2024

Using soil cores to assess the role of ion exchange in soils impacted by acid deposition: a case study from Sleepers River Research Watershed, Danville Vermont

Elliott Jaye Bloom

Recommended Citation
Bloom, Elliott Jaye, "Using soil cores to assess the role of ion exchange in soils impacted by acid deposition: a case study from Sleepers River Research Watershed, Danville Vermont" (2024). *UVM College of Arts and Sciences College Honors Theses*. 146.
https://scholarworks.uvm.edu/castheses/146

Using soil cores to assess the role of ion exchange in soils impacted by acid deposition: a case study from Sleepers River Research Watershed, Danville Vermont

An Honors Thesis by

Elliott Bloom

The University of Vermont

College of Arts and Sciences, Geography and Geosciences

Rubenstein School of Environmental Sciences

Advisor: Director of Geosciences and Associate Professor of Geochemistry Dr. Julia Perdrial

Committee Member: Associate Professor Carol Adair

Committee Member: Professor and Department Chair Shelly A. Rayback

April 12, 2024

Table of Contents

Abstract:

Shifts in acid deposition in the Northeastern United States have impacted forest soils in many watersheds with important trickle-down effects such as altered water quality in streams and rivers that are coupled and complex. For my research, my main question was “How do the characteristics of solution (acidity and ionic strength) impact soil geochemical reactions and the ensuing release of solutes (e.g. carbon, nitrogen, and major anions and cation species) from soils?” To address this question, I took advantage of archived samples, completed additional analyses, and integrated these new data into an existing dataset of soil leachate derived from intact soil core experiments. I then used these data for geochemical modelling to explore the various soil processes that could be occurring and changing in relation to acid deposition like ion exchange, aggregate breakup, and complexation and incorporated my observation into and updated conceptual model for soil processes.

1.0 Introduction

Shifts in acid deposition in the Northeastern United States have impacted forest soils in many watersheds and because soils are important sources for solutes in streams, water quality in streams and rivers have been impacted as a result (Ruckhaus et al., 2023). Because of these effects, acid deposition has received increasing attention in the research arena since the mid-1900s, emphasizing the connection between rain chemistry and ecosystem effects (Likens et al., 1972). These earlier investigations include studies of forest health (Matzner and Murach, 1995), soil dynamics (Driscol et al., 2001), and shifts in stream composition because of acid deposition (Skjelkvåle et al., 2001). For example, acid deposition leads to saturation of soil particles with protons, nitrates (NO_3) and sulfates (SO_4) from rain that replace base cations (e.g., Ca, Na, Mg) from soil exchange sites (Sposito et al., 2008). Such exchange happens when an ion in solution exchanges with an ion that is partially bonded to a soil particle's surface and is governed by both the solution concentration and ion affinity. Affinity, a general term for the ability of ions to be able to bond to a soil particle's surface, is a function of the hydrated radius of an ion, but other processes can affect it (Sparks et al., 2024). Ion exchange can be further regulated by a variety of interactions including the ion type, soil type, and other physical and chemical variables (Sparks et al., 2024). While ion exchange occurs at a molecular scale, it can have landscape-scale implications on mobility of toxins and availability and release of nutrients in the soil. During acid deposition, changes in ion exchange caused the so-called "cation stripping", where protons replaced base cations from soil exchange sites, changing stream composition, and depleting soils of important nutrients with trickle-down effects on plant health.

After the implementation of clean air acts in 1963 and later amendments, acid deposition decreased significantly (Driscoll et al., 2001; Likens et al., 1972) and previously impacted ecosystems began to recover from effects of acid rain. Specifically, soil and stream water pH increased, acid derived NO_3 and SO_4 loadings were reduced, and base cation content in soil increased slowly (Driscoll et al., 2001).

However, one aspect that puzzled the research community for years was a concurrent increase in dissolved organic carbon (DOC) concentrations in streams in many Northeastern forests, accompanying the decreases in acid deposition. This increase was unexpected because DOC is not a component of rain. Soils were investigated as important contributor to stream DOC, because waters entering streams typically first percolate through several soil layers and the near stream riparian zones before entering streams (Sparks et al., 2024). Because DOC is more readily dissolved in high pH solutions, the DOC increase was suspected to correspond to the change in pH (Monteith et al., 2007). More recently, an additional soil process was investigated, which involves changes in the physical conformation of soil particles in clumps. These so-called soil aggregates can accommodate organic material and other soil constituents and are more stable when surrounded by solutions with high charge density, as it was typical during the peak of acid deposition (Adler et al., 2021; Cincotta et al., 2019). These studies employed a combination of long-term analyses of stream water and intact soil core experiments to investigate the connection between solution chemistry, soil processes and stream impacts (Cincotta et al., 2019; Adler et al., 2021; Ruckhaus et al. 2023). Results from these soil core experiments from a local watershed, the Sleepers River Research Watershed (SRRW), indicated that indeed, DOC concentration in soil leachate increased when soil aggregates were breaking up, and that this break up was common when solutions were used that simulate regular (not acid) rain (Bristol et al., 2021).

A recent study from Ruckhaus et al (2023) integrated these findings into a conceptual model, that indicates that during recovery, aggregate breakup increases, resulting in a higher release of

DOC and lower release of dissolved inorganic nitrogen (DIN). However, this model does not include specific cation and anion species to further clarify processes within the soil cores (Fig. 1).

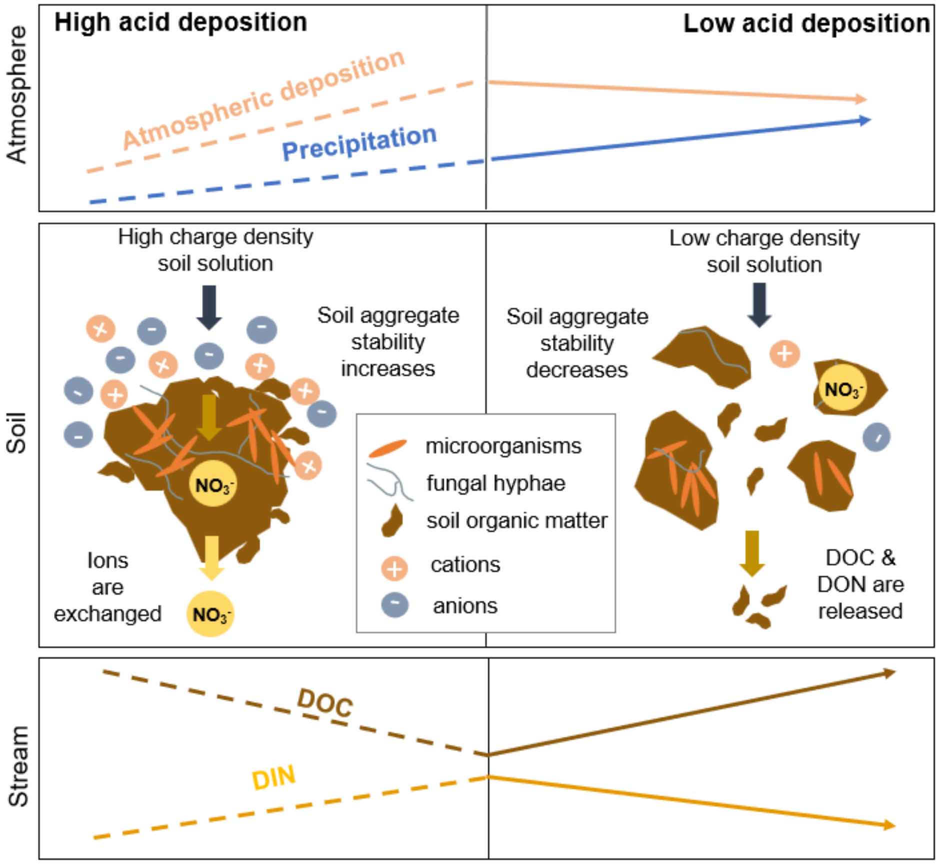


Figure 1: *Conceptual model of aggregate breakup in times of low acid deposition, leading to dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) release (Ruckhaus et al., 2023)*

These studies also found variations in carbon and nitrogen release (DOC, DIN, and dissolved organic nitrogen, or DON) by season and landscape position. For example, solute release from hillslope soil cores indicated build-up of materials that were periodically flushed during hydrological events (Adler et al., 2021), while cores from low-lying areas accumulated nutrients, but the high microbial and geochemical activity was suspected to cause losses in the concentration (Bristol et al., 2019). Additionally, soil core effluent generally showed higher concentrations of organic constituents in fall and winter samples (Bristol et al., 2021). In fall, leaf litter contributes high amounts of organic rich materials to soil, while winter soils accumulate materials due to processes under the snowpack that can be released during snowmelt (Ruckhaus et al., 2023).

Another process that is specifically important for DOC dynamics is complexation, where hydrated metal ions and ligands bond to form a metal-ligand complex (Sparks et al., 2024) Functional groups in DOC have a particular affinity to form complexes with polyvalent cations such as Ca, but also Fe and Al (Sparks et al., 2024). The latter two metals are typically not soluble at pH above 3, but can remain in solution as complexes, thus, especially in the context of DOC increases, organo-metal complexes should be considered for possible implications for water quality.

As the chemistry of precipitation that interacts with these soils continues to change, the quality of water that drains from soils and enters streams might also continue to change in complex ways that we need to prepare for. While previous research on soil cores offered many insights on a variety of processes in SRWW, most studies focused on DOC and nutrients, with little focus on the full speciation of all major solutes. Indeed, most studies did not analyze for the full suite of solutes, limiting our ability to fully understand specific processes and presenting a significant knowledge gap.

However, speciation using geochemical models allows for better constraining specific processes such as ion exchange and complexations. Speciation of soil solutes is the process of determining the distribution of ions in solution in their chemical forms. This is important as the chemical form and activity of an ion varies with soil solution composition (e.g. pH, ionic strength, presence of other ions) and can impact its mobility and availability in soil and solution (Sparks et al., 2024). Speciation models are based on thermodynamic data and solve a large number of equilibrium calculations for a variety of solutes iteratively until the best solution is presented. Many speciation models exist that have various inputs and capabilities. In this study, I used "Visual MINTEQ" due to its capabilities to calculate for DOC (Gustafsson et al., 2011).

My overall research objective was to complement the data set on soil core experiments with the complete suite of solutes necessary for geochemical modelling to investigate specific soil processes. For this I analyzed archived samples (2019-2023) for missing solutes, completed geochemical modelling, and analyzed these data for patterns in solute dynamics by treatments and additional parameters like seasons and landscape positions.

2.0 Methods

2.1 Study Area

SRRW is operated by the US Geological Survey (USGS) and located in northeastern Vermont (Fig. 2b). This location is collecting hydrological data since the late 50ies, and abundant geochemical data since the early 90ies (Shanley et al., 2022). The site comprises multiple nested sub catchments of forested and agricultural landcover. The 0.405 km^2 large, forested headwater catchment (watershed 9 = W-9) is the location of all samples and data presented in this study (Fig. 2c). The mountainous W-9 is situated between 524 and 672 m above sea level with primarily hardwood forest consisting of mostly birch, beech, and maple. Climate is temperate humid where temperatures vary from -30 to +30 °C (Pellerin et al, 2011). The watershed experiences frequent rain events with an average precipitation of between 38-45 inches distributed roughly evenly throughout the year (Runkel, 2004). Snow covers the ground from 20-30% of the year with spring stream water flow largely dominated by this snowmelt (Shanley et al, 2015).

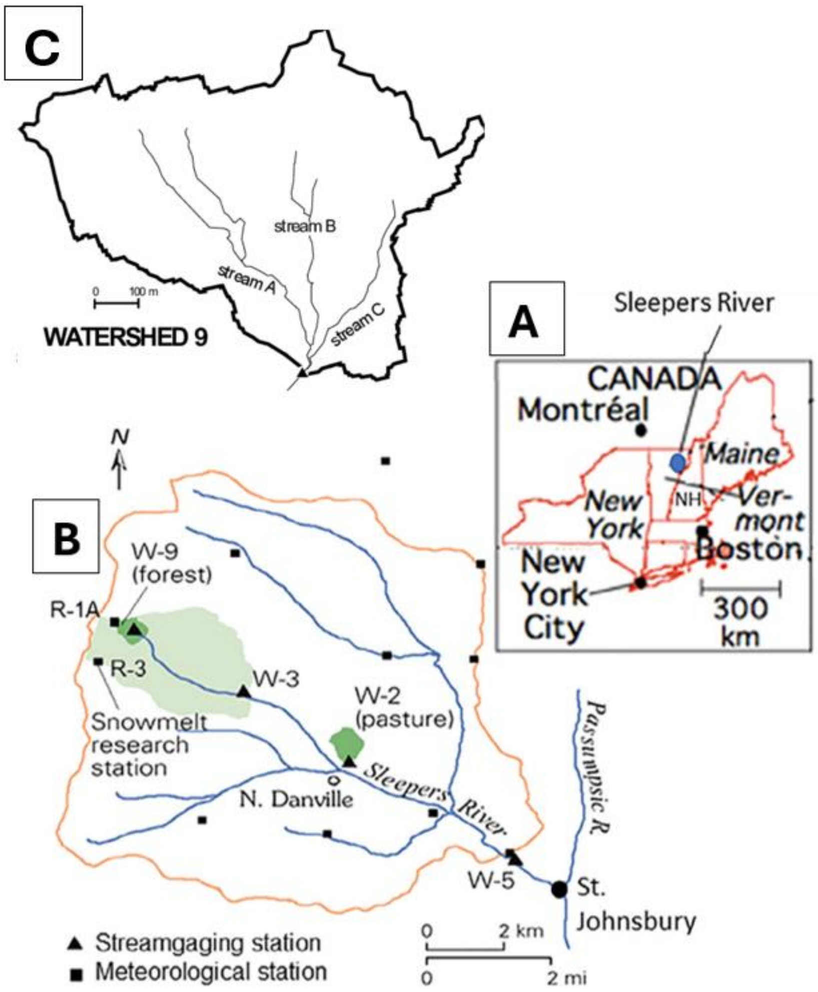


Figure 2: *Map of New England (A), Sleepers River Research Watershed (B) with stream locations (Shanley et al., 2002), and the forested headwaters (Watershed 9, C) (Sebestyen et al., 2009).*

SRRW, like the rest of the Northeast, has received a significant amount of acid deposition in the past decade which led to stripping of base cations and export of NO_3 from topsoil in the area (Shanley et al., 2000). The soil type in W-9 is primarily Inceptisols and Spodosols (Cincotta et al, 2019). Unlike many locations in the area, parent material for soil formation in SRRW contains carbonates, mostly in the 1-4m of basal (glacial) till that incorporates quartz-mica phyllite with interbedded calcareous granulite. The carbonate content buffers the pH of ground water and ensuing stream water, and deeper soil layers are not affected by the otherwise widespread calcium depletion (Armfield et al, 2019; Shanley et al., 2000).

2.2 Sample Collection

My data comes from soil cores that have been collected by previous researchers (Adler et al., 2021; Bristol et al., 2021; Cincotta et al., 2019; Ruckhaus et al., 2023) across seasons between 2019 and 2023, as well as from cores that I collected in 2023. All cores were collected using a polyvinyl chloride (PVC) pipe that was 5cm in diameter (Fig. 3a). The PVC pipe was inserted 10 cm into the ground in order to capture the soil organic horizon. Then, it was carefully removed to maintain the integrity of the soil core. Before sample collection, leaf litter was removed from the ground to avoid organic material that was not incorporated into the soil. In the winter months, snow was removed from the ground before collection (Fig. 3b & c). After sample collection, leaf litter and snow were returned to the location of sample collection. The samples were sealed using parafilm and sample tape, stored upright in 4 ℃ and transported back to the laboratory where experimentation happened within 24 hours of collection. Various number of samples were collected depending on the season and the student running the project.

Figure 3: *Samling of intact soil cores in winter. Polyvinyl chloride (PVC) pipes containing soil cores being stored upright (a), Ruckhaus, Perdrial, and Bloom hiking into Sleepers River Research Watershed (b), Perdrial and Ruckhaus clearing snow off of sampling area before sampling (c), Bloom hammering pvc pipe 10cm into ground to collect soil core (d).*

While sample collection was consistent through these years and studies, the use of terminology for landscape position was not. For example, Bristol et al. (2021) used the term “concave” for low lying landscape positions that tend to receive materials from upslope (including swales and riparian zones), and convex or linear convex for hillslope positions that tend to be source locations. In the case of Ruckhaus et al. (2023), and unpublished data from Bernadina Cordes, zones of confluence and low-lying landscape positions are exclusively riparian zones. To integrate terminology across functionality (accumulation or sourcing) and location (near stream or far stream), I use the overarching terminology "low-lying" landscape position for swales, concave and riparian zones, and hillslope for convex, linear and hillslope locations (Table 1. See Appendix 2 for detailed list of samples used in this paper).

	Fall		**Winter**		**Total**
	Low-lying	Hillslope	Low-lying	Hillslope	
Acid	0	1	2	5	**8**
Mixed	3	9	1	0	**13**
Recovery	3	1	2	3	**9**
Total	**17**		**13**		

Table 1: *The number of samples collected during each season by landscape position, season, and experimental treatment. For a detailed list of samples used in this paper, see Appendix 2.*

2.3. Soil core experiments

Soil core experiments were performed consistently across all research projects using procedures outlined in Cincotta et al. (2019) and Adler et al. (2021) within 24 hours of soil core collection, including experiments that I conducted. Cores were arranged vertically and fitted with a PVC cap and a filter inserted at the bottom to avoid loss of soil during experimentation and a nozzle to allow for the control of the flow out of the core. Each core was assigned a treatment solution and 120 mL was poured into the core and allowed to interact with the solution for five minutes. After five minutes, the solution was released from the core and collected for 4 minutes. The total volume of this solution was recorded, and the flushing is repeated one more time with the same treatment solution to allow for a total of two treatments per soil core. After experimentation, the soil was removed from the core, oven-dried, and massed.

The following treatment solutions were used: The acidification (A) analogue simulates the high ionic strength ($3*10^{-2}$ M) and low pH (~ pH=3) of rain during acid times of peak acid deposition and was generated with HCl and $CaCl_2$. The recovery solution (R) simulates the higher pH (~ pH=5) and low ionic strength ($<10^{-5}$ M) more typical for rain during times of recovery from acid deposition. The mixed solution (M) was designed to simulate the pH of the A solution (pH = 3 from HCl) with a ionic strength that is similar to the R solution (ionic strength $<10^{-5}$M) in order to test the two variables of acid rain (pH and ionic strength, Table 2)(Ruckhaus et al., 2023; Cincotta et al., 2019; Adler et al., 2021).

	pH	**DIC (mg/l)**	**Ca+ (mg/l)**	**K+ (mg/l)**	**Cl- (mg/l)**
Acid	2.9	0.21	460	NA	812
Mixed	3.3	0.23	0.15	0.71	10.6
Recovery	5.0	0.26	NA	NA	NA

Table 2: *Measured composition of inflow solutions prepared for the acid, mixed, and recovery treatments.*

2.4 Analytical Methods and Data Analysis

All effluent and aliquots of each inflow solutions were filtered using a 0.45 µm polyether sulfone membrane and stored in glass vials for carbon analyses and HDPE vials for cation and anion analyses. The pH of the liquid effluent was measured and recorded. Most studies focused on DOC dynamics, thus these data were largely available and had been analyzed using a Shimadzu Carbon Analyzer (Shimadzu, Columbia, MD, USA). Bristol et al. (2021) additionally analyzed for cations, but DIC data were missing, and Ruckhaus et al. (2023) analyzed anions, but DIC and cation data were missing (Table 3). I therefore complemented all datasets with missing analyses as follows:

For additional DIC analysis, I used a Shimadzu Carbon Analyzer (626 sample total, Shimadzu, Columbia, MD, USA) and for anions (Cl, NO_2, NO_3, PO_4, and SO_4) I used the Thermo Scientific Dionex Aquion Ion Chromatography System (199 samples total, Thermo Fisher Scientific, USA) in the Perdrial Environmental Biogeochemistry lab. To complement missing cation analyses (Al, Ca, Fe, K, Mg, Mn, Na, and Si) I prepared acidified dilutions that were measured in University of Vermont's Agricultural and Environmental Testing Lab using inductively coupled plasma-optical emission spectroscopy (142 samples total, ICP-OES).

Study	**Date Collected**	**Number of Samples**	**If needed, what?**	**Number of Samples analyzed for this study.**
Adler	10/16/2019	196	DIC	196
Bristol	10/11/2020	104	DIC	104
Ruckhaus	11/8/2020	111	DIC	111
Cordes	6/7/2022	57	DIC Anions Cations	171
Bloom	9/18/2022	50	Anions TDN Cations	150
Ruckhaus	3/5/2022	54	DIC TDN Anions Cations	216
Bloom	2/18/2023	38	Anions Cations	76

Table 3: *Complete list of archived samples that required additional analysis for dissolved inorganic carbon (DIC), total dissolved nitrogen (TDN), anions and cations. Note that not all data passed the quality check of electrical charge balance and are included in this study.*

Once all the solutes were analyzed, I used Visual Minteq 3.1, for speciation (Gustafson et al., 2011). Because of the importance of DOC in organic rich soils, I included DOC using the Stockholm Humic Model, which is a model used to describe the binding of protons and metals to humic (organic) substances and is integrated in Minteq 3.1 (Gustafsson et al., 2001). From speciation results, I used the electrical charge balance (EB) for quality checking each output and only used data with an EB of zero±10%. Further, I calculated the charge contribution (in milliequivalents = meq) for each solute and retained information on complexation between DOC and other solutes. For some investigations, total solute release (expressed in mg/kg or meq/kg) is more important than concentration. For this I used total liquid content in soil cores (existing water content + amount of treatment solution) and the dry soil mass to calculate the liquid to solid ratio for each core and multiplied this with the respective concentration for each solute. To investigate total release or retention of constituents in the soil core, I calculated the difference as effluent minus inflow. In this situation, positive values would represent constituents being released from the soil core and negative values would represent constituents being absorbed from the soil core.

For comparison between treatments (and in some cases between seasons and landscape positions), I used a t-test to investigate the statistical significance of differences between means. Further, I used a correlation matrix with excels data analysis tool to explore my data for liner correlations. The correlation coefficient (R) ranges between -1 (negative correlation) and 1 (positive correlation) and measures how strongly two variables move together.

3.0 Results

3.1. pH and solute concentrations in O-horizon leachate

Generally, pH values for effluent treated with low pH inflow solutions (2.9 for A and 3.3 for M, respectively, Table 2) are, on average, lower than for soil cores treated with the higher pH of 5 for R (Fig. 4) but vary greatly within each treatment. For example, A treatment effluent averages 2.9 ±1.9, M treatment effluent 3.3 ± 2.1, and R treatment effluent averages 5.1 ± 2.4. The difference between A and M pH is not statistically significant with a p-value of 0.5 while the difference between M and R and the difference between A and R are statistically significant (p-value <0.05). Accordingly, average effluent pH for A and M treatment is generally higher than inflow pH, while average R treatment effluent is very close to inflow pH (Fig. 4).

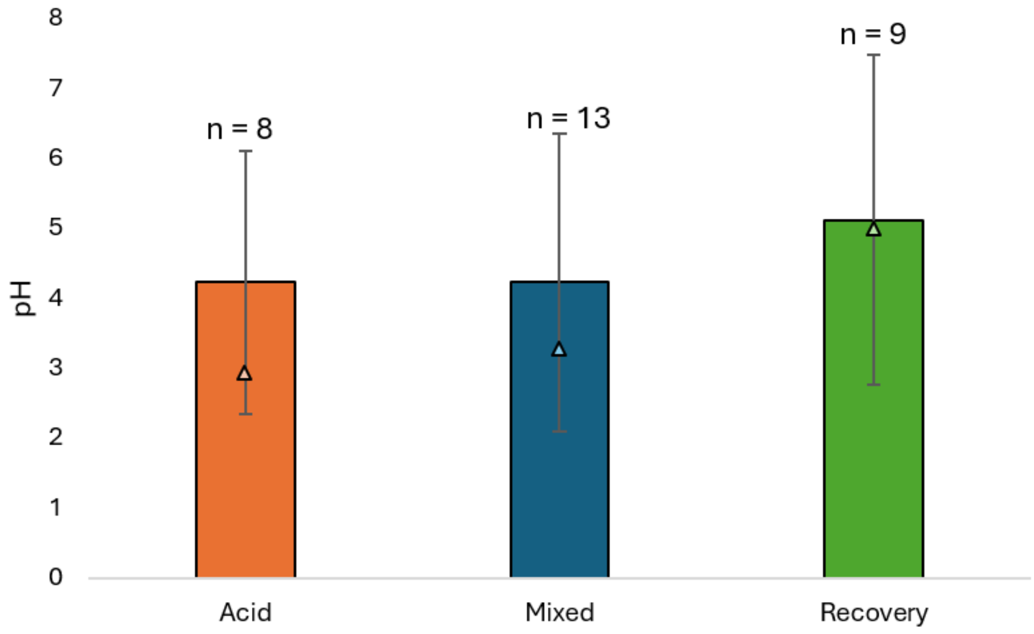


Figure 4: *Average effluent pH by treatment. The triangles represent the pH of the inflow solution.*

When comparing solute concentrations between treatments, concentrations of solutes generally decreased in the order of A, M, R, the exception is a slightly higher average in DOC concentrations for R treatments. Here, R effluent samples had the highest values (9.39 ± 5.14

mg/kg) compared to A (8.74 ± 4.47 mg/kg) and M treatments (8.74 ± 4.62 mg/kg) (Fig. 5). However, the difference between these values is not statistically significant with the p-value for all treatments around 0.3.

When comparing cation release between treatments, concentrations of cations tend to decrease in the order of A, M, and R treatments with the exception of Na which actually decreases by R, M, and A treatments. Anion release follows a similar pattern of decreasing by A, M, and R treatments, especially for Cl which had high levels for M treatments (Fig. 5).

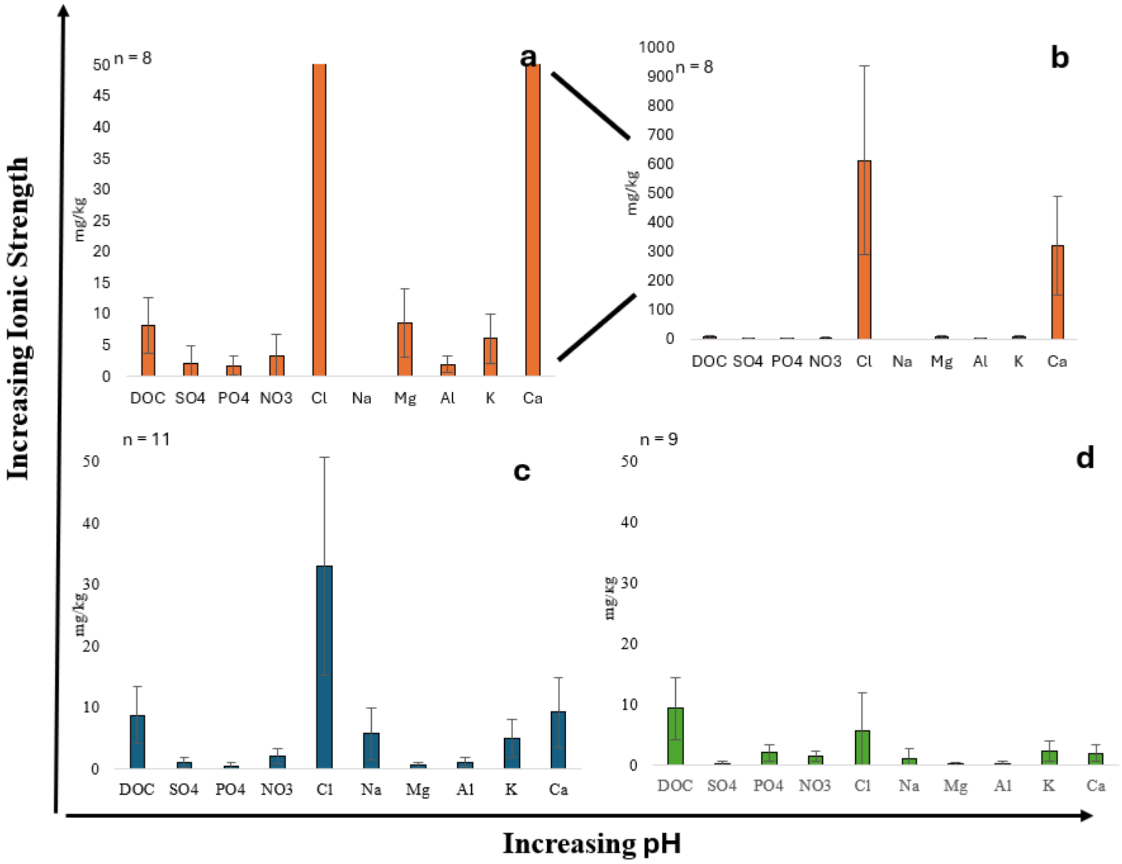


Figure 5: *Average solute concentration in mg/kg for effluent samples for cores treated with acid analogue with same axes ranges as other treatments (a) and full axis range (b), as well as cores treated with mixed analogue (c), and recovery solution (d).*

When expressing effluent concentrations in terms of charge density (meq/kg, Fig. 5), DOC has lowest values in R treatments (0.06 ± 0.04 meq/kg) compared to the A and M treatments (0.07 ± 0.05 meq/kg and 0.09 ± 0.09 meq/k).

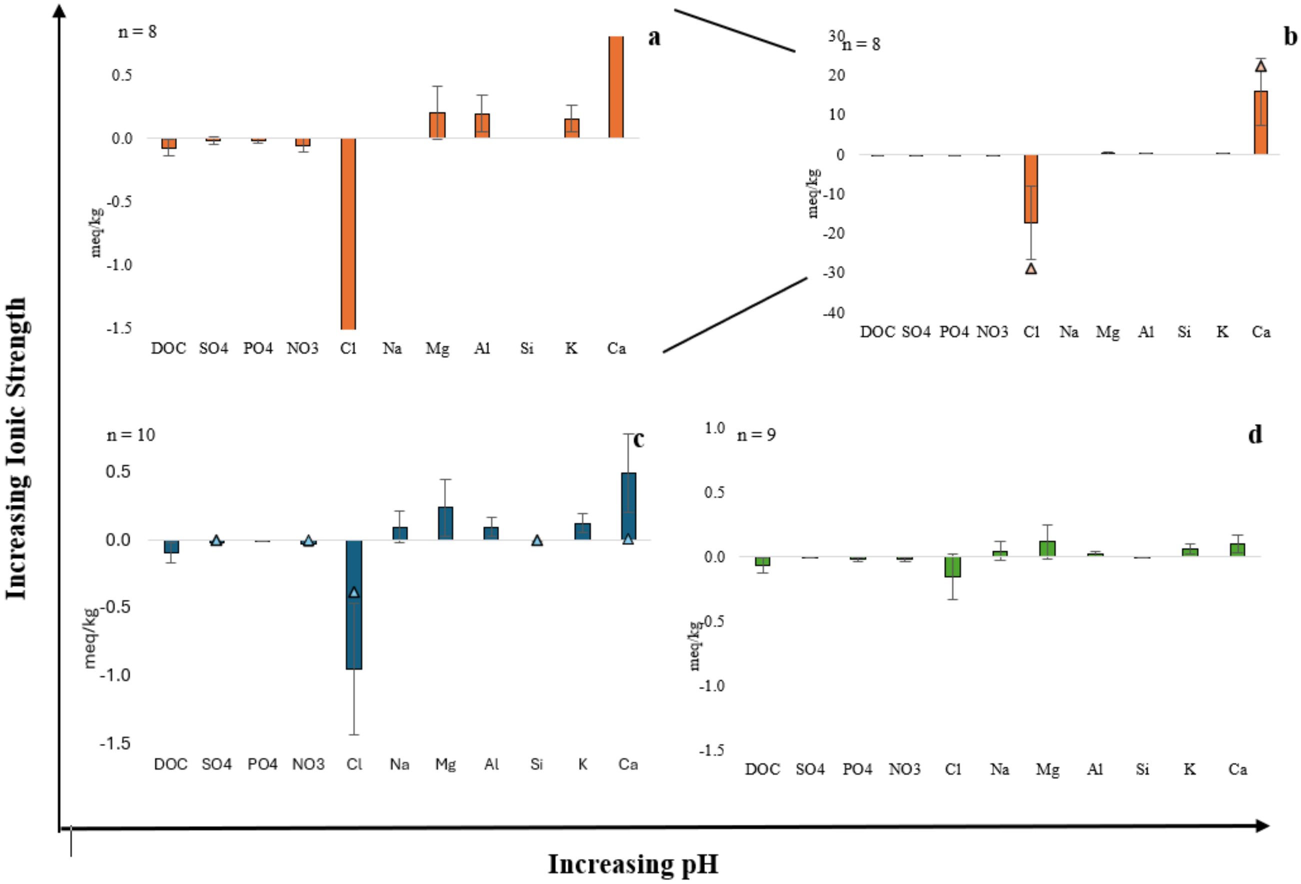


Figure 6: *Average solute concentration in meq/kg for effluent samples for cores treated with acid analogue with same axes ranges as other treatments (a) and full axis range (b), as well as cores treated with mixed analogue (c), and recovery solution (d). Inflow values are indicated with triangles.*

Similarly to concentrations expressed in mg/kg, other effluent solute concentrations in meq/kg vary by treatment as well, but this representation emphasizes the relatively high contribution of Al to positive charges in A treatment (0.19 +- 0.14 meq/kg, Fig. 6a). Negative charges for M treatments are mostly contributed through Cl (-0.94 +- 0.48 meq/kg, Fig. 6c), while positive charges also come from Al (0.096 +- 0.068 meq/kg), and additionally from Na, K (around 0.1 meq/kg) and mostly Ca (average 0.50 +- 0.29 meq/kg, Fig. 6c).

Effluent from R treatments has the lowest concentrations with negative charges coming from DOC and Ca, with around 0.07 meq/kg (p-value = 0.3) and 0.16 meq/kg (p-value = 0.013) (Fig. 6d) and cation charges are contributed through Na, K, Ca, and Mg.

3.2. Release and retention in soil cores: difference between inflow and effluent concentrations.

Another way of comparing the effect of treatment on effluent solute concentration is by displaying the change in concertation (Δ= effluent minus inflow, Fig. 7), where positive values indicate release from soil cores, while negative values indicate retention in the soil core.

The change in concentrations indicates that in the case of A treatment, soil retains Ca and Cl (Δ-7.2 meq and -12.5 meq, respectively, Fig. 4b) while releasing DOC, Al, K and Mg (Δ meq is positive for all, up to 0.57 meq for Mg). Soils treated with M and R do not retain solutes from inflow, but release solutes from soil (Fig. 7). Overall, the M treatments released more anions (Δ0.68+-0.51 meq) and cations (Δ0.4621+-0.473 meq) than the recovery solution that released Δ0.26 +- 0.16 meq of anions and Δ0.23+-0.17 meq of cations.

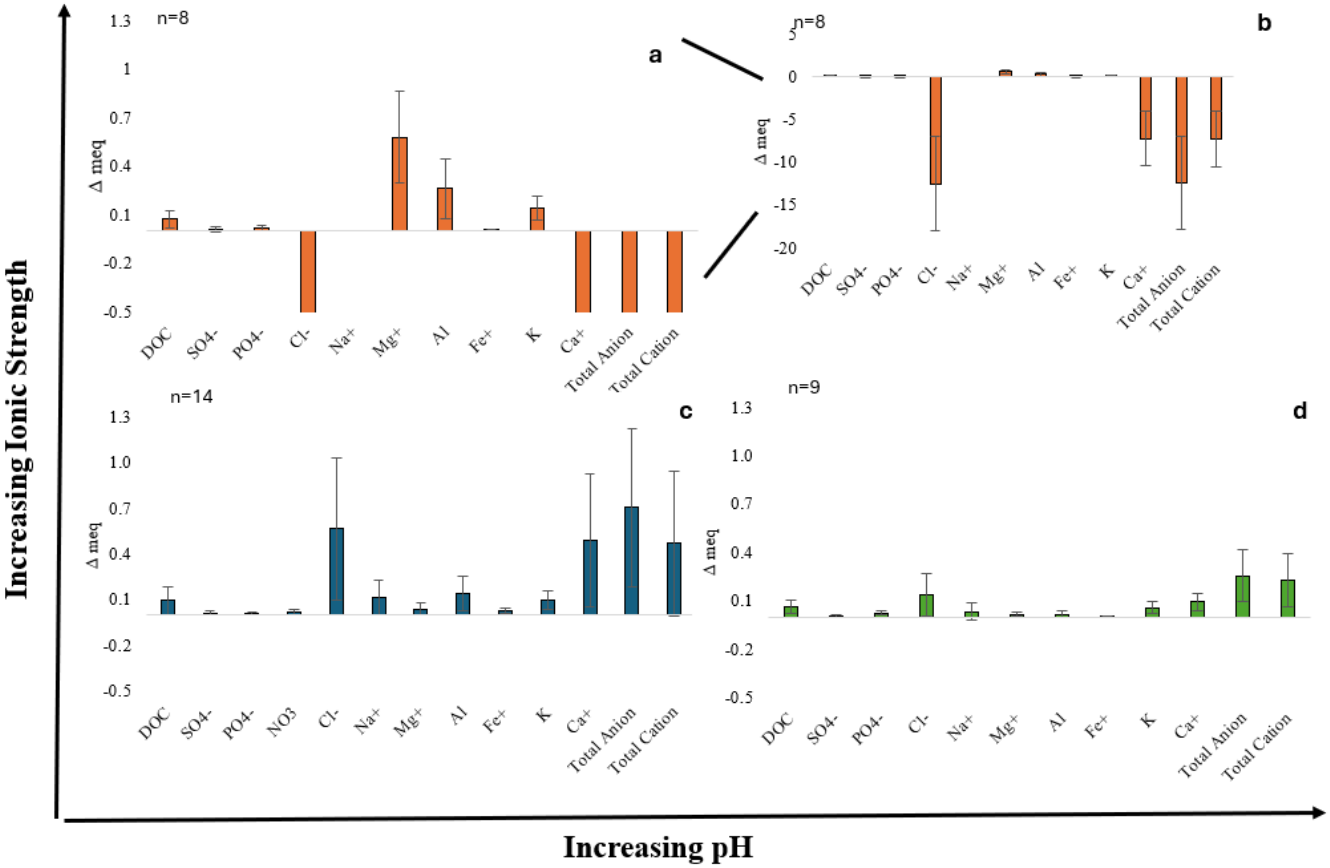


Figure 7: *Change in solute composition (=outflow minus inflow) expressed as Δmeq when treated with acid (a, see b for full scale), mixed (c), or recovery (d) inflow solution. Positive values indicate ion release from the soil core, negative values indicate ion retention in the soil core.*

This effect is conceptualized in Appendix 3, where inflow and effluent solution for all constituents are compared. A treatments released the greatest magnitude of cations and anions, decreasing with the M treatments and R treatments, respectively.

3.3. Seasonality and landscape position

Solute concentrations vary seasonally, however, because the number for samples for winter A treatments and fall M treatments is only 1, a comparison for these treatments is not possible. Samples with R treatment in contrast are available for winter (n=5) and fall (n=4) and generally show a similar pattern for both seasons, with anion charges dominated by DOC and Cl and positive charges dominated by Na, K, Ca, and Mg (Fig. 8). The main difference is that fall samples have a higher concentration of Ca (0.16 ± 0.09 meq/kg), Cl (0.28 ± 0.39 meq/kg), Na (0.09 ± 0.16 meq/kg), and Mg (0.24 ± 0.43 meq/kg) charges than winter samples. There is a large variability in the Cl, Na, and Mg of the fall samples.

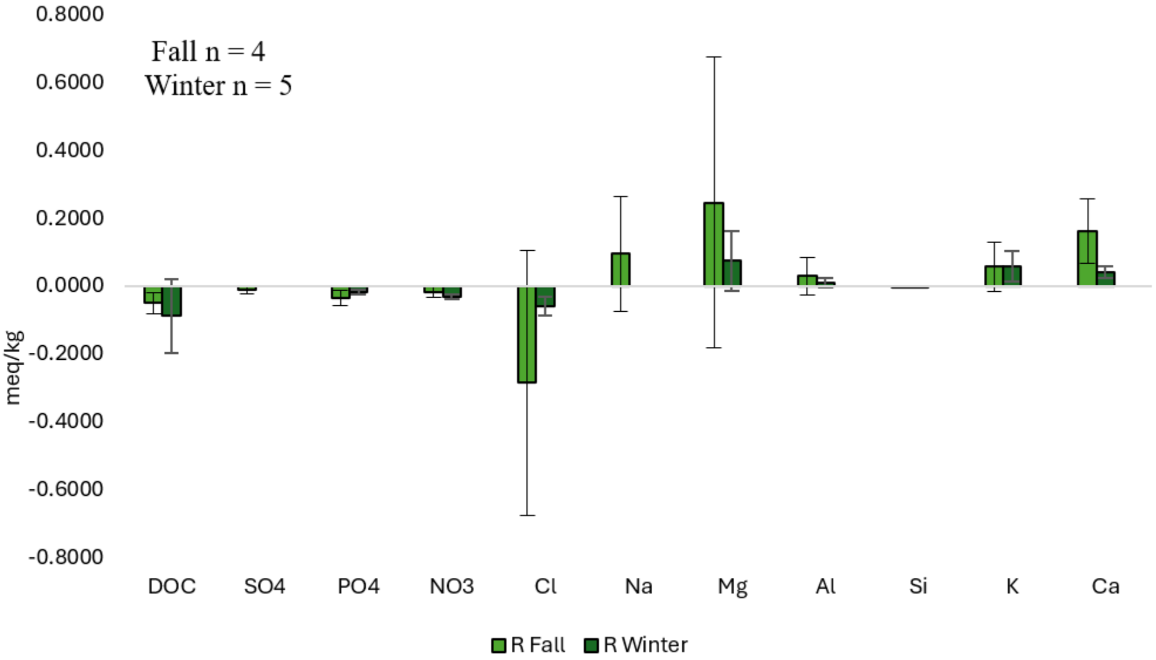


Figure 8: *Average solute concentration in soil leachate from soil cores in milli equivalents (meq) normalized to soil mass and leachate amount when leached with recovery solution.*

For many hillslope samples, the number of samples is low (n=2 for A and R treatments), however, for A treatments, hillslope soil cores contributed significantly more Al (0.26 = meq/kg, p=0.08) and K (0.18 = meq/kg, p=0.047 Fig. 9).

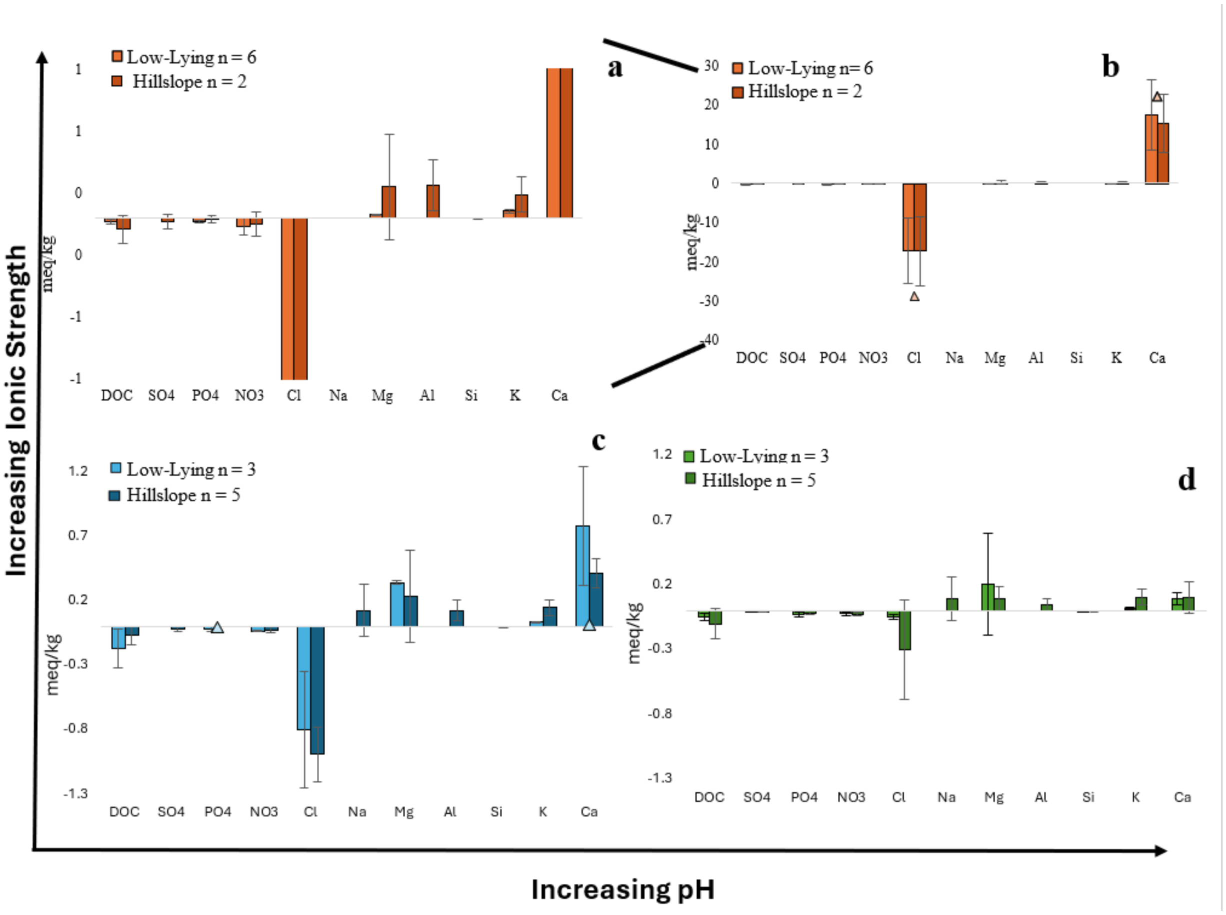


Figure 9: *Average solute concentration in soil leachate from soil cores in milli equivalents (meq) normalized to soil mass and leachate amount by landscape position when leached with acid rain analogue (a, see b for the full axis range), mixed solution (c) and recovery solution (d). Inflow solution concentrations are represented by triangles. If triangles are not present, inflow concentration was 0.*

3.4. DOC complexes

DOC in effluent solution is typically not associated with complexes but is mostly present as free species across seasons and landscape positions, ranging from 67% to 92% for A, M, and R treatment, respectively (Fig. 10).

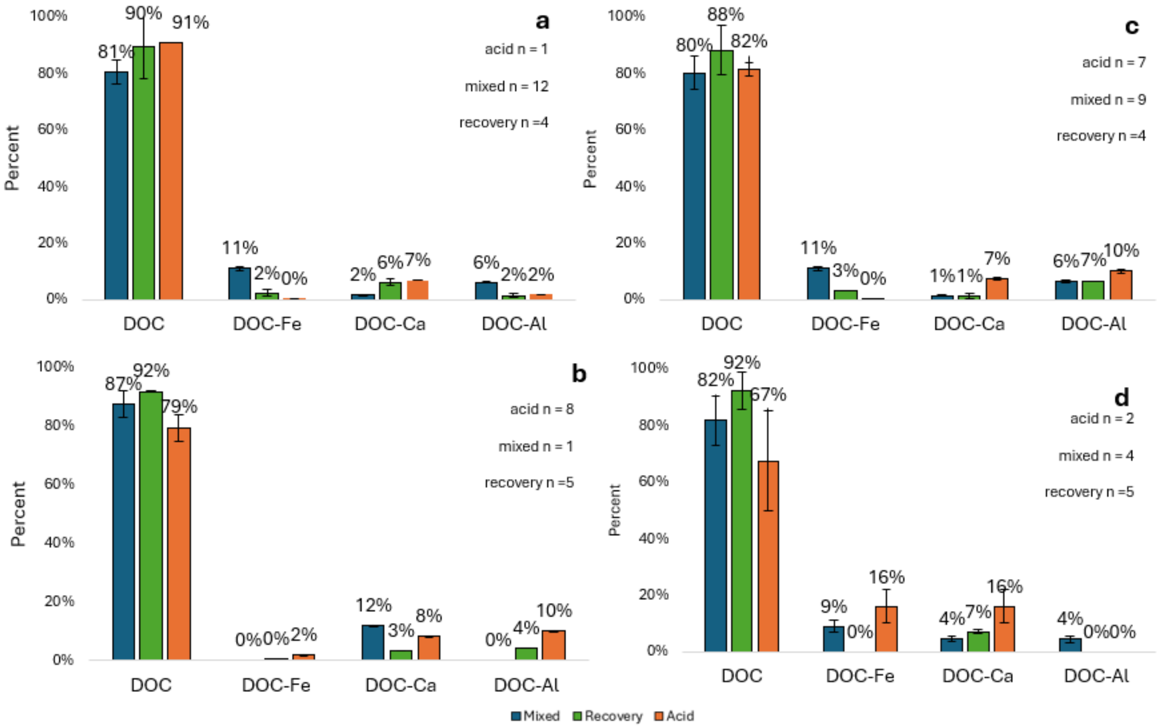
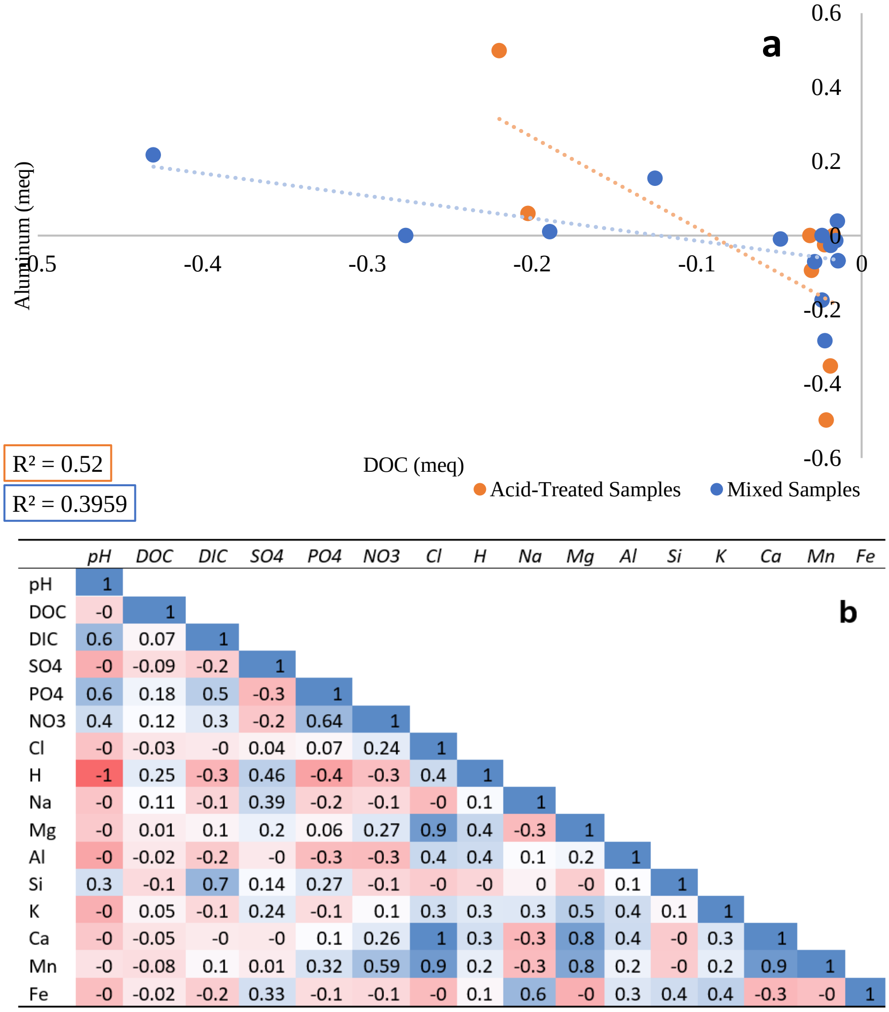


Figure 10: *Percentage of dissolved organic carbon (DOC) complexes with abundances above 1% for fall samples (a) and winter samples (b) as well as hillslope (c) and low-lying landscape positions (d).*

For both winter and fall, free DOC dominated with 80-92% with highest percentage for R in winter and A in the fall (Fig. 10a and b). DOC-Fe complexes had significantly lower percentages in the winter than the fall with percentages close to zero in the winter. In fall, M samples had the highest proportion for DOC-Fe averaging around 11%. DOC-Ca complexes are similarly prevalent in winter and in fall, except for the M samples that had an average around 12% in Winter. Finally, no DOC-Al was present in M sample in the winter, but they were present in fall with the highest percentage, around 6% (Fig. 10).

Samples were also compared by landscape position, either hillslope or low-lying. Like the winter and fall, DOC complexes were by-far the most prevalent in the sample with the highest value at 93% for hillslope recovery samples. DOC-Fe percentages were much lower, with the highest value at 10% for acid low-lying samples and all other DOC-Fe percentages at 1% or lower. DOC-Ca showed similar values with the highest percentage at 10% for acid low-lying samples and 8% for acid hillslope samples. Finally, no DOC-Al was found for low-lying samples, but mixed, recovery, and acid samples had DOC-Al at 2%, 7%, and 11%, respectively (Fig. 10).

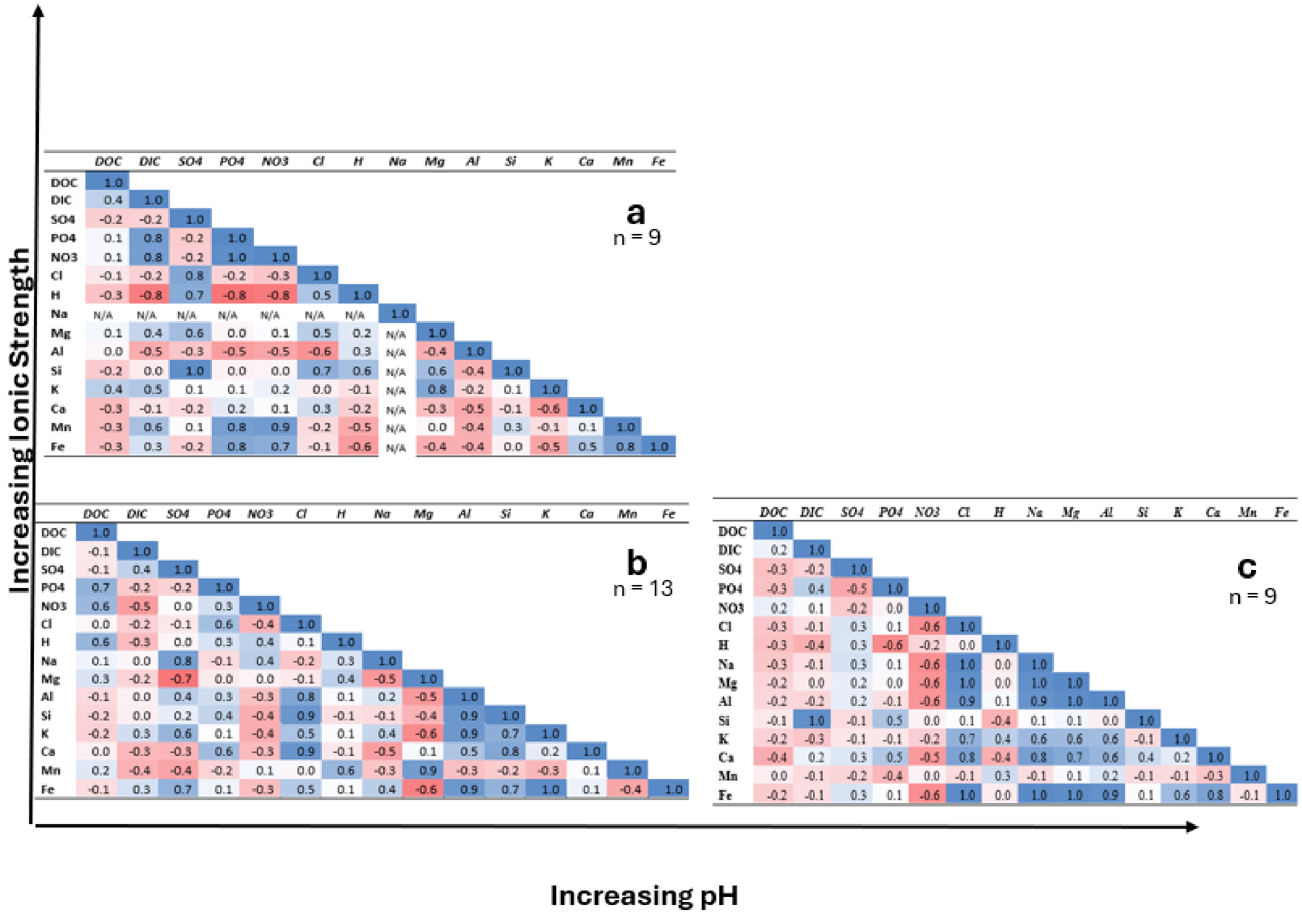
The correlation between DOC and Al was the strongest correlation with DOC at a r^2 value of 0.52 for acid treatment and an r^2 value of 0.39 for recovery treatments. (Fig. 11a). Ca had a strong correlation with Mg, Mn, and Cl with R values nearing 1 (or at 1 for Ca and Cl). Finally, Cl had a strong correlation with Mg, Mn, and Ca with R values close to 1 (or at 1 for Ca).



	pH	DOC	DIC	SO4	PO4	NO3	Cl	H	Na	Mg	Al	Si	K	Ca	Mn	Fe
pH	1															
DOC	-0	1														
DIC	0.6	0.07	1													
SO4	-0	-0.09	-0.2	1												
PO4	0.6	0.18	0.5	-0.3	1											
NO3	0.4	0.12	0.3	-0.2	0.64	1										
Cl	-0	-0.03	-0	0.04	0.07	0.24	1									
H	-1	0.25	-0.3	0.46	-0.4	-0.3	0.4	1								
Na	-0	0.11	-0.1	0.39	-0.2	-0.1	-0	0.1	1							
Mg	-0	0.01	0.1	0.2	0.06	0.27	0.9	0.4	-0.3	1						
Al	-0	-0.02	-0.2	-0	-0.3	-0.3	0.4	0.4	0.1	0.2	1					
Si	0.3	-0.1	0.7	0.14	0.27	-0.1	-0	-0	0	-0	0.1	1				
K	-0	0.05	-0.1	0.24	-0.1	0.1	0.3	0.3	0.3	0.5	0.4	0.1	1			
Ca	-0	-0.05	-0	-0	0.1	0.26	1	0.3	-0.3	0.8	0.4	-0	0.3	1		
Mn	-0	-0.08	0.1	0.01	0.32	0.59	0.9	0.2	-0.3	0.8	0.2	-0	0.2	0.9	1	
Fe	-0	-0.02	-0.2	0.33	-0.1	-0.1	-0	0.1	0.6	-0	0.3	0.4	0.4	-0.3	-0	1

Figure 11: *Example correlation of Al and dissolved organic carbon for acid and mixed treatment on their treatment (a). Linera correlation matrix for all samples, where dark blue colors indicate strong positive correlations and dark red colors represent strong negative correlation.*

When looking at correlations of solutes depending on treatment, solutes released from A treatments do not show strong correlations with DOC, but show strong correlations between H+ and DIC, SO_4 PO_4, and NO_3 (Fig. 12 a). DIC, PO_4, and NO_3 all have a strong negative correlation of r = -0.8 while SO_4 has a high positive correlation of r = 0.7. Solutes released from M treatments have the strongest correlation with DOC with PO_4 and NO_3 having r values around 0.6 and 0.7, respectively. M solutes also have a high correlation of H+ to Mn (r = 0.6), Mg (r = 0.4), and DOC (r = 0.6, Fig. 12 b). R solutes, however, do not show particularly high correlations of DOC or H+ to any solute (Fig. 12c).



	DOC	DIC	SO4	PO4	NO3	Cl	H	Na	Mg	Al	Si	K	Ca	Mn	Fe
DOC	1.0														
DIC	0.4	1.0													
SO4	-0.2	-0.2	1.0												
PO4	0.1	0.8	-0.2	1.0											
NO3	0.1	0.8	-0.2	1.0	1.0										
Cl	-0.1	-0.2	0.8	-0.2	-0.3	1.0									
H	-0.3	-0.8	0.7	-0.8	-0.8	0.5	1.0								
Na	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.0							
Mg	0.1	0.4	0.6	0.0	0.1	0.5	0.2	N/A	1.0						
Al	0.0	-0.5	-0.3	-0.5	-0.5	-0.6	0.3	N/A	-0.4	1.0					
Si	-0.2	0.0	1.0	0.0	0.0	0.7	0.6	N/A	0.6	-0.4	1.0				
K	0.4	0.5	0.1	0.1	0.2	0.0	-0.1	N/A	0.8	-0.2	0.1	1.0			
Ca	-0.3	-0.1	-0.2	0.2	0.1	0.3	-0.2	N/A	-0.3	-0.5	-0.1	-0.6	1.0		
Mn	-0.3	0.6	0.1	0.8	0.9	-0.2	-0.5	N/A	0.0	-0.4	0.3	-0.1	0.1	1.0	
Fe	-0.3	0.3	-0.2	0.8	0.7	-0.1	-0.6	N/A	-0.4	-0.4	0.0	-0.5	0.5	0.8	1.0

	DOC	DIC	SO4	PO4	NO3	Cl	H	Na	Mg	Al	Si	K	Ca	Mn	Fe
DOC	1.0														
DIC	-0.1	1.0													
SO4	-0.1	0.4	1.0												
PO4	0.7	-0.2	-0.2	1.0											
NO3	0.6	-0.5	0.0	0.3	1.0										
Cl	0.0	-0.2	-0.1	0.6	-0.4	1.0									
H	0.6	-0.3	0.0	0.3	0.4	0.1	1.0								
Na	0.1	0.0	0.8	-0.1	0.4	-0.2	0.3	1.0							
Mg	0.3	-0.2	-0.7	0.0	0.0	-0.1	0.4	-0.5	1.0						
Al	-0.1	0.0	0.4	0.3	-0.3	0.8	0.1	0.2	-0.5	1.0					
Si	-0.2	0.0	0.2	0.4	-0.4	0.9	-0.1	-0.1	-0.4	0.9	1.0				
K	-0.2	0.3	0.6	0.1	-0.4	0.5	0.1	0.4	-0.6	0.9	0.7	1.0			
Ca	0.0	-0.3	-0.3	0.6	-0.3	0.9	-0.1	-0.5	0.1	0.5	0.8	0.2	1.0		
Mn	0.2	-0.4	-0.4	-0.2	0.1	0.0	0.6	-0.3	0.9	-0.3	-0.2	-0.3	0.1	1.0	
Fe	-0.1	0.3	0.7	0.1	-0.3	0.5	0.1	0.4	-0.6	0.9	0.7	1.0	0.1	-0.4	1.0

	DOC	DIC	SO4	PO4	NO3	Cl	H	Na	Mg	Al	Si	K	Ca	Mn	Fe
DOC	1.0														
DIC	0.2	1.0													
SO4	-0.3	-0.2	1.0												
PO4	-0.3	0.4	-0.5	1.0											
NO3	0.2	0.1	-0.2	0.0	1.0										
Cl	-0.3	-0.1	0.3	0.1	-0.6	1.0									
H	-0.3	-0.4	0.3	-0.6	-0.2	0.0	1.0								
Na	-0.3	-0.1	0.3	0.1	-0.6	1.0	0.0	1.0							
Mg	-0.2	0.0	0.2	0.0	-0.6	1.0	0.0	1.0	1.0						
Al	-0.2	-0.2	0.2	-0.1	-0.6	0.9	0.1	0.9	1.0	1.0					
Si	-0.1	1.0	-0.1	0.5	0.0	0.1	-0.4	0.1	0.1	0.0	1.0				
K	-0.2	-0.3	-0.1	-0.1	-0.2	0.7	0.4	0.6	0.6	0.6	-0.1	1.0			
Ca	-0.4	0.2	0.3	0.5	-0.5	0.8	-0.4	0.8	0.7	0.6	0.4	0.2	1.0		
Mn	0.0	-0.1	-0.2	-0.4	0.0	-0.1	0.3	-0.1	0.1	0.2	-0.1	-0.1	-0.3	1.0	
Fe	-0.2	-0.1	0.3	0.1	-0.6	1.0	0.0	1.0	1.0	0.9	0.1	0.6	0.8	-0.1	1.0

Figure 12: *Correlation matrix of effluent from acid (a), mixed (b), and recovery (c) treatments. The numbers represent the correlation coefficient R. Dark blue coloring represents a strong positive correlation, the dark red coloring represents a strong negative correlation, and the lighter colors represent a weaker correlation.*

4. Discussion

Past work has been investigating the effect of rain chemistry on soil core leachate as analogue to soil flushing in Northeastern watersheds since 2018 (Cincotta et al., 2019; Adler et al., 2021; Ruckhaus et al., 2023) and contributed to our knowledge on carbon and nutrient release from soil to streams. However, without speciation, it was thus far difficult to investigate specific processes contributing to observed solute release in soils, limiting our capacity for future predictions as rain chemistry continues to shift. My research uses a more complete array of solutes and adds a piece to this puzzle.

4.1. Opening the Blackbox: exploring processes in soil cores

An important objective of my research was to use new results on speciation to identify the role of specific soil geochemical processes such as ion exchange, sorption, and complexation because of changing rainwater composition. Ion exchange is an important and fast process in soils and has been observed as "cation stripping" in many soils in the Northeast that received acid rain (Bristol et al., 2021), causing changes in soil and water quality. Indeed, my analyses of soil core effluent for solutions simulation past conditions (A and M treatments) are consistent with exchange reactions. For example, the decrease in Ca, with concomitant increase in Mg and K for A treatments (Fig. 5a, 6a and 7a) generally agrees with expected affinities for exchange sites in soils, which are higher for Ca than other base cations (Sparks et al., 2024). This means that Ca may have replaced K and Mg at exchange sites, resulting in the release of K and Mg and retention of Ca.

Further, pH is buffered by these soils and effluent pH is significantly higher than inflow pH (Fig. 4), which further emphasizes exchange as protons have a high affinity for soil sorption (Sokolova and Alekseeva et al., 2008). These results are in agreement with other studies in acid impacted areas in general (Cai et al.,2011)

One important caveat of this work is, however, that the composition of A treatment is not a realistic analogue for the chemistry of acid rain, because even though ionic strength and pH are appropriate, acid rain does not contain high levels of Ca. Instead, typical acid rain contains mostly protons SO_4^{2-} and NOx, and NH_3 in high concentrations (Driscoll et al., 2001). Therefore, we cannot over interpret the meaning of results related to Ca in A treatments. However, M treatments do not contain these unrealistic levels of Ca (but similarly low pH), and the fact that the general trend of buffering of pH with release of most cations (Ca, K, Al, Mg, and Na) is present in M treatments as well, indicates indeed that protons exchange base cations in soil cores (Fig. 4 and 5).

While exchange reactions are evident in the data, another important concept is the retention or sorption of solutes in the soils. My results from A treatments indicate that these soils have a large capacity for retaining significant amounts of Ca and Cl without exchanging and releasing other materials (Fig. 7b). In contrast, soils treated with M and R solutions do not significantly retain ions from solution (and ionic strength is so low that there is not much to retain), but release solutes instead (Fig. 7c & d). Even though A solutions are not the ideal rain analogue, the observation of the high retention capacity agrees with many other studies, including related to acid rain (Armfield et al, 2019).

Additionally, Adler et al. (2021) found that soils treated with acid rain analogues had not only larger soil particle size due to increased aggregate stability, but also released less DOC compared to other treatments. This might indicate that some of the retained solutes might be accommodated in more stable aggregate or colloidal associations in this case.

While exchange/sorption are important for species with high charge contributions (e.g. base cations, SO_4, or PO_4), DOC only has a low negative charge (ranging from -0.3 to -0.5, Sparks et al., 2024), and does not contribute to charges significantly (e.g. see low meq values in Fig. 6). Instead, DOC is known to form complexes and to act as a transport vector for metals such as Al and Fe that otherwise would not be mobile at a given pH (Sparks et al., 2024).

My results indicate that Ca, Na, and K increase along with DOC by mass (mg/kg) in M and R treatments (Fig. 5), however, correlation matrices do not indicate linear correlation between DOC and base cations in most cases (Fig. 12). Generally, my speciation results indicate that only a small fraction of DOC (typically below 10%) is complexed (Fig. 10), and because base cations typically occur as free ions anyway, these results are not surprising for base cations. However, complexation with DOC needs to be taken into account for Al and Fe at neutral pH (i.e. recovery simulations), where most (17.7%-75.9%) of Al and Fe are complexed to DOC (Fig. 10).

For the case of DOC and rain composition, previous research has emphasized, that especially low ionic strength in soil solutions (our M and R treatment) can lead to aggregate breakup (Adler, 2021, Cincotta et al., 2019, Ruckhaus et al., 2023), and release of DOC into solutions. Additionally, DOC also has a higher solubility at higher pH, thus R solutions should release higher amounts of DOC. My analyses indeed confirm this trend (e.g. Fig. 5), and results on complexes indicate that DOC (from either aggregate breakup or solubility effects) is largely not complexed in any treatments, but especially R solutions (Fig. 10). This means that even though solutes might have the same source, and could be co-transported, they are not necessarily functionally connected, and are mostly free to react with the environment.

4.2. Landscape position and seasonality: complexity through spatial and temporal variations.

Variations across temporal and spatial sales affects soil processes and nutrient release and add complexity to the results of my analyses. For example, past work has suggested a higher release of organic material from winter samples as solutes accumulate under the snowpack and are available to be flushed during snowmelt (Bristol et al., 2021). Such watershed scale processes increase variability in results that need to be investigated. While previous work Bristol et al., (2021) and Ruckhaus et al. (2023) includes experiments on 4 seasons (Spring, summer, fall and winter), samples for further analyses were only available for soils from Fall and Winter treated with R (Table 1 and 3).

In these results, the generally higher release of DOC and NO_3 from winter soils (Fig. 8) is consistent with results by Ruckhaus et al. (2023), who also found significantly higher release of DOC from winter soils. In this work, the authors suggested that fall plant detritus and over winter processes led to the accumulation of materials and labile DOC.

Indeed, my results show that fall soils contribute to higher concentrations for most solutes other than DOC (Fig. 8), indicating that recovery conditions allow for the mobilization of nutrients from the freshly fallen fall foliage and detritus, which is consistent with other studies that showed the importance of foliage and senescence to nutrient release within the soil (Wu et al., 2004). Senescence is closely related to Ca dynamics, not only because calcium makes up a part of the cellular membrane, but also because it acts as a messenger in the plant, helping it respond to biotic and abiotic stressors (Thor et al., 2019). Indeed, the higher percentage of DOC-Ca complexes (Fig. 8) might indicate that senescence is allowing for the release of Ca into the soil.

Within a given season, landscape position introduces additional variability, and data limitations limit my ability to make inferences to R and M treatments. For M treatments, low-lying soils tend to release more DOC, while for R treatments, most DOC comes from hillslopes (Fig. 9). These results are consistent with Adler (2021) who found that hillslope features treated with R leached significantly more DOC than acidification treatments. However, these results do not align with Bristol et al., (2021) who found that landscape position did not have a large impact on DOC mobility, but it was noted that large precipitation events occurred right before sampling. This variability in results may emphasize the impact of variable weather conditions on the amount and mobility of DOC in the soil.

For both treatments, speciation analyses confirm a high degree of DOC-Ca complexes in low-lying soils (Fig. 10) which is consistent with findings by Cincotta et al. (2019), who found close associations of DOC and Ca in aggregates due to the divalent nature of Ca.

Soil cores from hillslopes show more DOC-Al association, especially in R treatments (Fig. 10). Hillslopes generally have shallower organic horizons with mineral horizons being in proximity. Thus, these results might indicate some presence of weathering related Al that is available for complexation, however the data is not conclusive enough and more samples are necessary for further investigation.

4.3. Implications for current and future stream water quality and limitations of the study

The effect of changes on soil and stream water quality have been investigated for decades, and most work indicates that coupled and complex processes are at play in soil and their corresponding watersheds (Montieth, 2007). Effects of multiple overlapping drivers for solute release are difficult to disentangle, making predictions on future water quality difficult (Ruckhaus et al., 2023).

My research has similar limitations, however, the following should be taken into consideration:

Even though the use of the A rain analogues has its limitation, it still allows for insights on the soil and its processes, especially the high retention capacity of SRRW soils for solutes (here Ca and Cl, but likely for other materials as well, Fig. 7). In combination with the release into R and M treatments, these results agree with a significant legacy effect, i.e. these soils will likely continue to release accumulated materials from acid deposition until a new equilibrium is reached (Armfield et al., 2019).

While effluent of cores with acid treatment release on average slightly less DOC (Fig. 5), the difference to R and M treatments is less pronounced than in studies by Adler and Cincotta (Adler et al., 2021 and Cincotta et al., 2019). However, my results suggest that the observed increased release of DOC in response to recovery conditions (Ruckhaus et al., 2023; Adler et al., 2021; Cincotta et al., 2019) is mostly free DOC that does not contain a significant proportion of organo-mineral complexes (Fig 10). Thus, while the science community is concerned about water browning (Kritzberg et. al., 2020), at least my results indicate that metal mobilization is less of a concern.

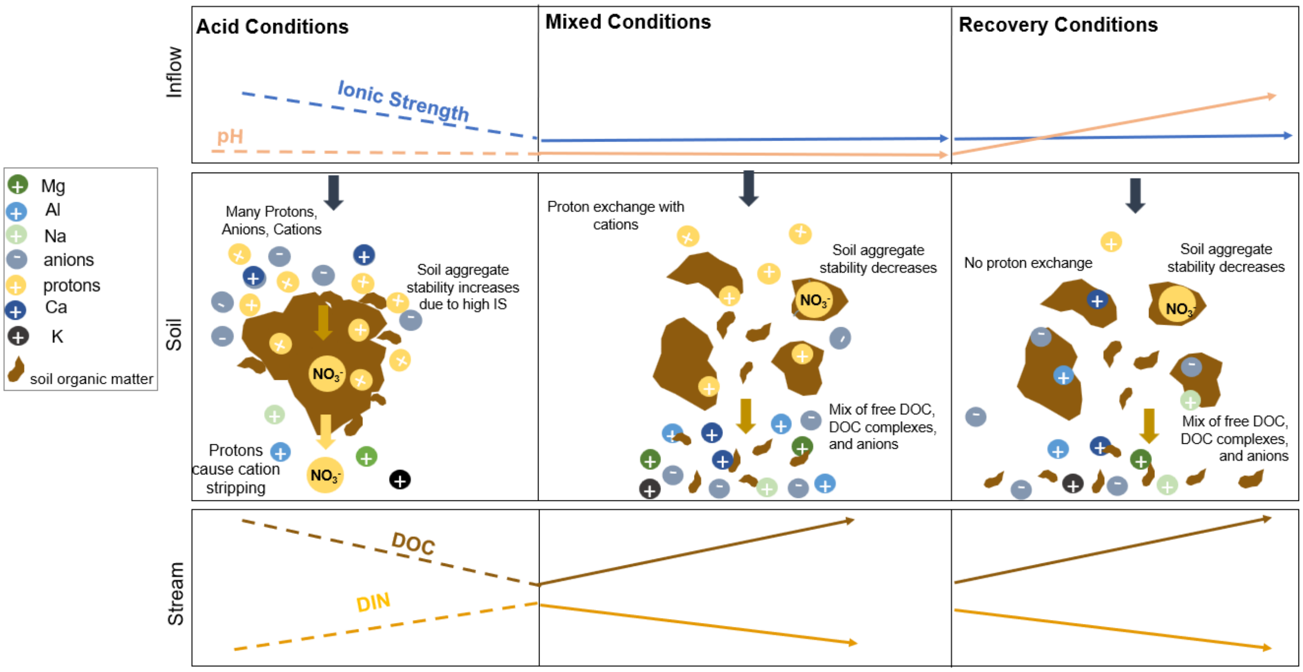


Figure 13: Conceptual model modified from Ruckhaus et al. (2023), showing the release of cations and anions in response to different treatments.

My results allowed me to adjust the existing conceptual model with these additional data. The M conditions show the primary driver of cation release to be proton exchange, resulting in a large release of cations into the stream. However, in R conditions, the primary driver of cation release is due to aggregate breakup, instead of proton exchange. This results in a slightly smaller, but still release of aggregates into the stream water.

My study has some limitations, one of which is the aforementioned challenge with the A solution. An additional limitation is the availability of data and conditions under which samples were collected. For example, much of the experimental process and sample collection was not performed with solute speciation and geochemical modelling as an objective but focused on carbon and nitrogen dynamics alone. This resulted in sample and data gaps across seasons and landscape positions, that did not produce statistically significant results, and more data is necessary.

Finally, these samples were collected in a singular, specialized watershed in Vermont, there are limitations to what systems this can be applied too. While learning about nutrient dynamics is incredibly useful to understanding large scale change, this work may not be applicable to all systems and environments.

5.0 Conclusions

Nutrient release from soils is driven by a complicated mixture of conditions. Precipitation, bedrock composition, seasonality, and landscape position are just a few that have shaped the framing of this study. While release of solutes during recovery conditions seem to show mostly aggregate breakup as leading to nutrient release, mixed conditions show evidence for a mixture of aggregate breakup and proton exchange being responsible for the large release of solutes.

However, there is still much to be explored within this topic. In general, this research should be continued to better understand these processes with the goal of understanding the full suite of inflow and effluent analytes. Furthermore, a stronger understanding of the connection between precipitation volume and, in particular, DOC, release may help guide scientific understanding of the future of Northeastern streams as precipitation increases due to climate change.

6.0 Acknowledgements

I am incredibly thankful to Manya Ruckhaus, Dina Cordes, Bren Cable, and Niara Hicks who braved days in the field to collect samples with me and trained me in the lab. I also want to thank all the graduate students in the Perdrial lab who came before me, they not only collected many of the samples that I used, but also laid the groundwork for my study. I am very grateful to the UVM Agricultural and Environmental Testing Lab who processed my IC samples, allowing me access to a complete dataset. I am also grateful to my friends, family, and partner, who listened to me talk endlessly about a topic that I never fully explained. Finally, I cannot express how thankful I am to Dr. Julia Perdrial, who has provided me with endless support, advice, and kindness over the years I have spent in her lab. She has not only provided me with the skills, knowledge, and guidance needed to tackle this project, but also has been an amazing roll model for a young woman in science.

7.0 References

Adler, T., Underwood, K. L., Rizzo, D. M., Harpold, A., Sterle, G., Li, L., Wen, H., Stinson, L., Bristol, C., Stewart, B., Perdrial, N., & Perdrial, J. N. (2021). Drivers of Dissolved Organic Carbon Mobilization from Forested Headwater Catchments: A Multi-Scaled Approach. *Frontiers in Biogeoscience*.

Armfield, J., Perdrial, J., Gagnon, A., Ehrenkranz, J., Perdrial, N., Cincotta, M., Ross, D., Shanley, J., Underwood, K., & Ryan, P. (2019, March 5). Does Stream Water Composition at Sleepers River in Vermont Reflect Dynamic Changes in Soils During Recovery From Acidification? *Frontiers in Earth Science*, *6*. https://doi.org/10.3389/feart.2018.00246

Bristol, C. (2021). Assessing the impact of changes in acid deposition on dissolved organic carbon mobilization from two forested headwater catchments: A combined lab and field study. University of Vermont.

Cai, M., Johnson, A. M., Schwartz, J. S., Moore, S. E., & Kulp, M. A. (2011). Response of soil water chemistry to simulated changes in acid deposition in the Great Smoky Mountains. *Journal of Environmental Engineering*, *137*(7), 617–628. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000354

Cincotta, M. M., Perdrial, J. N., Shavitz, A., Libenson, A., Landsman-Gerjoi, M., Perdrial, N., Armfield, J., Adler, T., & Shanley, J. B. (2019). Soil Aggregates as a Source of Dissolved Organic Carbon to Streams: An Experimental Study on the Effect of Solution Chemistry on Water Extractable Carbon. *Frontiers in Environmental Science*, *7*. https://doi.org/10.3389/fenvs.2019.00172

De Vries, W., Posch, M., & Kämäri, J. (1989). Simulation of the long-term soil response to acid deposition in various buffer ranges. Water, Air, and Soil Pollution, 48, 349–390. https://doi.org/10.1007/BF00283336

Gustafson, J.P., 2011, Visual Minteq ver. 3.1. https://vminteq.lwr.kth.se/

Gustafsson, J. P. (2001). Modeling the Acid–Base Properties and Metal Complexation of Humic Substances with the Stockholm Humic Model. Journal of Colloid and Interface Science, 244(1), 102-112. https://doi.org/10.1006/jcis.2001.7871

Kritzberg, E.S., Hasselquist, E.M., Škerlep, M. *et al.* Browning of freshwaters: Consequences to ecosystem services, underlying drivers, and potential mitigation measures. *Ambio* **49**, 375–390 (2020). https://doi.org/10.1007/s13280-019-01227-5

Likens, G. E., Bormann, F. H., & Johnson, N. (1972). Environment: Acid rain. *Environment, 14,* 33-40.

Matzner, E., & Murach, D. (1995). Soil changes induced by air pollutant deposition and their implication for forests in central Europe. *Water, Air, and Soil Pollution, 85,* 63–76. https://doi.org/10.1007/BF00483689

Monteith, D. T., Stoddard, J. L., Evans, C. D., de Wit, H. A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B. L., Jeffries, D. S., Vuorenmaa, J., Keller, B., Kopácek, J., & Vesely, J. (2007). Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, *450*(7169), 537–540. https://doi.org/10.1038/nature06316

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., & Bergamaschi, B. A. (2012). Taking the pulse of snowmelt: In situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry, 108*, 183–198. doi:10.1007/s10533-011-9589-8.

Ruckhaus, M., Perdrial, J., Seybold, E., Underwood, K., Shanley, J., Li, L., Stewart, B., & Kincaid, D. (2023). Disentangling the separate and intersecting pathways of carbon and nitrogen response to overlapping drivers. *Frontiers in Water*.

Runkel, R. L., Crawford, C. G., and Cohn, T. A. (2004). “Load estimator (LOADEST): a FORTRAN program for estimating constituent loads in streams and rivers,” in USGS Techniques and Methods Book 4, Chapter A5, eds S. M. Westenbroek, J. Doherty, J. F. Walker, and V. A. Kelson (Reston, VA: U.S. Geological Survey).

Skjelkvåle, B. L., Stoddard, J. L., Jeffries, D. S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D. T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., & Worsztynowicz, A. (2001). Regional scale evidence for improvements in surface water chemistry 1990-2001.

Shanley, J. B., et al. (2022). Hydrology and biogeochemistry datasets from Sleepers River Research Watershed, Danville, Vermont, USA. *Hydrological Processes, 36*(2), e14495. doi:10.1002/hyp.14495.

Shanley, J., et al. (2014, November 27). Water's Way at Sleepers River watershed - revisiting flow generation in a post-glacial landscape, Vermont USA. *Hydrological Processes, 29*, 2447-2459. Wiley Online Library. doi:10.1002/hyp.10407.

Shanley, J. B., et al. (2002). Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA. *Hydrological Processes, 16*(3), 589-609. USGS

Publications Warehouse. doi:10.1002/hyp.312. Retrieved from https://pubs.usgs.gov/publication/70024760.

Shanley, J. B. (2000). Sleepers River, Vermont: A Water, Energy, and Biogeochemical Budgets Program site. U.S. Geological Survey. https://doi.org/10.3133/fs16699

Sebestyen, S. D., et al. (2009). Using high-frequency sampling to detect effects of atmospheric pollutants on stream chemistry. USGS Publications Warehouse. Retrieved from https://pubs.usgs.gov/publication/70176164.

Sokolova, T., & Alekseeva, S. (2008). Adsorption of sulfate ions by soils (A Review). Eurasian Soil Science, 41, 140-148. https://doi.org/10.1134/S106422930802004X

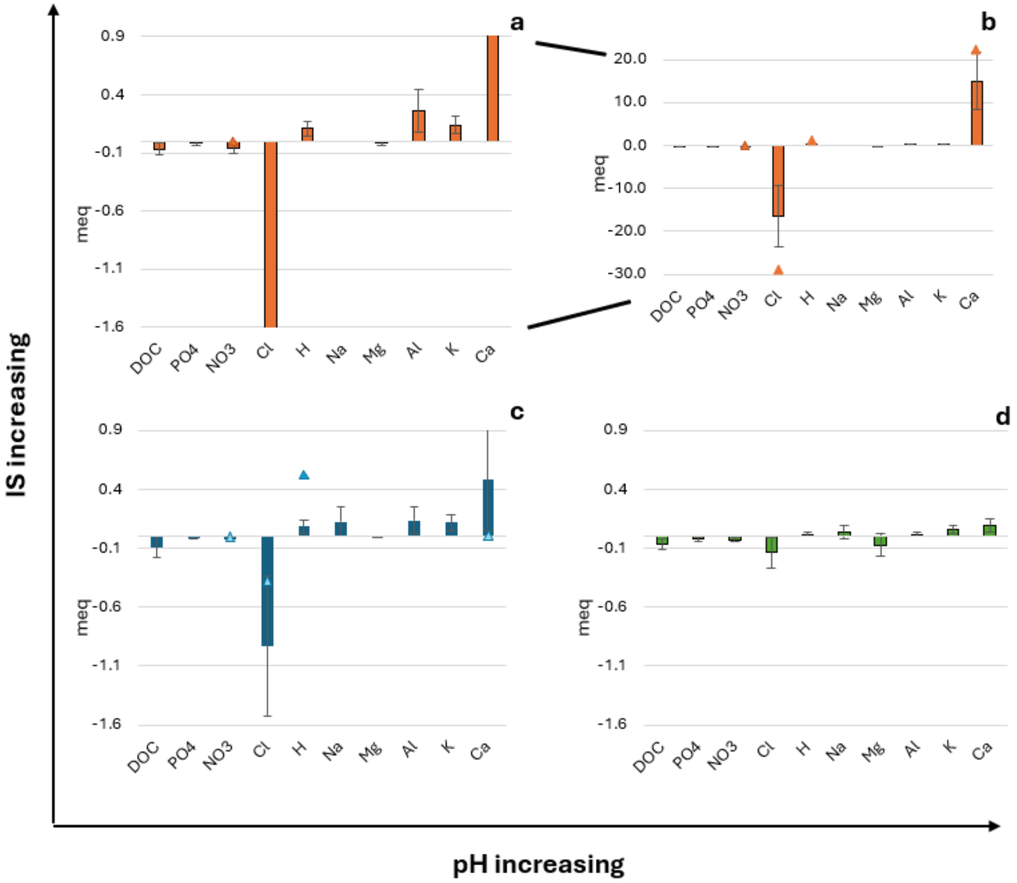
Sparks, D. L., et al. (2024). Ion exchange processes. In *Environmental Soil Chemistry* (pp. 283–302). Academic Press, an Imprint of Elsevier.

Sposito, G. (2016). *The Chemistry of Soils*. doi:10.1093/oso/9780190630881.001.0001.

Thor, K. (2019). Calcium-Nutrient and Messenger. Frontiers in Plant Science, 10, 440. https://doi.org/10.3389/fpls.2019.00440.

Wu, C., Wang, Z., & Fan, Z. (2004). “Significance of senescence study on tree roots and its advances”. Ying Yong Sheng Tai Xue Bao, 15(7), 1276-1280. PMID: 15506114.

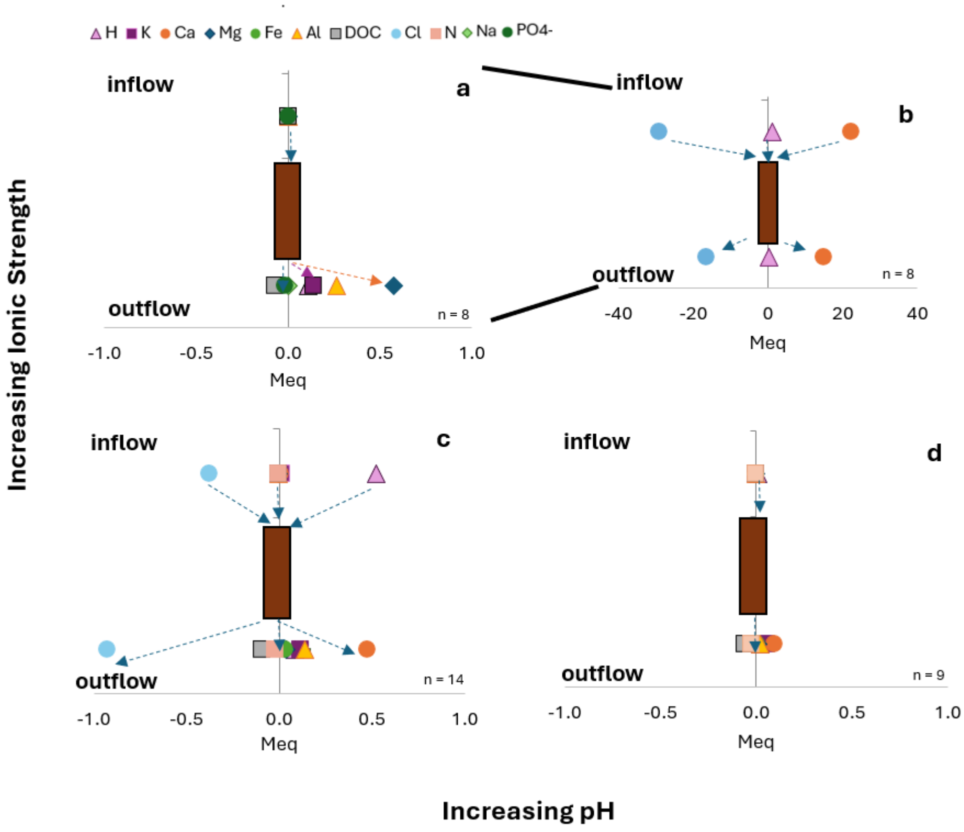
8.0 Appendix:



Appendix 1: Average solute concentration in meq for effluent samples for cores treated with acid analogue with same axes ranges as other treatments (a) and full axis range (b), as well as cores treated with mixed analogue (c), and recovery solution (d). Inflow values are indicated with triangles.

Sample Number	Treatment	Landscape Position (as defined by original researcher)	Landscape Position (as defined in this study)	Season
531	Acid	Hillslope	Hillslope	Fall
371	Acid	Hillslope	Hillslope	Winter
374	Acid	Hillslope	Hillslope	Winter
401	Acid	Hillslope	Hillslope	Winter
410	Acid	Hillslope	Hillslope	Winter
512	Acid	Hillslope	Hillslope	Winter
497	Acid	Riparian	Low-lying	Winter
519	Acid	Riparian	Low-lying	Winter
195	Mixed	Linear Convex	Hillslope	Fall
166	Mixed	Linear Convex	Hillslope	Fall
28	Mixed	Concave Convex	Low-lying	Fall
68	Mixed	Concave Convex	Low-lying	Fall
525	Mixed	Hillslope	Hillslope	Fall
552	Mixed	Hillslope	Hillslope	Fall
22	Mixed	Linear Convex	Hillslope	Fall
139	Mixed	Linear Convex	Hillslope	Fall
167	Mixed	Linear Convex	Hillslope	Fall
193	Mixed	Linear Convex	Hillslope	Fall
194	Mixed	Linear Convex	Hillslope	Fall
560	Mixed	Riparian	Low-lying	Fall
420	Mixed	Riparian	Low-lying	Winter
372	Recovery	Hillslope	Hillslope	Winter
405	Recovery	Hillslope	Hillslope	Winter
510	Recovery	Hillslope	Hillslope	Winter
164	Recovery	Linear Convex	Hillslope	Fall
541	Recovery	Riparian	Low-lying	Fall
568	Recovery	Riparian	Low-lying	Fall
569	Recovery	Riparian	Low-lying	Fall
397	Recovery	Riparian	Low-lying	Winter
419	Recovery	Riparian	Low-lying	Winter

***Appendix 2**: Table showing every sample used for data analysis in this study, the treatment, landscape position (both original and defined for this study), and season.*



Appendix 3: *Average solute concentrations in milli equivalents (meq) when leached to acid (a, see b for full axis range), mixed (c), and recovery rain analogues (d).*