully record the onset of acidification; thus, pre-disturbance data does not exist. For example, HBEF exhibits one of the most complete and longest records of catchment data in the United States, beginning as early as the 1960s (Holmes & Likens, 2016). However, even these datasets only capture acidification at its peak and document the progressive reduction in acid deposition (Driscoll et al., 2001). Thus, it is difficult to assess if a system returns to a pre-disturbance level (i.e., resilience, **Figure 5-1**).

Despite this lack of data, we have indirect evidence on system resistance and resilience in this context. For catchments that experienced decreased acidification which ultimately contributed to DOC increases, it is reasonable to assume that increased acidification had the opposite effect and that stream DOC declined (for example, in response to the accumulation of C stores in the watersheds) during this time (dashed line in **Figure 5-1**). Additionally, recent research by Armfield et al., 2019, indicates that acidification might have led to the accumulation of legacy C stores at SRRW and that soils released their stored material in response to shifts in geochemical conditions like reduced acidification. Their study found significant decreases in riparian soil Ca concentrations

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between their repeated soil measurements in 2017 and archived soils from the late 1990s in similar locations. Because of the strong link between Ca and organic matter in general (Rowley et al., 2018; Rowley et al., 2021) and at SRRW (Cincotta et al., 2019), DOC and Ca, releases from legacy stores increased stream DOC at this site. Conceptually, the response of DOC, in this case, may indicate low resistance to change in geochemical conditions and high resilience by potentially restoring pre-acidification conditions.

The large-scale experimental treatment at HBEF provides additional insights into resistance and resilience despite lacking pre-disturbance data and emphasizes the highly catchment-dependent response to a disturbance. The treated watershed, HBEF-T, received wollastonite mineral applications in 1999 that artificially buffered the pH of this sub-watershed. The treatment led to a temporary pH increase in soil and stream water as wollastonite pellets dissolved (**Figure 4-1b**) (Battles et al., 2014; Cho et al., 2009; Peters et al., 2004). Simultaneously, this temporary and artificially induced pH increase seems to be superimposed on the general and ongoing trend of pH increases across all watersheds (**Figure 4-1**). In this case, the pH response from the wollastonite treatment indicates high resilience. However, stream DOC concentrations did not respond to the temporary spike in pH, and DOC_{FA} concentrations did not change (**Figure 4-2b**), which conceptually would indicate resistance to change for both the artificial short-term and natural long-term shifts in geochemical conditions. Indeed, the continued supply of DOC during repeat flushing at HBEF (**Figure 4-6**) suggests little-to-no supply limitation, further emphasizing the stable conditions at HBEF.

My experiments can also be viewed in this context, where DOC release from soils is investigated in response to shifts in acid deposition. Since the sampled soils already

experienced long-term acidification followed by a reduction in acid deposition (time X_0 to X_1 in **Figure 5-1**), the recovery treatment could be seen as a forward simulation (forward arrow from $X_{Present}$). In contrast, the acidification treatment serves as a backward simulation (backward arrows from $X_{Present}$) (**Figure 5-1**).

In general, the considerable soil response at SRRW from experimental treatments (for most seasons) agrees with the strong stream DOC_{FA} response and aligns with the forward versus backward simulation (**Figure 5-1**). In turn, for HBEF, the lack of response to treatments for all watersheds is in agreement with the lack of covariance between stream pH and DOC_{FA} trends (keeping the limitation of sample availability in mind). Overall, this suggests that SRRW DOC_{FA} might return to a base level when system recovery is achieved (resilience); however, more data on seasonal variability will be necessary to evaluate HBEF in this context of resistance and resilience.
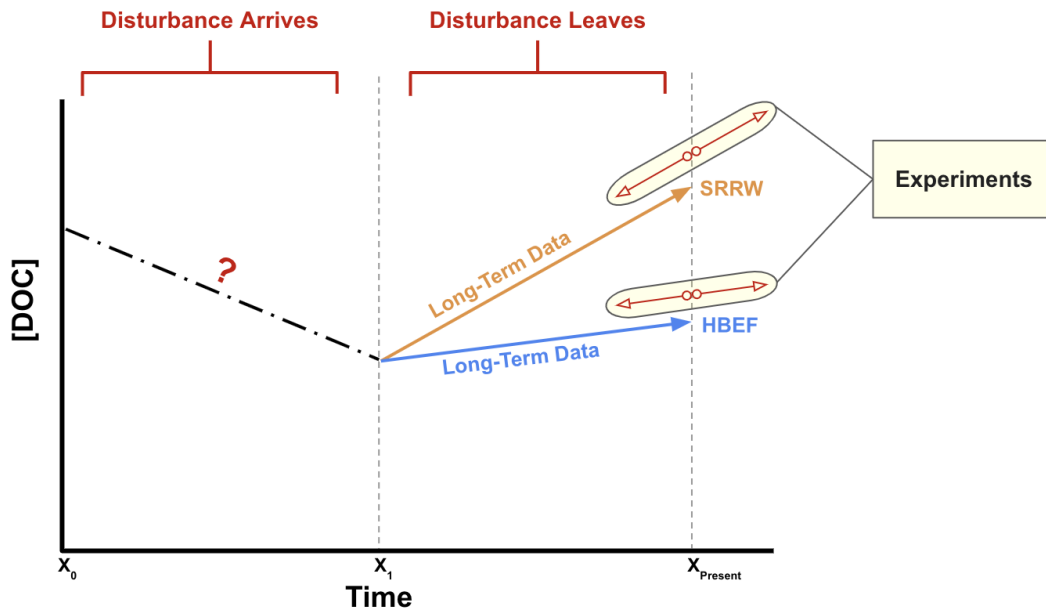
Figure 5-1 A conceptual model of dissolved organic carbon (DOC) concentrations over time for investigating a prolonged disturbance.

5.5. Limitations and adaptations

COVID-19: the largest limitation of my study is the reduced access to field sites due to the COVID-19 pandemic. For instance, I planned on sampling SRRW in winter, early spring, late spring, early summer, and fall, but due to COVID-19, I could only sample in winter, spring, and fall. The travel restrictions vastly reduced the samples I was able to collect to understand temporal dynamics at SRRW. More importantly, my original plan included several field trips to HBEF to fully constrain the effect of Ca in soils on DOC release. To elaborate, I did not have access to Ca data and/or samples as COVID-19 made most fieldwork impossible. Thus, I do not have insights on the specifics of Ca dynamics (stream and experiments) but have Ca data from the soil leaching experiments, which could provide additional insights. As a result, I only have HBEF samples from the fall. I accommodated COVID-19 restrictions by adding long-term data analyses and conceptualizing my work in the resistance and resilience context.

Data availability: HBEF and SRRW have published a significant amount of water quality data, which requires immense effort and quality control. The impressive long-term datasets allowed me to put my experiments in some context, but even these data have gaps. To illustrate, the timeframes for pH data extend much further back in time than DOC data. Even the available DOC data are scarce, and HBEF-HC has a significant data gap, prohibiting the detection of continuous long-term trends. Moreover, HBEF-BC was not sampled due to access restrictions, even though it has more long-term DOC data than HBEF-HC.

Spatial and temporal variability: Additionally, my experiments at SRRW and HBEF stress the difficulty of assessing catchment resistance and resilience across scales

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where catchment-specific processes vary across seasons, landscape positions, or both (e.g., temporal variations in spatial catchment connectivity). Moreover, I do not have seasonal SRRW aggregate data or pre-treatment HBEF aggregate data. And the differences in timing between the repeated flushing and how DOC is flushed are not readily understood across seasons. Additionally, how the timing and location further impact the soil's response to the treatments and other potential seasonal effects are unknown for HBEF in this study. As a result, another future experiment could compare SRRW and HBEF across seasons to add a temporal component.

Additional drivers: I focused on shifts in acid deposition; however, DOC is significantly controlled by precipitation amount. In particular, changes to the climate system have led to increasing precipitation amounts in the NE United States, both in the total event frequency and the occurrence of larger magnitude events (Arnone et al., 2011; Campbell et al., 2009; Guilbert et al., 2014; Jentsch et al., 2007; Seneviratne et al., 2012) and annual precipitation increased by 9.5 ± 2 mm/decade over the last century (**Figure 2-1**) (Campbell et al., 2011; Hayhoe et al., 2007; Keim et al., 2005; *National Atmospheric Deposition Program (NRSP-3)*, 2020). Furthermore, the increased persistence of rainfall events (i.e. more back-to-back wet days) that is observed in recent years in the NE (Guilbert et al., 2015) may impact DOC dynamics tough other processes than just flushing. For example, this persistence can lead to higher soil moisture and water tables, limiting aerobic C respiration and leading to accumulation of C in soils. Shifts in persistence of respiration can also impact vegetation structure, overall changing C cycling at an ecosystem level. While flow-adjusted DOC concentrations allow us to remove the hydrological component

of changes in precipitation patters, it does not address ensuing changes in biogeochemical cycling or changes in water residence times.

As a result, there is currently insufficient knowledge on the controls and feedback between processes (that operate on different time scales) to predict how watershed DOC export will respond under future climatic scenarios and more work needs to be done in this context (Campbell et al., 2009; Raymond & Saiers, 2010; Wen et al., 2020). While DOC release due to reduced acid deposition will likely return to a base level, climate change-induced DOC dynamics will become more critical and need careful investigation.

Chapter 6: **CONCLUSION AND FUTURE RESEARCH**

The investigation of watersheds that share many similarities and distinct differences is useful when examining the effect of regional disturbances on stream response (here DOC). My long-term data analyses showed that differences in extent and timing of shifts in stream pH versus DOC_{FA} could not be simply related to differences in bedrock composition but are likely much more complex. SRRW shows a strong progressive increase in DOC_{FA} concentrations (despite the weakest increase in stream pH). Conversely, HBEF only begins to exhibit increases in DOC_{FA} over the recent decade despite a significant and consistent increase in pH. I could not investigate many of my original research questions on Ca controls on DOC due to the pandemic, which offers many opportunities for further research.

However, my study confirmed that acknowledging and investigating the complexity of unique catchment-specific processes is essential. Such processes vary by season and landscape position and can superimpose signals of catchment attributes in comparative studies. For example, for my soil sampling, antecedent conditions (precipitation events) before sampling greatly affected my experimental findings. Signals of a response to a regional and long-term driver might be partially hidden in the "noise" generated by the large temporal and spatial variability. An iterative approach that investigates catchment processes in tandem with larger-scale patterns is a possible way forward, and more work is necessary to disentangle these signals.

However, my research showed that independent of changes in discharge, stream DOC is changing in all locations. This means that discharge-driven increases in DOC due to climate change are likely exacerbated by additional processes that liberate DOC. This

could be a transient effect if recovery from acidification is the main driver, but this could also be due to other dynamics. Namely, change in temperature, shifts in wetland coverage, etc.

My approach of conceptually investigating resistance and resilience might also provide further opportunities for research. By using resilience and resistance framing, I conceptually linked how experimental data relates to long-term data through forward and backward simulations and its possibilities and limitations. Another study may investigate this or explore other response variables to a disturbance such as nitrogen species or other pieces, as I only examined DOC.

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APPENDIX 1

Figure A-1 Long-term stream water dissolved organic carbon (DOC) time series for a. Sleepers Research Watershed, SRRW, b. Hubbard Brook Experimental Forest, HBEF-T (treated), c. HBEF-HC (hydrological control), and d. HBEF-BC (biogeochemical control). Data are derived from DOC (mg/L) concentrations and discharge (Q) (ft3/s).
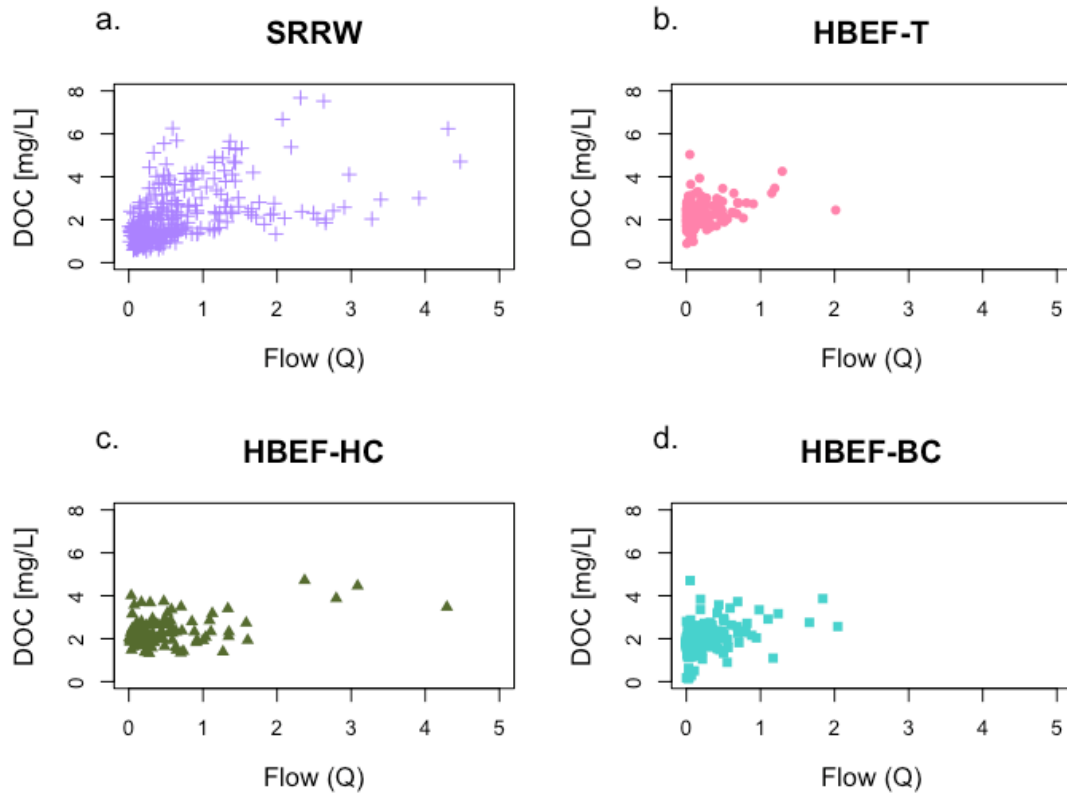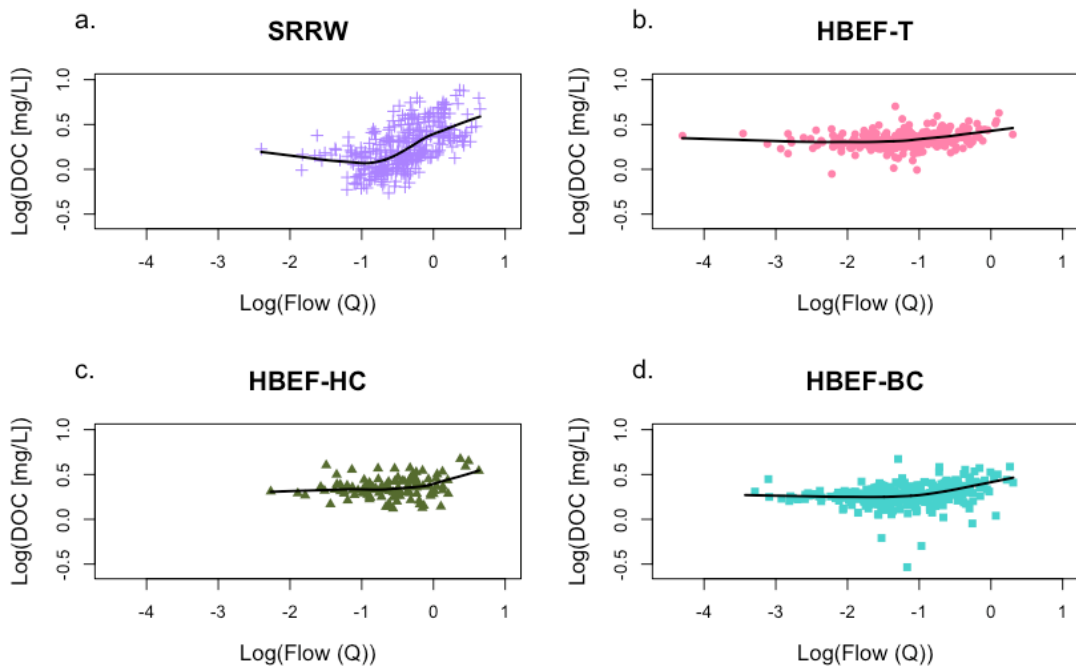
Figure A-2 Long-term stream water dissolved organic carbon (DOC) time series for a. Sleepers Research Watershed, SRRW, b. Hubbard Brook Experimental Forest, HBEF-T (treated), c. HBEF-HC (hydrological control), and d. HBEF-BC (biogeochemical control). Data are derived from log-transformed DOC (mg/L) concentrations and discharge (Q) (ft3/s), lines are generated from LOWESS fit (log-DOC ~log-Q) with a smoothing span of 67%.
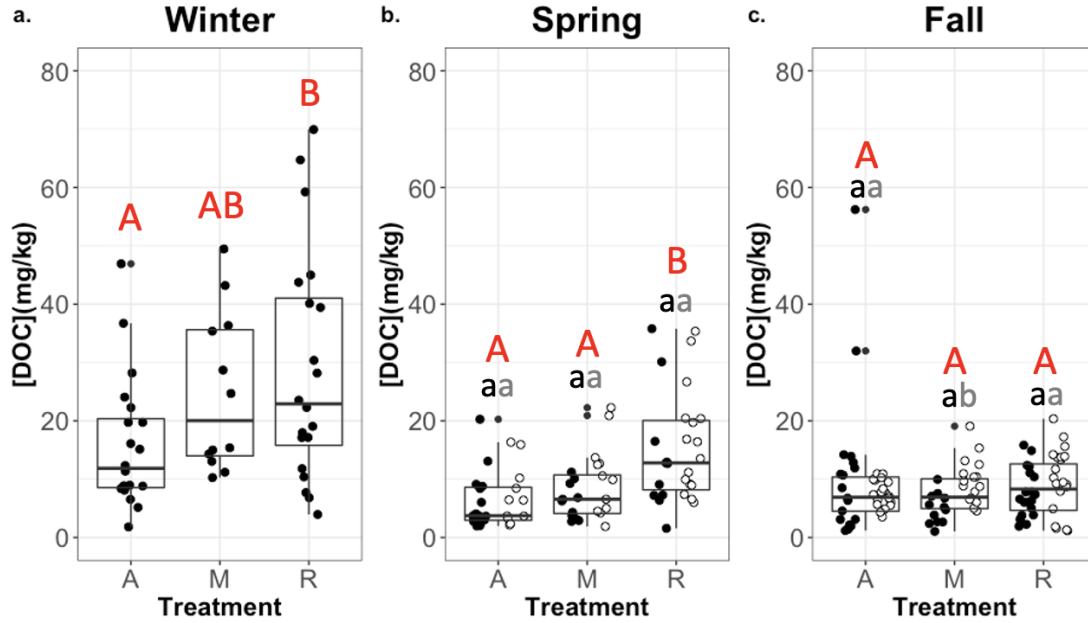
Figure A-3 Sleepers River Research Watershed seasonal soil core leaching experiments displaying data from 4 flushing's and comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) within a watershed for a. Winter, b. Spring, and c. Fall. Filled circles represent concave landscape (CC), and open circles represent linear convex hillslope (LV). Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by treatment for both landscape positions combined (upper case letter) and for each landscape position separately (lower case letter, CC= black letter, and LV = grey letter).

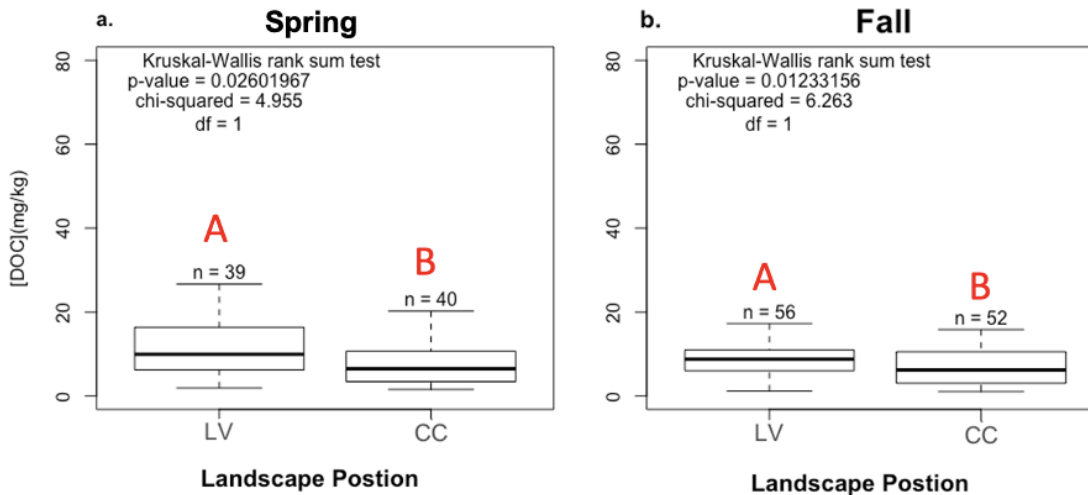
Figure A-4 Sleepers River Research Watershed seasonal soil core leaching experiments displaying data from 4 flushing's and comparing landscape positions, linear convex hillslope (LV), and concave landscape (CC) within a watershed for a. Spring, and b. Fall. Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by landscape positions for all treatments combined.
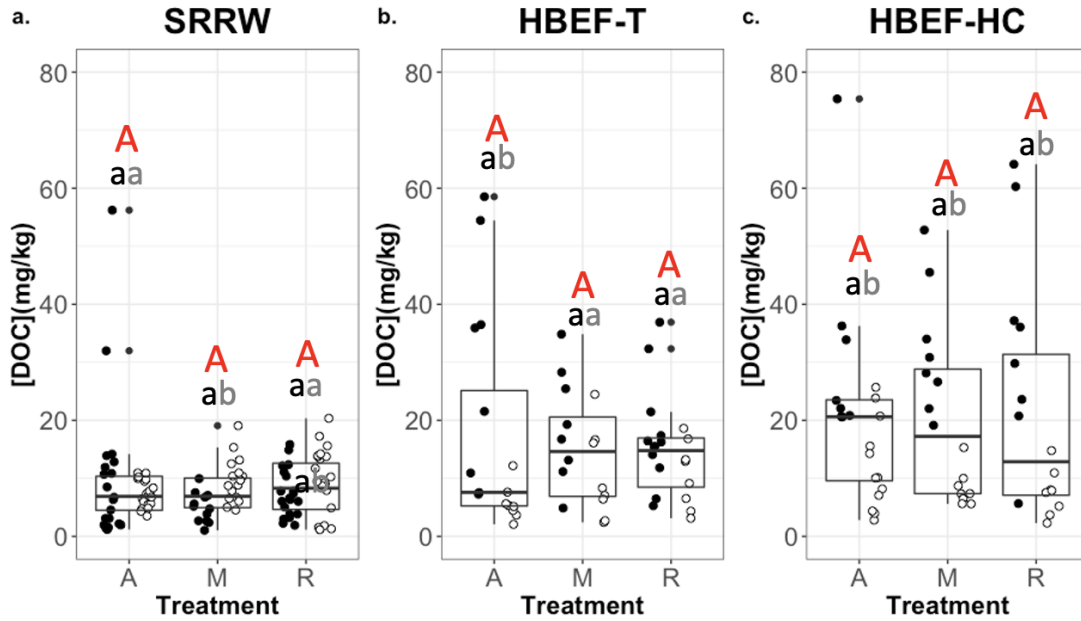
Figure A-5 Fall 2020 soil core leaching experiments displaying data from 4 flushing's at a. Sleepers River Research Watershed (SRRW), b. Hubbard Brook Experimental Forest, HBEF-T (treated), and c. HBEF-HC (hydrological control) comparing treatments (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) within a watershed. Red capital letters indicate statistically significant ($\alpha \leq 0.05$) differences across landscape positions within a watershed and season. Filled circles represent concave landscape (CC), and open circles represent linear convex hillslope (LV). Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by treatment for both landscape positions combined (upper case letter) and for each landscape position separately (lower case letter, CC= black letter, and LV = grey letter).

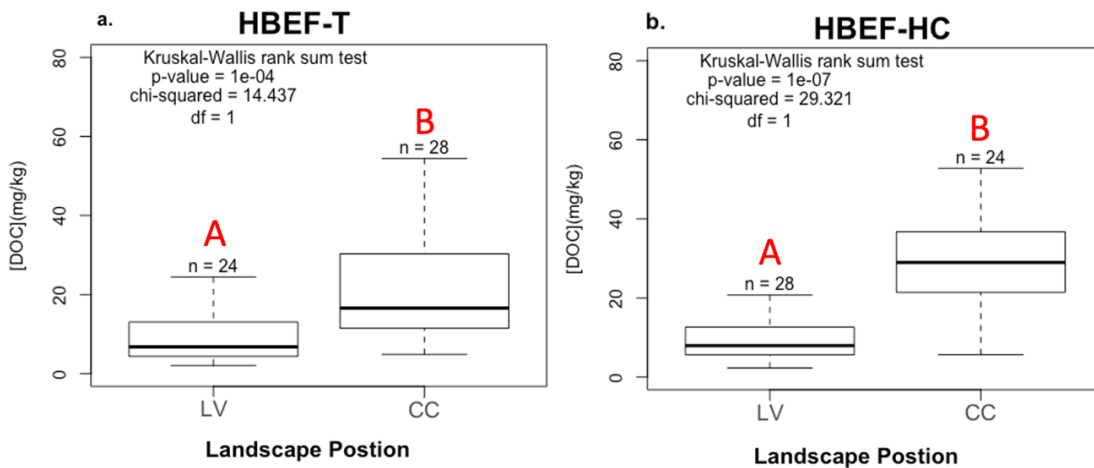*Figure A-6 Fall 2020 soil core leaching experiments displaying data from 4 flushing's comparing landscape positions, linear convex hillslope (LV), and concave landscape (CC) within a watershed a. Hubbard brook Experimental Forest, HBEF-T (treated) and b. HBEF-HC (hydrological control). Letters indicate statistically significant ($\alpha \leq 0.05$) differences of means by landscape positions for all treatments combined.*
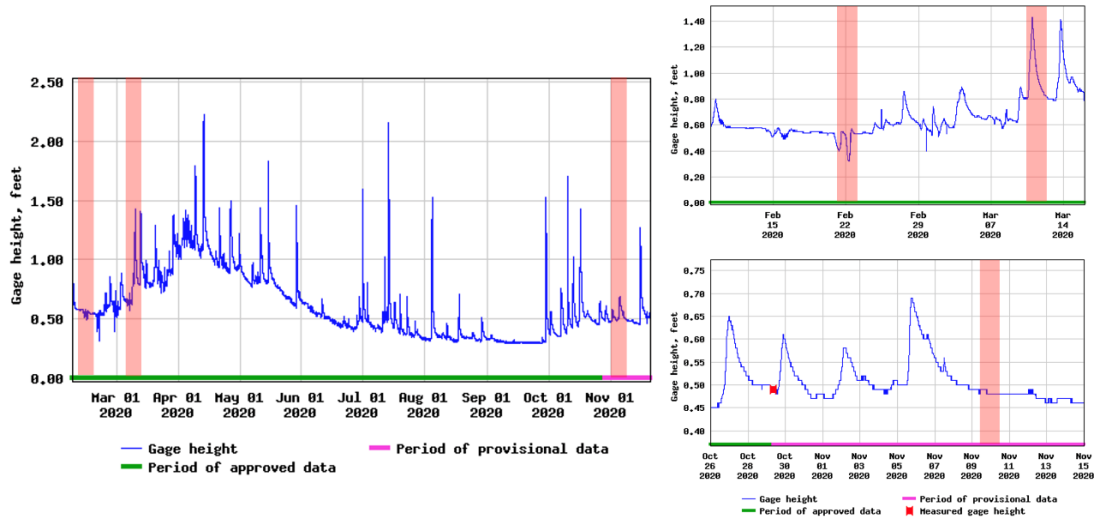
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Figure A-7 Sleepers River Research Watershed instantaneous gage height (ft) at W-3. W-3 is a larger watershed that encompasses W-9, where samples were collected for this study. W-3 has a slightly larger flow and delayed response but provides up-to-date stage height information to determine antecedent conditions before sampling SRRW. Dates near the sampling collection times are highlighted in red (data from U.S. Geological Survey, 2001).
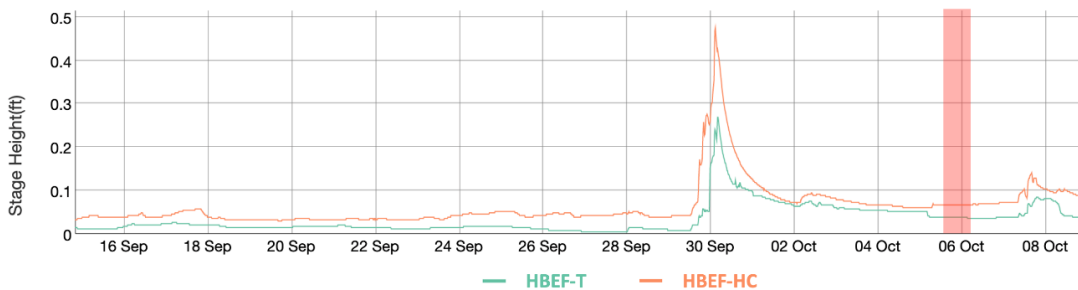

Figure A-8 Raw instantaneous gage height (ft) sensor data for Hubbard Brook Experimental Forest at HBEF-T (treated) and HBEF-HC (hydrological control). The date near the sampling collection is highlighted in red (data from Hubbard Brook Ecosystem Study, n.d.)

Table A-1 Sleepers River Research Watershed Experiments compared by treatment (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) and landscape positions (linear convex hillslope, LV, and concave landscape, CC) across the season. Letters across a single row indicate statistically significant ($\alpha \leq 0.05$) differences between seasons. Statistically significant p-values are bold.

Treatment	Landscape Position	Month			p-value
		Winter	Spring	Fall	
A		a	b	b	**4.6 x 10⁻²**
M		a	b	b	**4.3 x 10⁻³**
R		a	a	b	**1.3 x 10⁻³**
	LV	a	b	b	**2.8 x 10⁻⁴**
	CC		a	a	2.2 x 10⁻¹
A	LV	a	b	b	**3.3 x 10⁻²**
M	LV	a	a	b	**2.0 x 10⁻²**
R	LV	a	a	b	**4.2 x 10⁻²**
A	CC		a	a	7.2 x 10⁻¹
M	CC		a	a	4.2 x 10⁻¹
R	CC		a	b	1.7 x 10⁻²

Table A-2 Fall 2020 experiments compared by treatment (A, high IS, low pH), (M, low IS, low pH), and (R, low IS, high pH) and landscape positions (linear convex hillslope, LV, and concave landscape, CC). Letters across a single row indicate statistically significant ($\alpha \leq 0.05$) differences between watersheds, Sleepers River Research Watershed (SRRW), Hubbard Brook Experimental Forest, HBEF-T (treated), and HBEF-HC (hydrological control). Statistically significant p-values are bold

Treatment	Landscape Position	Watershed			p-value
		SRRW	HBEF-T	HBEF-HC	
A		a	a	a	1.3×10^{-1}
M		a	a	a	5.2×10^{-2}
R		a	a	a	1.2×10^{-1}
	LV	a	a	a	9.0×10^{-1}
	CC	a	b	b	**5.0×10^{-6}**
A	LV	a	a	a	4.3×10^{-1}
M	LV	a	a	a	6.0×10^{-1}
R	LV	a	a	a	5.6×10^{-1}
A	CC	a	a	a	8.5×10^{-2}
M	CC	a	b	b	**2.1×10^{-2}**
R	CC	a	b	b	**2.5×10^{-3}**