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Mechanisms of carbon and nutrient release from acid impacted soils: Investigating competitive sorption and aggregate dispersion

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COLLEGE OF ARTS
AND SCIENCES

Geology Department

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Abstract

Dissolved organic carbon (DOC) and associated nutrients are of critical importance to natural biogeochemical cycling. In recent decades, increased amounts of DOC have been observed in Northern Hemisphere surface waters recovering from acid deposition. Such increases in DOC can have significant implications for the productivity of surface waters, yet the mechanisms controlling DOC release are yet to be understood. As soils are one of the primary sources of DOC in surface waters, this study attempts to identify mechanisms controlling DOC release from soils in the context of changing deposition chemistry.

Two experiments were designed to investigate two soil-related processes that can lead to the liberation of DOC and nutrients from riparian zone (RZ) and hillslope (HS) soils. First RZ soils collected from the Sleepers River USGS research station were used to conduct a flow through experiment using simulated sulfate impacted and non-impacted soils. In this experiment DOC solution was infiltrated to test the effect of competitive sorption between DOC and sulfate, however this effect could not be confirmed. In a second experiment, a batch approach was used to test the effect of pH and ionic strength (IS) on aggregate dispersion in both RZ and HS soils. Results reveal that IS, not pH, strongly controlled DOC release in all soils presumably by impacting soil aggregation. Release of DOC and P was similar for RZ vs. HS soils, however N release was significantly higher from RZ soils, indicating soil type and landscape position matter for nutrient release. Together these results indicate that changes in deposition IS more than pH or sulfate additions play a major role in the release of DOC and nutrients from soils at Sleepers River, likely due to the connection between IS and soil aggregate dispersion.

<u>Introduction</u>

The Importance of Dissolved Organic Carbon

Dissolved organic carbon (DOC) plays a crucial role in our environment. DOC influences productivity within aquatic ecosystems, serves as a critical transport vessel for nutrients and metals, and greatly influences photic depth of surface waters via light attenuation (Gergel et al. 1999; Porcal et al. 2009; Thrane et al. 2014). DOC is also the most labile fraction of carbon (C), which means it is readily processed by microorganisms that can transfer DOC into the greenhouse gas CO_2 (Gougoulias et al. 2014; Sondergaard & Middelboe 1995).

Freshwater ecosystem nutrient condition is often a function of DOC and its nitrogen (N) and phosphorus (P) constituents (Gerson et al. 2016). DOC in surface waters can be either autochthonous (produced on site) or allochthonous (produced elsewhere and transported); hence DOC has important implications for nutrient flow into and within aquatic systems. Because DOC serves as a source of energy at low trophic levels, the success of all aquatic organisms, including microorganisms and macrophages, ultimately depends on it.

The relationship between DOC and acidity additionally plays an important role in surface water nutrient availability. DOC compounds contain weak acid constituents, and can consequently impact surface water acidity (Perdue et al. 1980; Porcal et al. 2009) by releasing H^+ ions in high ambient pH (>5.5), or acting as a buffer in more acidic waters (Clair et al. 2011). Surface water acidity determines the solubility and consequent bioavailability of N and P (USGS 2016).

Not only do vital elements such as N and P co-vary with DOC, metals can also be complexed with organic matter compounds, including dissolved complexes (Gergel et al. 1999;

Porcal et al. 2009). Such organo-metal associations can keep metals in solution and mobile under conditions where the metal itself would not be stable.

Furthermore, light attenuation throughout the water column is governed in large part by chromatic (or colored) dissolved organic matter (CDOM), the light absorbing component of DOC (Thrane et al. 2014), particularly in lakes of low to moderate productivity (Houser 2006). Light attenuation determines photic depth, greatly influencing the vertical range of photosynthetic organisms throughout the water column. Due to the great importance of DOC in surface waters, it is monitored carefully across the globe.

Changes in DOC and Nutrient Constituents

Increased concentrations of DOC have been observed throughout Northern Hemisphere surface waters over the past three decades (Evans et al. 2006; Worrall & Burt 2004). This was exemplified by the UK Acid Waters Monitoring Network, which reported a 91% increase in DOC concentrations in UK lakes and streams between 1988 and 2006 (Evans et al. 2006).

Given the ability of DOC to act as a nutrient transport vessel, increases in allochthonous DOC offer the potential to provide limiting nutrient additions to aquatic ecosystems, a contribution that is of particular importance for P (Gerson et al. 2016). This connection might lead to increased productivity such as surface water algal blooms, however the outcome of nutrient additions is highly dependent on the previous environmental conditions. For example, increases in CDOM concentrations associated with allochthonous DOC may reduce the range and level of productivity due to increased light attenuation by CDOM making less light available to photosynthetic organisms. Multiple studies have shown that there is a threshold at which light attenuation by DOC limits productivity (Seekell et al. 2015a; Seekell et al. 2015b). A clear,

oligotrophic northern lake, for example, may be expected to have increased its primary productivity in the previous few decades, while a eutrophic, low elevation lake may have done the opposite as any increase in CDOM would limit photosynthesis (Seekell et al. 2015a).

The strong connection between DOC, nutrients, and differing responses of productivity to variations in both lends additional urgency to identifying drivers for DOC increases. Specifically which drivers are prominently responsible for DOC increases is highly debated in the scientific community, but recovery from acidification is put forth as one potential driver (Clark et al. 2010; Seifert-Monson et al. 2014).

Acid Deposition, Recovery, and DOC

Acid deposition was a result of previously high levels of atmospheric N oxides and sulfur dioxide (SO_2), which led to the formation of strong acids. As one of the chief acidifying agents of anthropogenic acid deposition, sulfuric acid (H_2SO_4) supplies protons (low pH) and sulfate (SO_4^{2-}) ions to soils, substantially increasing acidity and ionic strength (IS). In decades following the clean air act and subsequent legislation, the amount of SO_2 and resulting H_2SO_4 deposition has decreased substantially, with the result of decreased inputs of hydrogen ions and anion concentrations (Driscoll et al. 2001).

Reduction of sulfur loading is one of the most significant atmospheric chemistry changes to have occurred in recent decades, and is widely correlated with increases in DOC concentrations (Evans et al. 2006; Porcal et al. 2009). Across hundreds of study sites, changes in anion composition of atmospheric deposition have been shown to relate to DOC increases, particularly in regions where acid deposition has declined significantly (Porcal et al. 2009). Decreases in acidity, sulfate concentration, and IS are all suggested as drivers for increased DOC

release associated with recovery from acid deposition (Porcal et al. 2009), although research is currently mostly limited to correlations. It is difficult to decipher between the influence of acidity and ionic components however as the changes occurred together (Clark et al. 2006), and it is difficult to determine what specific mechanisms exist that may explain the relationship between deposition recovery and DOC changes. To date, it is unclear if decreases in acidification are related mechanistically to increases in DOC.

This study seeks to experimentally isolate the influence of sulfate additions, pH changes, and IS changes on DOC release from soils, and offers a mechanistic link to explain how these changes may control DOC release.

Potential Mechanistic Links between Recovery and DOC

1) **Mechanism 1: Competitive Sorption**

Competitive sorption is the process where two chemical species compete for the same sorption sites on a surface. The prolonged deposition of sulfate onto acid impacted soils might have saturated sorption sites on the surface of soil particles with sulfate. Both sulfate and DOC share an affinity for binding sites on soil particles and aggregates, consequently putting them in competition (Eimers et al. 2008; Gobran et al. 1998; Kerr & Eimers 2012).

During recovery from acid deposition, sulfate concentrations decreased and soil binding sites occupied by sulfate may have gradually been filled with binding DOC. While Kerr and Eimers (2012) discuss that this could theoretically increase DOC adsorption in soils, consequently decreasing flux into surface water, this would not be a long-term effect: as soils gradually recovered from acid deposition, sulfate would have quickly been replaced by DOC. With higher capacity for C stores within the soil, hydrological events may be able to create

higher DOC flux into surface waters at concentrations too high to be processed quickly in the environment, resulting in overall higher surface DOC. The connection between DOC and soil sulfate content has already been tested in a field study using sulfate amendments on peatland soils (Seifert-Monson et al. 2014), as well as in a laboratory analysis utilizing a sequential soil horizon leaching technique (Gobran et al. 1998).

2) **Mechanism 2: Aggregation and Dispersion**

Aggregation occurs when soil particles are able to bind to one another, creating "aggregate" structures within soils. Aggregates contain a variety of components, including minerals, clays, microorganisms, and other organic material (Nimmo 2005; Totsche et al. 2018), where ratios depend on the soil composition (Fig. 1). This aggregation process is capable of physically surrounding and protecting organic matter, preventing its dissolution and release.
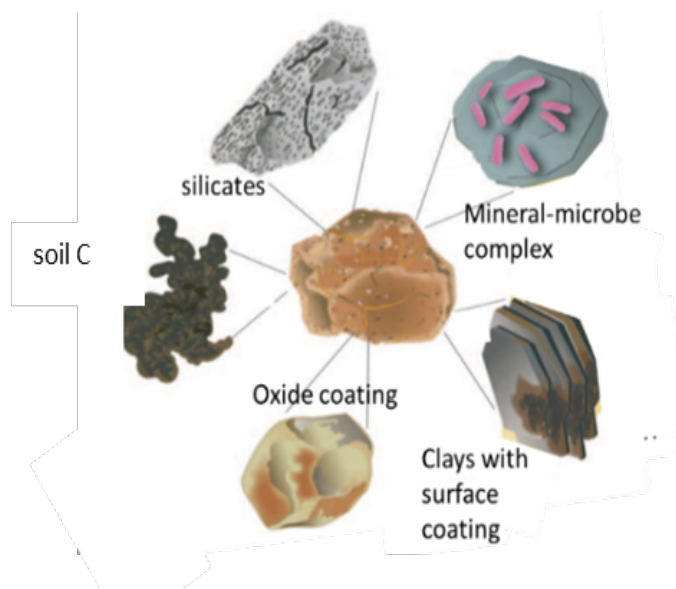

Figure 1: Components of a soil aggregate. *Modified from (Chorover et al. 2007).*

Cation bridging

Cation bridging contributes to aggregation by providing a means of connecting outwardly negatively charged soil constituents (often clay particles or bacteria) that would otherwise repel one another, and occurs in the presence of cations in soil solution. These binding forces are strongest with polyvalent cations (e.g. Ca^{2+}), which can bond to multiple separate particles with outward negative charges (Wuddivira & Camps-Roach 2007). Solutions containing higher concentrations of cations consequently promote aggregation in soils.

Aggregation is not however solely dependent on polyvalent cations. The presence of monovalent cations, specifically hydrogen ions in the context of acidity, can increase aggregation. Organic acid compounds found in soils (humic and fulvic acids) typically aggregate, contributing to microaggregation. The compounds are significantly influenced by pH, and as pH increases the hydrogen bonding and Vander Waals activity between them weakens, reducing the strength of these forces (Schnitzer & Khan 1978). High pH in soils can also increase negative charge on organic molecules, which in turn reduces complexation by contributing to negative charge dispersal (Rengasamy & Olsson 1991). Consequently, aggregation should dominate at low pH, effectively sequestering DOC, while dispersion should dominate at high pH, releasing DOC into leached soil solution.

Ionic strength effects on the diffuse double layer

In addition to cation dominated interactions, soil particle aggregation is also influenced by the overall IS of the surrounding solution. At the surface of outward-facing negatively charged clay particles, two "layers" of distinct charge patterns can be identified, forming a "diffuse double layer" (Fig. 2). Cations in soil solution are attracted to a negatively charged clay particle, forming a layer of tightly grouped cations (Moore & Reynolds 1997). The close

grouping of these positive charges consequently attracts anions or negative poles of aqueous compounds, which in turn attracts a less tightly grouped layer of cations. This pattern continues, dissipating charge into a "diffuse" layer, together with the tightly grouped layer forming the diffuse double layer (Fig. 2, Moore & Reynolds 1997).

In soil solution of higher IS, the attractive forces within the diffuse double layer are stronger and compress the diffuse double layer until Van der Waals attractive forces overwhelm the repulsive charge forces, and aggregation occurs (Derjaguin & Landau 1941; Verwey 1947). Hence, soil solutions of high IS should have a greater potential to protect organic matter by fostering aggregation.
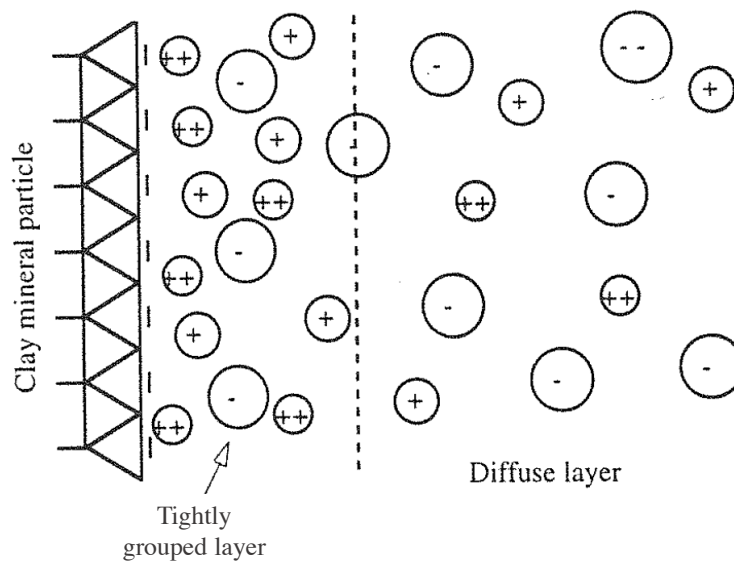

Figure 2: Visualization of the diffuse double layer. *Modified* from (Moore & Reynolds 1997).

The Role of Landscape Position in DOC and Nutrient Dynamics

Differences in landscape position can have large impacts on the type and amount of soil C and resulting DOC (Parry et al. 2015; Sadro et al. 2012). In many cases, the watershed landscape explains much of DOC and total organic carbon characteristics in surface waters, especially where aquatic systems are dependent on allochthonous DOC over autochthonous DOC (Gergel et al. 1999).

The influence of landscape is particularly relevant when considering riparian zone (RZ) compared with hillslope (HS) DOC release from soils into surface waters, as most stream water DOC is sourced either from HS soils or near-stream RZ soils. As RZ soils border surface waters, water travels through or over RZ soils immediately prior to entering streams or lakes. Therefore, RZ soils have a great influence on DOC discharge variations (Vidon et al. 2010; Winterdahl et al. 2011). HS soils on the other hand make up a larger area through which water flows prior to reaching the near stream RZ.

Landscape slope also greatly influences the amount of DOC exported from soils to surface waters. HS soils typically have shallower organic rich horizons and shorter residence times for water flow (Frost et al. 2006; Parry et al. 2015), which consequently decrease the quantity of DOC extracted from these soils. Hence, slope has been shown to be negatively correlated with DOC and P export (Frost et al. 2006; Parry et al. 2015; Sadro et al. 2012). Additionally, catchments with steeper slopes tend to have more organo-mineral soil, which is better able to retain DOC during rainfall (Parry et al. 2015). As a result of each of these factors, HS soils tend to contribute smaller quantities of DOC to surface waters when compared with RZ soils (Dick et al. 2015).

Hypotheses

Considering competitive sorption and aggregation as potential mechanisms impacting changes in DOC, and considering the potential modulating effect of soils from different landscape positions, a set of experiments was designed to examine the influences of recovery on DOC leaching from soils. These experiments used two main approaches, a flow through analog to test competitive sorption (DOC vs. sulfate) and a set of batch experiments where solution chemistry (pH and IS) was altered. Changes in DOC quantity were monitored for soils from HS and RZ locations.

It was hypothesized that 1) sulfate saturated soils have a greater affinity for DOC sorption than sulfate free control soils (competitive sorption effect), 2) low pH soil solution fosters aggregate-driven C retention in soils more than neutral pH soils (cation bridging effect), 3) high IS soil solution promotes aggregate formation and C retention in soils (IS effect on the diffuse double layer), and lastly that 4) DOC and associated nutrient release will vary with landscape position and will be greatest for RZ soils and lower for HS soils.

Materials and Methods

Field Site

The USGS Sleepers River watershed was selected for the project because this area has been studied intensively over several decades (Shanley et al. 2015). It is located in northeastern Vermont and consists of a set of nested catchments (Fig. 3b) including the well-studied sub-watershed W-9 (Fig. 3a). Soils are established mostly over glacial till on slopes of varying degrees (3-16%). Typical for many forested systems in the NE, the site has been heavily impacted by acid deposition.
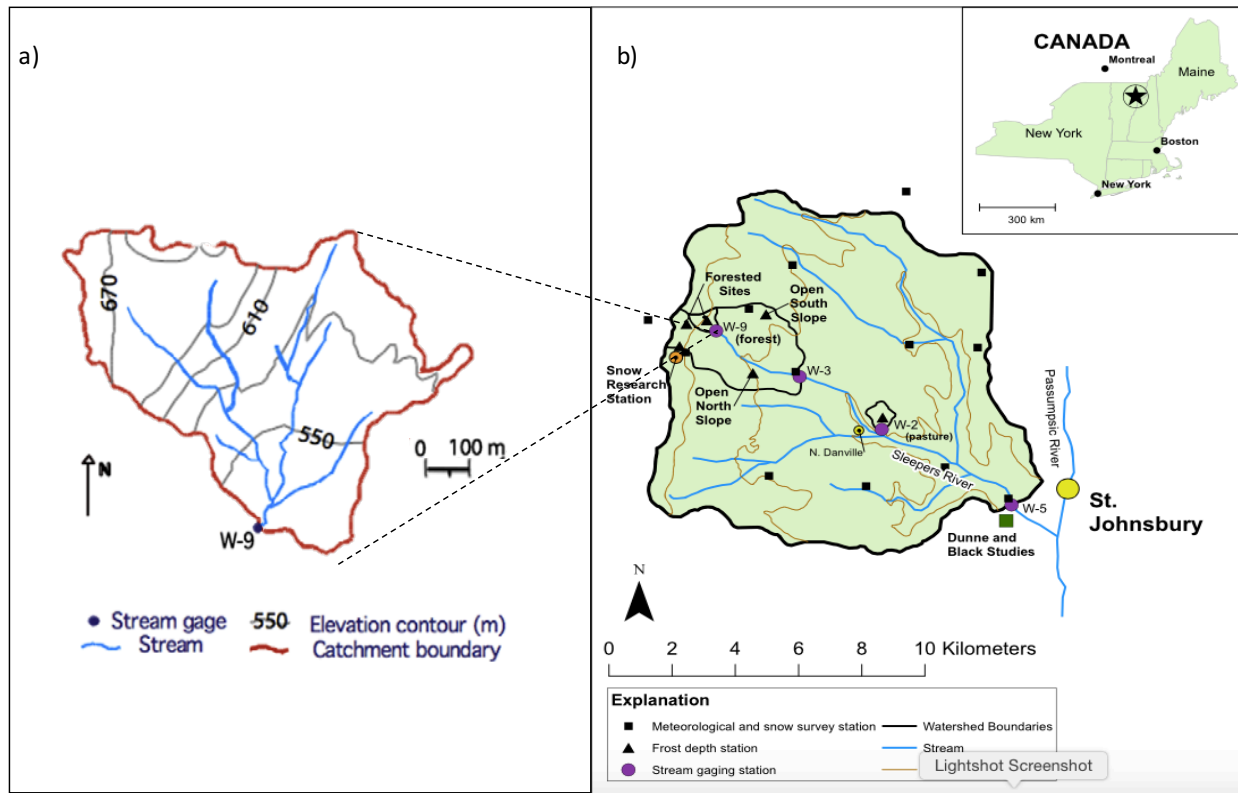
Figure 3: a) The W-9 catchment area within b) Sleepers River Watershed. *Modified from (Mayer et al. 2010; Shanley et al. 2015)*

Sample Collection

All samples were collected from W-9, which exhibits variably steep hillslopes of well drained inceptisols and flat RZs bordering the perennial streams with thick histosols. In some areas the RZs resemble waterlogged wetlands. Samples were taken from both HS and RZ soils to represent the typical pedologic units in this experiments. Three stream-flow transects were sampled in the Summer of 2016 by graduate students in the UVM Geology Department.

Two subsamples from these soils were used for the first set of experiments (flow through). Both samples were collected from the top 15cm of RZ soils along a stream bank using

a handheld bucket auger during the Summer of 2016. The samples were stored in plastic bags until the implementation of this project in February of 2017.

For the second set of experiments (aqueous soil extracts) samples were collected from each of the three transects in the Fall of 2017 from both RZ and HS soils. At each transect, three RZ and three HS soils were collected, amounting to a total of eighteen soils, nine RZ and nine HS. Effort was made to avoid decaying trees, heavily rooted areas, and other sources of excess organic matter that were likely to include disproportionate quantities of organic matter not reflective of the ambient soil composition. Collection was conducted again using handheld bucket augers, and consisted of a depth range of 0-15cm. Immediately after collection, the 15cm soil column was mixed for homogeneity, and transported in sealed plastic bags in order to maintain field moisture.

Experimental Setup

1) **Flow Through Leachate**

In order to simulate percolation of soil solution, a flow through experiment was designed in which simulated solution was fed through soil "packets" using suction (Fig. 4). These soil packets consisted of small quantities (~0.5g) of dried and sieved (2mm) soil contained between two 0.7μm combusted glass fiber filters. Each of the two soils were placed in duplicate onto the center of the bottom glass fiber filter, leaving approximately 2mm from the edge uncovered (Fig. 4). The second glass fiber filter was then placed on top of the soil sample to form the soil packet, and the filter pod was secured around it.

The primary function of the upper glass fiber filter was to prevent the addition of particles from the infiltrating solution and to disperse added solution across the surface area of

the soil packet. The bottom glass fiber filter was used to filter particulates from the soil out of the effluent solution.

To test the effect of sulfate on the soil's ability to take up DOC, soil was first saturated with sulfate (0.07 mM Na_2SO_4, stage 1) and then leached with leaf litter leachate as a DOC source (stage 2). In both stages influent and effluent solution were collected for analyses. In order to test for the effect of competitive sorption it was necessary to examine DOC sorption in comparable non-sulfate impacted soils. Hence corresponding blank experiments were prepared where soil was treated with Millipore double deionized (DDI) water instead of Na_2SO_4 solution (stage 1).

Each infiltration consisted of the application of 15ml of experimental solution onto the top filter and used a small amount of suction to aid percolation. In order to allow for interaction time between the soil and infiltrating solution, the vacuum was turned off for one minute after the first three drops of solution escaped through the bottom of the soil packet into the lower chamber of the filter pod. After one minute the vacuum was reapplied until all solution had flowed through the soil packet. This step was repeated 5 times for a total of 75ml of infiltration.

The leaf litter leachate was prepared from dried leaves collected from a typical northern hardwood forest at BREE EPSCoR sites in northern VT. All leaves were allowed to air dry under ambient laboratory conditions. 5 grams of leaf litter were added to 210 grams of DDI water and shaken on a reciprocal shaker at 180rpm for 20 minutes, a technique modified from Schreeg et al. (2012). Following shaking, leachate was filtered through a 0.7µm glass fiber filter, diluted with DDI water, and stored in glass amber bottles until experimentation.

Figure 4: Filter setup for sulfate flow through experiment. An open top soil packet is seen resting on the bottom section (effluent collection) of a Nalgene filter pod.

2) Batch Experimental Approach with Aqueous Soil Extracts

Aqueous soil extract experimental setup

Field moist soils were used for the batch experimental approach. In order to enable use of fixed solid/solution ratios in all experiments existing soil moisture was taken into account. For this, gravimetric soil water was determined on a subset of all soils.

To prepare each soil for aqueous extraction, approximately 7g of each field moist soil was massed out in duplicate, one per treatment. Treatment solution was added respectively to reach a 1:5 soil to solution mass ratio, factoring in soil water already contained within the sample. Samples were shaken on low (180rpm) for one hour, and immediately afterward were centrifuged for thirty minutes at 3000rpm to remove solid components. Vacuum filtration through 0.45μm glass fiber filter was used to remove any remaining particulate matter, preparing the solution for analysis of dissolved components. Solution was transferred to and stored in amber glass bottles in order to prevent any light driven modifications in DOC.

Treatment solutions

In order to test the effect of varying pH and IS on DOC mobilization from soils, a series of batch experiments was performed where soils were extracted with solutions of varying composition. To test the effect of pH on DOC release, two solutions of differing pH were used, sodium sulfate (Na_2SO_4) and H_2SO_4. Consistent IS was maintained by preparing the Na_2SO_4 at an IS of 0.005 mol/L and the H_2SO_4 at pH 4, brought to IS 0.005 mol/L with Na_2SO_4. For this set of batch experiments, one RZ and one HS soil was chosen from each of the three transects, amounting to six experimental soils, 3 RZ soils and 3 HS soils.

In order to test for IS effects, solutions of varying IS were prepared. DDI water served as the low IS solution, while a H_2SO_4 - Na_2SO_4 (pH 4, IS 0.005 mol/L) solution served as the higher IS solution. The choice of H_2SO_4 in the preparation of this solution was intended to be representative of natural precipitation chemistry during historical acid rain events. For this set of batch experiments all eighteen soils were included, amounting to eighteen experimental soils, 9 RZ soils and 9 HS soils.

Sample and Data Analysis

A Shimadzu Total Organic C Analyzer was used to measure DOC and total N for all samples within 48 hours of sample preparation. Sulfate was measured via ion chromatography in the UVM Ross Lab. Total P was measured via Inductively Coupled Plasma (ICP) analysis.

One way, paired t-tests were conducted for acidity and IS analyses, while one-way equal variance t-tests were used to examine landscape driven differences. In order to understand the influences on nutrient concentrations, multiple regression was utilized to examine influences on N and P. Microsoft Excel was used for the production of graphical display. The Excel data

analysis extension was used for multiple regression model construction. An alpha value of 0.05 was used to assess significance throughout the study.

<u>Results</u>

Flow Through Experiment on Competitive Sorption

Sulfate saturation resulted in no major changes in DOC sorption vs. release in flow through experiments using soil packets. Compared to the average influent solution for soil replicate 1 (12.55$\pm$0.38 mg/L), DOC concentration was lower in the first stepwise effluent solution for both the sulfate treated soil (11.16$\pm$0.30 mg/L) and the sulfate free, DDI treated control (11.16$\pm$0.95 mg/L, Fig. 5). Concentrations stabilized at influent levels after the first infiltration step (Fig. 5). For replicate 2, the first stepwise effluent for the sulfate treated soils (9.36$\pm$0.31 mg/L) and the DDI treated control (8.85$\pm$0.86 mg/L) were at influent DOC concentration (9.32$\pm$0.52 mg/L), with effluent concentrations ranging slightly above influent levels after the first infiltration step (Fig. 5).

Cumulative sorption of influent derived DOC (calculated as the cumulative sum of the difference between influent and effluent DOC) revealed no significant difference between sulfate saturated and control soil samples. However, significant differences were seen between the two soil samples (Fig. 6). Leachate of soil replicate 1 showed positive cumulative C sorption (i.e. DOC was effectively attenuated by this soil) while soil replicate 2 showed negative cumulative sorption (Fig. 6). For this soil (replicate 2) DOC effluent was, with the exception of the first infiltration step, consistently higher than effluent DOC concentration.

Effluent sulfate concentrations where highest for the sulfate treated soils in the first infiltration step (0.05$\pm$0.01 mg/L) but approached influent leaf litter leachate sulfate

concentrations thereafter (Fig. 7). Sulfate concentrations remained at influent levels for both control soils, with the exception of a small peak at the second effluent solution from replicate 1 (0.26 mg/L, Fig. 7).

Figure 5: Effluent DOC concentration for all five stepwise infiltrations of both soils (replicates 1 and 2) by leaf litter leachate. Both sulfate impacted (Na_2SO_4 infiltrated) and control (DDI infiltrated) soils are included. Concentrations were not normalized to the amount of soil because DOC is present in leaf litter leachate.

Figure 6: Cumulative sorption of DOC to RZ soil for sulfate impacted (Na_2SO_4) and control (DDI) samples. Measurements are taken after each of five stepwise flow-through infiltrations.
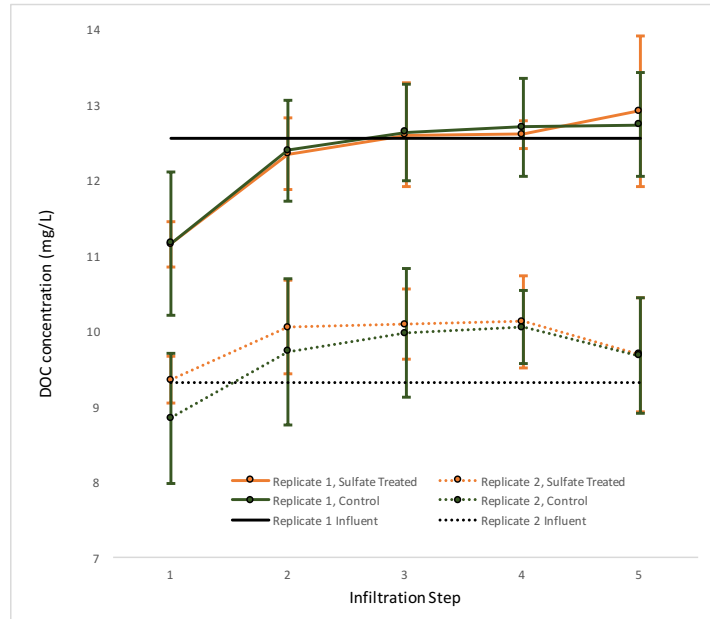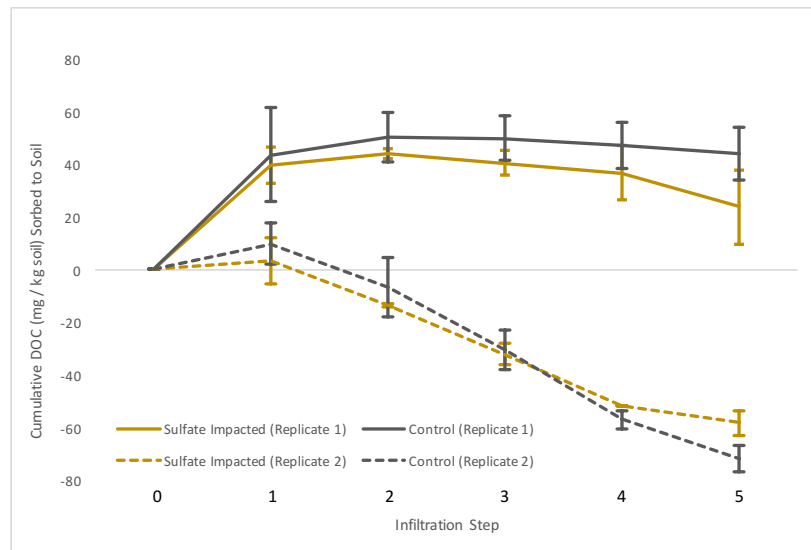
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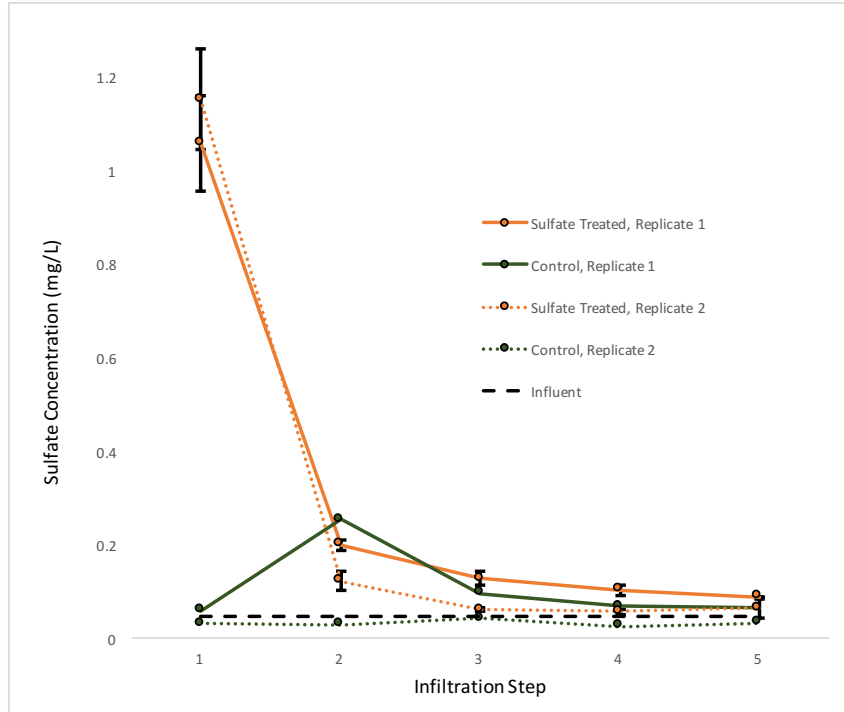
Figure 7: Effluent sulfate concentration for all five stepwise infiltrations of both soils (replicates 1 and 2) by leaf litter leachate. Both sulfate impacted (Na_2SO_4 infiltrated) and control (DDI infiltrated) soils are included (note that no duplicates were included for the control).

Extraction - Aggregation vs. Dispersion in Batch Experiments

In order to investigate the effect that pH and IS have on soil leachate DOC and nutrient concentrations, aqueous soil extracts of all eighteen samples were analyzed for DOC, N, and P.

1) **pH**

pH (4 vs. 7) did not have a large effect on the amount of DOC leached from soils. Average extracted DOC was slightly lower for pH 7 extract (45.26 ± 29.79 mg/kg) compared with pH 4 extract (49.05 ± 30.84 mg/kg). The large variability in extractable DOC between samples is apparent in large error bars (Fig. 8), and is primarily a result of one sample with starkly higher DOC concentrations than the other samples. Regardless, a paired t-test revealed significance ($p=0.046$) for one tailed differences in DOC between treatments.
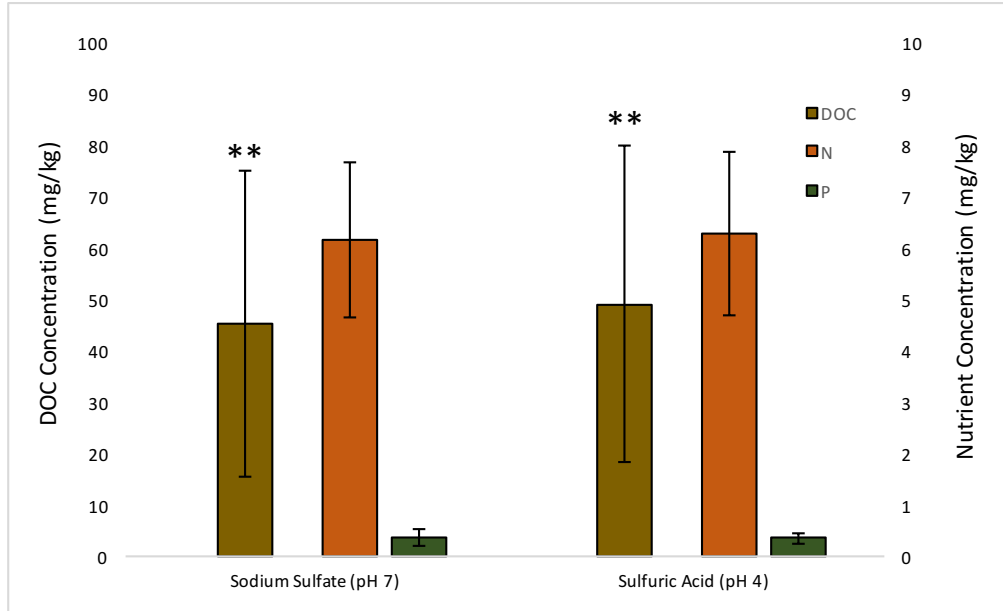
Figure 8: Average extracted DOC, N, and P concentrations by neutral (pH=7) and acidic (pH=4) solution [n=12 (DOC, N), n=10 (P)]. Stars indicate significant difference at a 0.05 alpha level.

Variability of N in soil extract was less pronounced and the difference between pH 7 (6.17±1.51 mg/kg) and pH 4 (6.29±1.60 mg/kg) in average N content was not significant (p=0.419). Similarly, the difference between average P content in pH 7 (0.37±0.17 mg/kg) and pH 4 (0.36±0.10 mg/kg) was found not to be significant (p=0.460) for one tailed differences between treatments. Due to inaccuracies in ICP analysis, only 10 of 12 total effluent samples were used in P data calculations. Excluded sample data is included in the appendix.

2) Ionic Strength

Variations in IS impacted DOC release more than nutrient (N, P) release. Variability in DOC was lower compared to the pH treatment. Mean DOC content in low IS extract (IS = 0.000 mol/L, 33.37±13.30 mg/kg) was significantly higher than the high IS extract (IS=0.005 mol/L, 23.25±9.75 mg/kg, p<0.00001, Fig 9a).
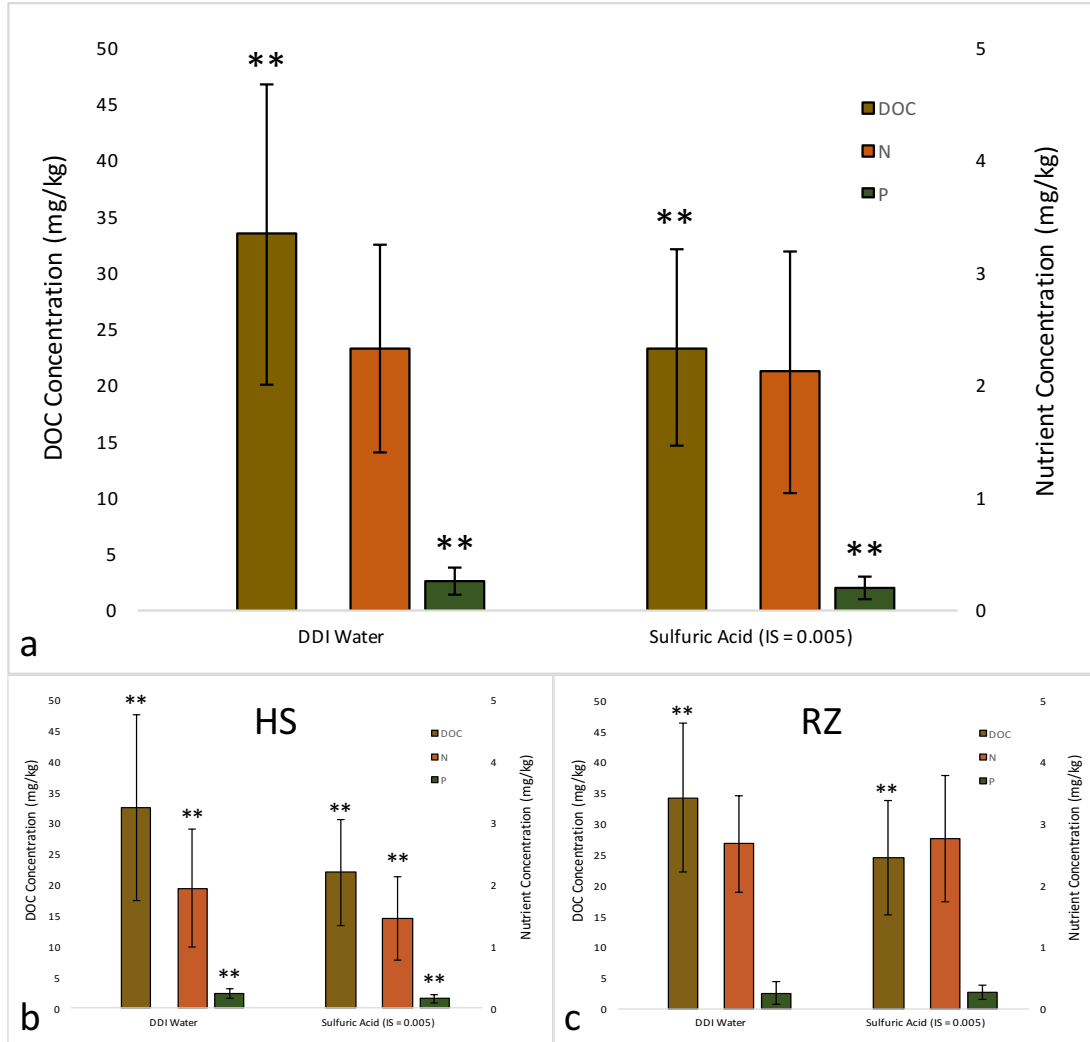
Figure 9: Average extracted DOC, N, and P concentrations by deionized (DDI water) and high IS (IS=0.005 mol/L) solution for a) all samples [n=36 (DOC, N), n=26 (P)], b) HS samples [n=18 (DOC, N), n=16 (P)], and c) RZ samples [n=18 (DOC, N), n=10 (P)]. Stars indicate significant difference at a 0.05 alpha level.

Differences in N between high IS (02.11±1.01 mg/kg) and low IS (02.31±0.02 mg/kg) treatments (ignoring soil type) were found not to be significant (p=0.077, Fig. 9a), however P release was significantly higher in low IS extract (0.25±0.12 mg/kg) compared with high IS extract (0.19±0.10 mg/kg, p=0.036). Considering both soil types separately however, concentrations were significantly lower in the high IS treatment of HS soils for both N (p=0.004) and P (p=0.003, Fig. 9b), while in RZ soil IS treatments were not significantly different for N

(p=0.323) or P (p=0.458, Fig 9c). DOC was consistently lower in high IS treatments in both HS soils (p=0.002, Fig. 9b) and RZ soils (p=0.0001, Fig. 9c). Compared to pH treatments, N concentrations were lower relative to DOC concentrations. Due to inaccuracies in ICP analysis, only 26 of 36 total effluent samples were used in P data calculations.

3) Landscape Position

Composition of extract varied by soil type (covariant with landscape position), however not for all analytes. Average DOC released from RZ soils was higher (29.36±11.61 mg/kg) than HS soils (27.26±13.01 mg/kg), however an equal variance t-test revealed one-tailed differences between soil types to not be significant (p=0.306). P similarly yielded insignificantly higher concentrations (p=0.092) in RZ extract (0.26±0.14 mg/kg) compared with HS extract (0.20±0.08 mg/kg). Differences in N however were large, resulting in significantly higher N in RZ extract (2.72±0.89 mg/kg) compared with that of HS (1.71±0.84 mg/kg, p=0.001).
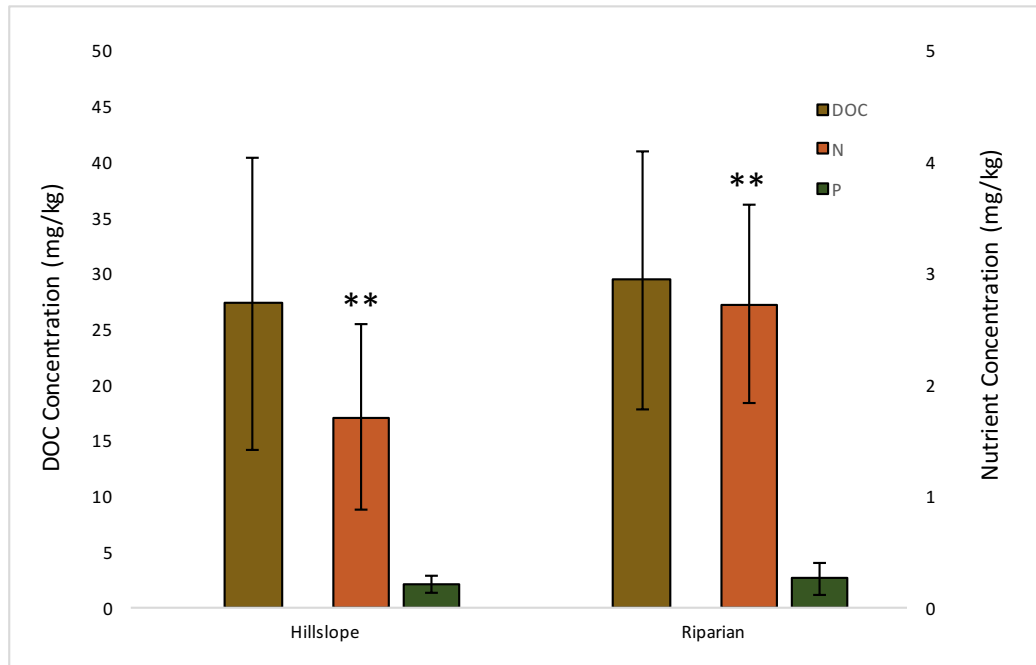

Figure 10: Average extracted DOC, N, and P concentrations from HS and RZ soils [n=36 (DOC, N), n=26 (P)]. Stars indicate significant difference at a 0.05 alpha level.

Given the greater concentrations of N and P in RZ extract, multiple regression analysis was run to determine predominate predictors of N in experimental soils. Relevant regression information can be found in the appendix. Considering DOC, treatment (IS), and topography (soil type) as predictors, multiple regression output identified a much stronger predictor model for N ($p<0.00001$) than for P ($p=0.37$). DOC and topography were both found to be significant predictors of N, while no predictors showed significance for P. Closer examination of topography as a predictor of N shows a lower C:N ratio in RZ soils compared with HS soils, regardless of treatment. This is also reflected by the presence of differences in N but not DOC seen between soil types (Fig. 10). The C:N ratio appeared also to be lower in high IS solution compared with low IS solution, which is reflected by the absence of differences in N between IS treatments where differences in DOC are seen (Fig. 9a). These ratio differences are less extreme than those between soil types, as treatment was not found to be a significant predictor for N ($p=0.12$) in IS regression analysis, while topography was significant ($p=0.0001$).

Discussion

The original hypotheses state that changes in soil solution chemistry have profound effects on DOC and nutrient release from soils through mechanisms of competitive sorption and aggregation vs. dispersion. Indeed, some of these mechanisms can explain the behavior of solutes in these experiments, however, the response is more varied than was expected. In the following section each mechanism is discussed, the role of landscape position is commented on as a modulating factor, and the results are put into a broader context.

The Role of Competitive Sorption in Flow Through Experiments

It was hypothesized that sulfate saturated soils have a greater affinity for DOC sorption than sulfate free control soils. It was hence expected that in these experiments DOC would decrease while SO_4^{2-} in sulfate impacted soil leachate would increase (hypothesis 1). It was observed that in both replicate soils DOC concentrations were low in the first effluent, while SO_4^{2-} concentrations were high (Fig. 5 & 7). This suggests that DOC from leaf litter is either diluted by solution already present in the soils (from either DDI or Na_2SO_4 treatment) or that DOC is indeed sorbed on soil sorption sites in this first step. After this first infiltration, DOC and sulfate concentrations approached that of the infiltration solution, indicating that whichever process occurred was completed rapidly.

However, no difference existed between the sulfate free control and the sulfate treated soils, providing little evidence of competitive sorption between DOC and sulfate in this experiment. This is in contrast with other studies that have clearly shown evidence of competition between DOC and sulfate (Gobran et al. 1998) and decreases in soil pore water DOC due to sulfate additions (Seifert-Monson et al. 2014). In one of these studies larger quantities of soils and multiple soil horizons were used (Gobran et al. 1998), while in another sulfate amendments were added in situ and soil pore water was collected directly from the amended field site (Seifert-Monson et al. 2014).

pH effects were reported by Gobran et al. (1998) as a possible reason for the absence of competitive sorption. Their results indicate that soil retention of sulfate is increased at lower pH (<4) while DOC retention is increased at higher pH (>4). Both solutions in the soil packet flow through analysis had a neutral pH where, according to this logic, DOC outcompetes sulfate for binding sites. Were this the case, the initial sulfate saturation would have sorbed primarily to

open binding sites, not those already occupied by DOC, and the later infiltration of DOC would have saturated those sites in the same sorbed concentrations as open sites (DDI control). In this case, no differences in DOC sorption would be seen between treatments, as was seen in the results of this study.

Another reason for the differing results between this study and previous work could be the experimental setup. Only a small amount of soil with relatively high amounts of liquid was used which presumably led to the fast saturation of soil by influent DOC. This limits the ability to examine differences in sorption patterns that may have been visible were there a greater ratio of soil mass to influent solution. Hence, adapting this experiment to increase the quantity of soil is warranted, possibly via the use of column infiltrations, as this would make minute differences in sorption and leaching patterns clearer.

Another factor could be the small amount of time allowed for soil-solution interaction during the sorption step. In previous experiments sulfate sorption was achieved either by sequentially infiltrating multiple horizons (Gobran et al. 1998) or amending in situ soils (Seifert-Monson et al. 2014). In both cases a much greater interaction time was allowed between infiltrating solution and soil. It is clear that more work is necessary in order to confirm the influence of sulfate-DOC competitive sorption on soil DOC release.

The Role of Aggregations vs. Dispersion in Batch Experiments

It was hypothesized that the cation bridging effect leads to aggregate-driven C retention in soils at low pH compared with soils at neutral pH, and it was predicted that the greatest DOC and associated nutrient release would be seen at neutral pH (hypothesis 2). In opposition to the hypothesis, slightly higher DOC concentrations were seen in pH 4 solutions compared with pH 7

(Fig. 8). However, confident extrapolation from these results is limited due to the large variation in concentration between samples within treatments, the small sample size (n=12), and the fringe significance level (p=0.046). Furthermore, no difference was found between nutrient concentrations. This may be in part due to the tendency of nutrient concentrations to correlate with DOC, and differences between DOC were minimal.

These results suggest that aggregation through proton driven cation bridging is not a likely mechanism for DOC release in these soils. This is supported by a previous soil column flow through experiment conducted by Munch et al. (2002), who found influent solution pH differences (pH 4 vs. pH 5.8) to have little influence on DOC release from soils. However, other studies have shown pH to greatly influence DOC release from soils via dissolution of organic matter, rather than via aggregate dispersion. Specifically, pH was found to be a key factor determining organic matter solubility under reducing conditions, with more DOC being released at pH 7.4 vs. 5.5 (Grybos et al. 2009). It therefore is still necessary to consider pH influences when assessing DOC release from soils.

It was also hypothesized that high IS soil solution promotes aggregate formation and C retention in soils through compressing the diffuse double layer, leading to aggregation (hypothesis 3). In this case it was expected that a greater release of DOC and associated nutrients would be seen at low vs. high IS. As hypothesized, low IS extracts yielded significantly higher DOC concentrations across all samples, and higher N and P concentrations for HS samples (Fig. 9). The lack of significance between N concentrations under different IS treatments in RZ samples can likely be attributed to the variation in N by soil type (Fig. 10) confounding IS driven N differences in RZ soils (Fig. 9c). Such variation may also explain the same phenomenon for P concentrations, however less P variability was found between soil types (Fig. 10). Low IS

solutions simulate rain and soil solution recovering from acid deposition, hence these results could suggest that recovery from acidification may allow more DOC and associated nutrients to be released from soils, although with C:N:P ratios varying according to soil type.

Regarding DOC, these results are in agreement with a study by Hruška et al. (2009) which found that increased stream DOC in a European catchment was driven by reductions in IS rather than pH, however they did not provide an explanation for this observation. In their soil column flow through experiment Munch et al. (2002) also confirmed that increases in IS decreased effluent DOC, however they express uncertainty regarding the relative influence of cation bridging vs. diffuse double layer effects, and do not look further into the specific mechanism.

Our understanding of the role of the diffuse double layer in aggregation indicates that aggregation is likely also influenced by the decrease in deposition IS, where aggregates are less likely to be maintained in low IS solution (Moore & Reynolds 1997). Given the tendency of soil aggregates to physically trap and protect OM, aggregate breakup likely serves as a mechanism controlling DOC and possibly nutrient release in light of recent low deposition IS. In HS soils both P and N did correspond with changes in DOC between IS strength treatments, which could indicate that this aggregate dispersion driven mechanism is likely to increase surface water nutrient loading along with DOC. Such an effect might be of importance because increased nutrient loading may lead to changes in productivity and consequent trophic structure. However, as HS soils tend to contribute less DOC to surface waters relative to RZ soils (Dick et al. 2015; Frost et al. 2006; Parry et al. 2015) and these results showed greater differences in nutrient release between IS treatments in HS soils compared with RZ soils, nutrient loading increases may be limited.

It was additionally hypothesized that DOC and associated nutrient release will vary with landscape position and will be greatest for RZ soils and lower for HS soils (hypothesis 4). Interestingly, only N showed significant differences by soil type with higher N in RZ extract. This difference in N and C:N ratio is likely a result of the tendency of the riparian zone to remove nutrients from upland sources (Vidon et al. 2010). Microbial activity may also differ between HS and RZ soils. Breakdown rates of C compounds can be limited by anoxia in RZ soils due to frequent saturation of these near stream soils. Microbial breakdown of C compounds often converts C and nutrients to more bioavailable forms (Gougoulias et al. 2014), which may explain the higher values for N and the lower C:N ratio seen in RZ soils compared with HS soils.

Continuing Research – Is there a Link between these Results and Soil Processes?

The experiments in this study were designed to test a specific set of hypotheses related to two main mechanisms that could explain the release of DOC from soils when precipitation and soil solution chemistry change. However, in order to fully understand the mechanisms contributing to changes in surface water DOC, a direct connection must be drawn between this series of experiments and soil processes. For example, in order to determine if changes in IS really lead to aggregate dispersion, aggregates have to be observed. This thesis is part of a larger research project that examined change in aggregate size with particle size analysis as a function of IS. Results show that aggregates after low IS treatment effectively decrease in size and release more DOC (Cincotta et al. in prep). This same project investigated the characteristics of DOC released through aggregate breakup because DOC and nutrient bioavailability (assessed through incubations and using spectral methods) have implications for productivity and DOC variability. These results are currently written up for a publication.

Conclusions and Global Relevance

IS was the strongest determining factor of DOC release, supporting the hypothesis that DOC release is highest at low IS. While DOC release differences were identified at different pH levels, the results were in opposition to the hypothesis that DOC release would be highest in higher pH soils. Moreover, any differences in DOC release between pH treatments cannot confidently be confirmed, hence the significance of aggregation in acidic solution remains unconfirmed. The occurrence of competitive sorption additionally could not be confirmed, because DOC effluent patterns were identical for sulfate impacted and control (DDI) soils. These results prevent the confirmation of the first hypothesis, that DOC-sulfate competitive sorption will result in higher DOC effluent concentrations late in the experiment. However, further analysis of competitive sorption may reveal more nuanced DOC-sulfate interactions that were not apparent due to inadequate soil mass and solution pH above that seen during acid deposition recovery.

The significance of IS in determining DOC release and the connection between IS and the diffuse double layer enhance our understanding of the primary mechanisms responsible for the widespread increase in DOC which have occurred in recent decades. Isolating the mechanisms controlling DOC release from soils will allow us to better predict how surface waters may be impacted by recovery from acid deposition. As the diffuse double layer is dependent on negatively charged particle surfaces and pore water IS, knowledge of watershed soil composition can potentially allow us to interpret how changes in IS may influence aggregate breakup and consequent DOC release. Such an understanding is particularly relevant in areas still recovering from acid deposition.

Implications

Considering aggregation as the primary mechanism controlling recent increases in surface water DOC, predictions can be made regarding the future trend of surface water DOC concentration. The reduction of IS in precipitation is a result of a recovery from years of atmospheric pollution, and as such should approach an equilibrium state. As a result, continued increases of surface water DOC in the long term are unlikely. Rather, DOC concentrations should reach a new equilibrium state in response to stabilizing deposition IS. Trophic structure changes dependent on DOC would theoretically follow this pattern, stabilizing in response to DOC reaching an equilibrium state.

This successive stabilization however would only follow if atmospheric deposition changes were the dominant driver of changing DOC release from soils. Other factors, including increasing atmospheric temperatures and storm event frequency, have the potential to alter DOC release quantities as well, and would not be predicted to level out in the same manner as deposition chemistry.

Future Work

More research is necessary however to support the results of this study before they can be applied at a broad scale. The results of this study may be system specific, particularly as they indicate that soil type influences DOC and nutrient release, implying that future results will vary by location and soil type. Additionally, a small set of samples was used which further limits the accuracy of the study.

It is also important to continue research efforts related directly to this study, as our understanding of the observed DOC release mechanisms is still incomplete, and consequences of

recovery are related to both DOC concentrations and components. Presently changing surface

water DOC concentrations have influence over water quality via nutrient inputs and light

attenuation. Hence, efforts are being made in the UVM Geology Department to further

understand the specifics of DOC release mechanisms in light of recovery from acid deposition.

Treatment	Sample	1	2	3	4	5	6	Average
pH 7	DOC	23.15	32.72	103.54	38.82	26.54	46.76	45.26
	Nitrogen	6.12	5.09	8.70	5.59	4.51	7.00	6.17
	Phosphorus	0.42	0.49	0.21	0.27	0.60	0.26	0.37
pH 4	DOC	28.95	42.07	110.16	42.49	26.69	43.94	49.05
	Nitrogen	6.80	6.20	8.98	6.36	5.02	4.38	6.29
	Phosphorus	0.38	0.49	0.38	0.29	0.41	0.24	0.36

Table 1: DOC, N, and P values (mg/kg soil) for all samples included in the pH experiment. Red shading indicates inaccurate values produced by ICP analysis; any sample with inaccuracy and its corresponding paired sample were not included in data analysis.

Treatment	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Average
DDI	DOC	42.98	39.29	32.19	30.84	37.33	20.35	23.53	37.53	59.48	27.59	58.11	21.47	21.19	26.10	25.93	50.20	36.66	9.85	33.37
	Nitrogen	3.59	3.57	2.87	2.79	2.30	1.51	2.09	2.26	3.64	2.02	2.88	1.36	1.45	2.26	2.35	2.99	1.69	0.00	2.31
	Phosphorus	1.11	1.32	1.10	0.94	0.34	0.26	0.14	0.15	0.12	0.26	0.23	0.25	0.34	0.50	0.54	0.28	0.23	0.08	0.25
H2SO4	DOC	24.14	30.42	26.46	24.30	21.10	14.23	17.04	24.88	44.87	16.22	33.46	14.36	14.30	16.49	21.69	37.33	23.22	14.01	23.25
	Nitrogen	3.88	4.59	3.31	2.32	1.66	0.97	1.95	1.92	2.85	1.15	1.80	1.29	1.62	1.85	2.91	2.49	1.12	0.36	2.11
	Phosphorus	0.13	0.29	0.28	0.30	0.23	0.16	0.15	0.16	0.24	0.17	0.23	0.17	0.41	0.53	0.36	0.15	0.06	0.09	0.20

Table 1: DOC, N, and P values (mg/kg soil) for all samples included in the IS experiment. Red shading indicates inaccurate values produced by ICP analysis; any sample with inaccuracy and its corresponding paired sample were not included in data analysis.

Regression Statistics					
Multiple R	0.81				
R Square	0.66				
Adjusted R Square	0.62				
Standard Error	0.61				
Observations	36				
ANOVA					
	df	SS	MS	F	Significance F
Regression	3	22.66	7.55	20.29	1.50E-07
Residual	32	11.91	0.37		
Total	35	34.58			
	Coefficients	Standard Error	t Stat	P-value	
Intercept	0.02	0.35	0.06	0.96	
DOC	0.06	0.01	5.92	1.38E-06	
Topography	0.90	0.20	4.40	1.13E-04	
Treatment	0.36	0.22	1.61	0.12	

Table 2: Multiple regression output with Response=N, Predictors=[DOC concentration, Topography, Treatment], where treatment indicate low vs. high IS, and topography indicates RZ vs. HS soils.

Regression Statistics					
Multiple R	0.36				
R Square	0.13				
Adjusted R Square	0.01				
Standard Error	0.11				
Observations	26				
ANOVA					
	df	SS	MS	F	Significance F
Regression	3	0.04	0.01	1.11	0.37
Residual	22	0.26	0.01		
Total	25	0.30			
	Coefficients	Standard Error	t Stat	P-value	
Intercept	0.24	0.07	3.72	0.00	
DOC	0.00	0.00	-0.32	0.75	
Topography	0.06	0.04	1.38	0.18	
Treatment	-0.06	0.05	-1.21	0.24	

Table 3: Multiple regression output with Response=P, Predictors=[DOC concentration, Topography, Treatment], where treatment indicate low vs. high IS, and topography indicates RZ vs. HS soils.

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