Final Report

Impacts of salt loading on nutrient and metal processing in stormwater bioretention

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Executive Summary

This project leveraged a controlled greenhouse study along with a field study to understand how de-icing salts impact water quality performance of stormwater bioretention and bioinfiltration systems. Results were fairly similar between the two studies. However, insights from the field study were much more variable and somewhat challenging to interpret, demonstrating the value of also having a semi-controlled greenhouse study. The greenhouse experiment also allowed the ability to explore possible system modifications, such as addition of a subsurface internal water storage zone.

Overall, results indicate that stormwater bioretention is an effective management practice for removing nutrients, sediment, and metals. For nitrogen, bioretention often provides decent removal, but may be subject to some leaching early on, depending on organic matter content of topsoil. However, presence of an internal water storage zone can ensure consistently excellent nitrogen retention, even with salinity changes. Nitrogen performance is also strongly linked to plant health, and thus can be reduced when salt toxicity affects plant health.

Bioretention generally does a very good job of removing phosphorus, sediment, and metals. Average removal efficiencies generally exceeded 85 % in the mesocosm study. Removal efficiencies were more variable in the field study; while sediment retention was excellent (generally >90 %), phosphorus and metals removal ranged from 87 % to slightly negative, indicating net export of some metals. Phosphorus, sediment, and metals all suffered reduced removal efficiencies (4-10 % reduction in average removal in the greenhouse study) under increased salt, with some periods of metals export. Better phosphorus removal was observed with addition of internal water storage in greenhouse experiments.

While performance of bioretention can be enhanced by use of salt tolerant plants and presence of an internal water storage zone, it is clear that salt has detrimental effects on water quality performance in stormwater bioretention and bioinfiltration systems. Given the other documented detrimental impacts of de-icing salts on downstream water bodies, pursuing strategies to reduce salt application to roads, parking lots, and sidewalks is also critical.

Key Restoration Question

How do different levels of salt present in a BMP due to road application impact the BMP's nitrogen removal efficiency and export rates out of the BMP of pollutants such as heavy metals?

Introduction

A variety of salts are typically applied as deicers to roads, parking lots, and sidewalks in advance and during winter storm events in the mid-Atlantic region. These salts wash off of these surfaces during winter and spring rain or melt events and make their way to groundwater and downstream waterbodies. There is increasing recognition of the associated broad-scale salinization of freshwaters that is occurring (Kaushal, Likens, et al., 2018). Salts can have direct toxic impacts on biota, but can also have indirect undesired consequences through their interactions with biogeochemical processes, such as mobilization of base cations and nutrients (Haq et al., 2018; Kaushal, Gold, et al., 2018; Van Meter & Swan, 2014).

Stormwater Best Management Practices (BMPs), also called Stormwater Control Measures (SCMs), are designed to receive, detain, and treat runoff from impervious surfaces. During deicer flushing events, these BMPs can receive concentrated inputs of salts that make their way through the BMP soil media and interact with vegetation and soil media, making BMPs potential hotspots for some of these undesired biogeochemical interactions. Limited research over the last decade has begun to investigate a subset of these phenomena.

Lab-scale research on impacts of sodium chloride on soil media has found reduced infiltration, and increased leaching of organic matter, nitrogen (N) and phosphorus (P), major cations, and zinc, copper, and lead with salt additions; this leaching of metals and cations is presumably from exchange of incoming sodium with existing base cations and metals associated with the soil media (Kakuturu & Clark, 2015; Soberg et al., 2014, 2020). Lab-scale studies focusing on use of salt-tolerant plants in stormwater treatment in Australia did find improved N removal, even with increased salt load, in plants considered more salt-tolerant such as *F. nodosa* or *J. kraussii* (Szota et al., 2015). Monitoring of outdoor planted bioretention mesocosms in Ontario, Canada did not observe significant reductions in infiltration rates due to salt influxes, likely due to countering effects of freezing and salts. Despite accelerated loading to mimic multiple years of stormwater inputs, all mesocosms regardless of salt load removed metals at adequate rates and did a similarly poor job of removing total N and P. Vegetation impacts on these phenomena were unclear, despite improved survival of *Panicum virgatum* and *Aster nova angliae* 'Red Shades' (Denich et al., 2013a).

There has been limited investigation digging into the specific factors or processes contributing to observed phenomena. One critical process affecting N removal is denitrification, the microbially-mediated transformation of reactive nitrate to N gases N_2O and N_2 (Groffman et al., 2006). Denitrification is particularly of interest because it completely removes N from the stormwater BMP, whereas N immobilized in vegetation or complexed with metals could potentially become available again. A broad investigation of salt impacts on bioretention soil biogeochemistry found striking changes in soil bacterial communities but did not identify obvious implications for nutrient processing as it relates to salt impacts (Endreny et al., 2012). Investigation of denitrification in roadside versus more pristine wetlands found that denitrification consistently reduced in response to chloride additions, but that reductions were less in the more chronically-exposed roadside soils (Lancaster et al., 2016).

A more in-depth and comprehensive understanding is needed of biogeochemical phenomena resulting from deicing salt inputs, in order to understand the implications on processing and removal of nutrients, metals, and sediment. It is also important to understand where certain design modifications or management strategies could aid in increasing the resilience of BMPs to salt inputs.

Hypotheses

Our overarching hypothesis was that *increased salt loading into stormwater BMPs is correlated to overall increased export or decreased removal efficiency of N and metals (Cu and Zn)*.

However, we believe that there are important interactions between the inflowing salt load as well as the hydrologic regime. For example, increased soil moisture and greater hydraulic residence times in stormwater BMPs could moderate impacts of salt loading on N removal, but saturated conditions may also have detrimental impacts on phosphorus and metals. *Specifically, the addition of internal water storage could improve the removal of nitrogen and moderate the impacts of salt but may increase effluent concentrations of phosphorus and heavy metals.*

Previous work also indicates that vegetation plays a substantial role in N removal, and can also impact metals removal. We hypothesize that the *presence of vegetation improves N and metals removal, compared to no vegetation.* With regards to the interaction of vegetation and salinity, we envision two possible hypotheses: *that there is no difference in N and metals retention in vegetation according to magnitude of salt loading, or that there is a decrease in N and metals retention in vegetation with increased salt loading, due to stress on the vegetation.*

Methods

The proposed study combines both a field monitoring study of actual stormwater control measures, along with a semi-controlled greenhouse study, in order to adequately address the above hypotheses.

Field monitoring of two basins

Our focal region is the City of Lancaster, located in southeastern Pennsylvania. Lancaster has several hundred stormwater BMPs installed, in order to manage stormwater and associated pollutant inputs to its combined and separate municipal storm sewer systems. Green stormwater infrastructure, or ecologically-based stormwater BMPs, are a critical part of their 2017 Combined Sewer Overflow Consent Decree. Their major BMP types include bioretention basins/swales, infiltration trenches, permeable pavement, tree trenches, and detention basins. We chose

Lancaster due to its extent of stormwater BMPs representative of those in the Chesapeake Bay watershed, but also because we leveraged existing partnerships cultivated with municipal staff as well as instrumentation installed as part of two internal Penn State grants.

The first component of this research is an intensive field investigation of water quality and biogeochemical dynamics in two stormwater bioretention basins in Lancaster. The sites were selected such that one has a higher salt input and one has a lower salt input. The bioretention basins monitored in the field were selected from the City's existing 138+ bioretention basins, in coordination with our City of Lancaster partners. We aimed to keep all other factors beyond salt input as similar as possible.

The final selected basins were both located in Brandon Park in Lancaster. Both basins were constructed in 2012 with similar initial soil specifications and plant palettes. After some challenges with initial plant establishment, plantings were replaced in 2018. One basin, referred to as the Brandon Park High, or BH, basin, receives runoff from Wabank St adjacent to the park. Runoff is first routed through an initial pre-treatment SCM and into the main bioretention basin. Because this basin receives loads directly from this well-trafficked road, it is considered the high salt basin. The second basin is referred to as the Brandon Park Low, or BL, basin as it receives relatively lower salt loading. It is located adjacent to the park's basketball courts and parking lots. Runoff from the parking lot is first routed through a pre-treatment SCM and then into the main bioretention basin. The BH basin is 260 m^2 and has 0.6 m bioretention soil mix underlaid by 0.3 m aggregate. The BL basin is 325 m^2 in area 0.6 m bioretention soil mix underlaid by 0.2 m aggregate. The bioretention soil mix was specified as loamy sand with 2-4% organic matter. Both basins include underdrains, although the underdrain pipes were capped and not in use at the time of the study. Common plants include *Carex sprengelii* and *Eupatorium purpureum*.

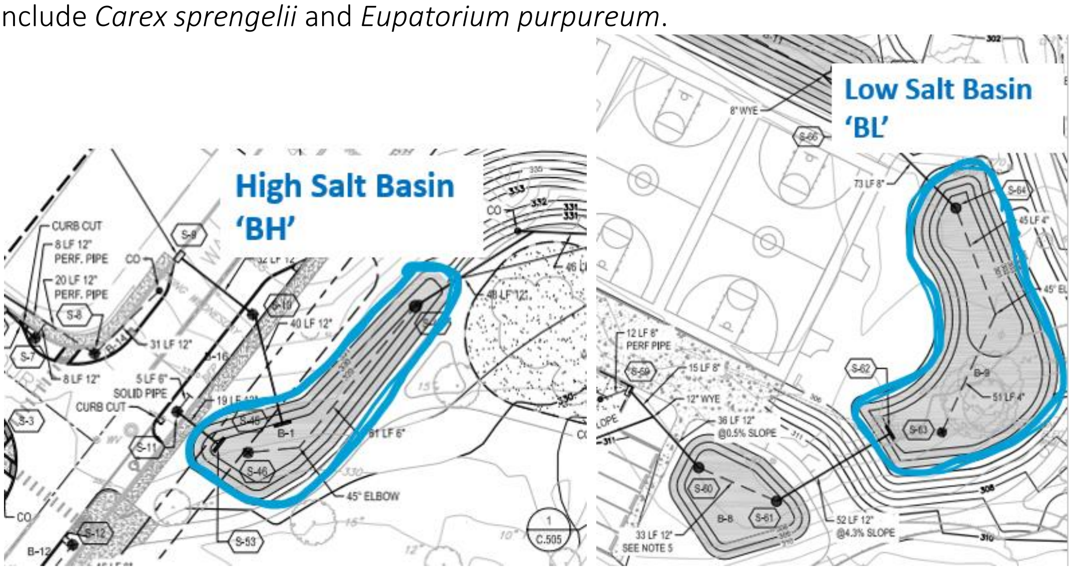

Figure 1. Drawings of two monitored stormwater bioinfiltration basins in Lancaster, PA

Because both of these basins did not have operational underdrains, the primarily mode of water loss was via exfiltration to underlying soils. The basin soils were instrumented with METER soil electrical conductivity and moisture (TEROS12) sensors that permit continuous monitoring. Four sensors (two at 3 cm depth, and two at 6 cm depth) were installed for the continuous monitoring of the soil parameters at both sites. The sensors were located approximately 1-2 meters from the inlets.

Stormwater sampling for nutrients, sediment, and metal loads was conducted between January 2022 and May 2023. We installed ISCO automated samplers at the inflow locations to each basin in order to sample runoff during selected storm events. At the high basin, the ISCO sampler was coupled with an area-velocity meter that was installed in the primary inflow pipe. The sampler was programmed to collect water samples throughout the storm event using flow-weighted sample collection. For outflow samples, Soil Moisture Corp. 0.3 m and 0.6 m depth soil water samplers were installed in each basin. Water was pumped out from these lysimeter-style samplers after selected storm events. Inflow and outflow water samples were collected and a subset filtered to 0.45 µm as soon after the event as possible. This initial sample collection was conducted by Franklin and Marshall undergraduate researchers. Samples were refrigerated and retrieved imminently by Penn State researchers and returned to Penn State- University Park for analysis. Sampling was completed in May 2023 after continued issues with vandalism of the ISCO sheds in that spring.

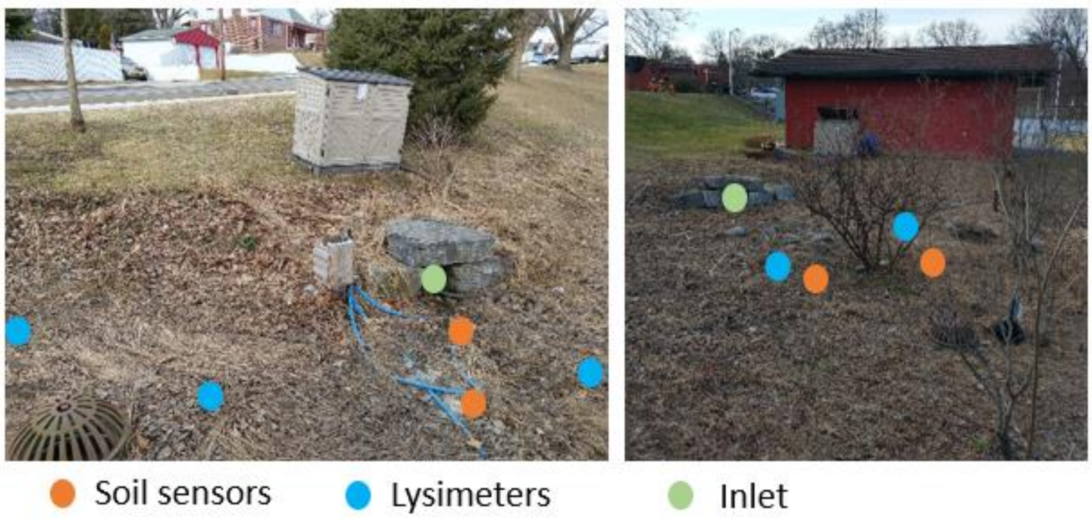

Figure 2. Brandon Park 'High Salt' basin (BH) site at left, and Brandon Park 'Low Salt' (BL) site at right. Sheds housing ISCO automated samplers used for inflow sampling are shown, along with soil sensors, and lysimeter locations (underground soil water samplers for treated outflow).

After initial collection of water samples by Franklin and Marshall research assistants, the samples were transferred to Penn State-University Park campus, where they were processed in the Kappe Environmental Engineering Lab. Nitrate and chloride were analyzed on filtered samples via Dionex ion chromatograph while total dissolved nitrogen was analyzed on filtered samples via Shimadzu TOC-VCSH+TNM-1. Composite unfiltered samples were analyzed for metals by the Penn State Laboratory for Isotope and Metals in the Environment. These samples first underwent an acid hotplate digestion for environmentally available metals per EPA method 200.7, and then were analyzed via ICP-OES for major cations, phosphorus, and selected trace metals (Cr, Cu, Ni, Pb, Zn). An additional unfiltered sample was used for analysis of total suspended solids (TSS) by USGS method I-3765-85. We then compare event-mean concentrations for chloride, nutrients, and metals, and ultimately the removal rate of each of these in each basin for each event.

For both of these intensively monitored basins, additional environmental measurements will be made to aid in understanding of biogeochemical processes underlying observed removal rates. Soil samples were taken at five points within each basin for analysis of N via combustion and metals content via Mehlich 3 digestion and ICP analysis. Plant samples were also taken at five points within each basin for analysis of metals via acid digestion and ICP analysis and N content via combustion. Analysis was conducted at the Penn State Agricultural Analytical Services Lab.

Rainfall and air temperature data was accessed from Millersville University Climatology Center for additional interpretation of data. This weather station was located approximately at 5.5 km from the sites, hence the rainfall obtained from this station served as a close estimate of rainfall at the Brandon Park.

The data obtained from laboratory analyses were then analyzed using R Statistical Computing Language via RStudio. For individual rainfall events that generated inflow and outflow samples from the basins, the removal efficiency of a given parameter (X) by the bioinfiltration basins was calculated by using the following relationship:

$$Removal\ efficiency\ (\%) = \frac{X_{in} - X_{out}}{X_{in}}\ x\ 100$$

where, X_{in} is the inflow concentration of a given parameter, and X_{out} is the outflow concentration of the given parameter. Because outflow from the basins exfiltrated to underlying soils, outflow volume was not monitored, and thus loads were not evaluated.

Simple linear regression models (lm function in R) were used to evaluate the linear relationships of removal efficiency with different variables, such as amount of rainfall and the soil conductivity. Similarly, Pearson correlation coefficient was also used for identifying any correlation between any two variables.

Bioretention mesocosm experiment

The second major component of the project is the mesocosm experiment. While it is ideal to quantify function of stormwater BMPs *in situ* when possible to understand how various environmental constraints manifest in a certain water quality performance, this type of monitoring is costly and more challenging to adequately tease apart the relative impact of certain variables. Thus we complemented our intensive *in situ* monitoring with a mesocosm experiment which is intended to systematically evaluate several variables which we hypothesize could impact stormwater treatment under the influence of deicing salts. While the primary focus of the field experiment is evaluating the impact of differing salt input loads, the mesocosm experiment allowed for incorporation of hydraulic regime and vegetation as additional factors (Figure 4).

Specifically, there are two hydraulic regimes, free draining and internal water storage (IWS), where an upturned elbow is used to maintain a subsurface saturated zone. Vegetation treatment included no vegetation and two different native, salt-tolerant plants that tolerate a wide range of moisture. We selected *Panicum virgatum* (switchgrass) and *Eupatorium purpureum* (Joe Pye weed), based on both plants being common in the selected field experimental basins as well as other SCMs in our region. We specifically used the *Panicum* 'Cape Breeze' and *Eupatorium purpureum* 'FLOREUPRE1' Euphoria™ Ruby varietals based on their slightly smaller stature for experimental purposes and availability from our plant source, North Creek Nurseries. The salt load treatments included low and high salt inputs in late winter/ early spring, roughly corresponding to concentrations anticipated in runoff from a smaller side road or parking lot (low) and a main arterial road (high). Because the greenhouse study was initiated before the field study, salt concentrations were determined from other studies. Each combination of treatments had four replicates, resulting in 48 total mesocosms.

These mesocosms were constructed from 15 cm diameter SDR 35 PVC columns, following typical bioretention recommendations, with 43 cm loamy sand bioretention topsoil underlain by 33 cm sand, and a 10 cm gravel layer. 7.5 cm at the top of each mesocosm was reserved for ponding. The topsoil had 5-6% organic matter by mass. The sand was amended with woodchips (debarked oak/maple) to provide a carbon source for nitrogen removal, with amendment at 20% by volume. Mesocosms with an IWS zone had an outlet structure with an upturned elbow elevated to 30 cm. These mesocosms were located in a greenhouse where temperatures generally mimicked typical diurnal and seasonal changes, while not going below freezing. Planting of vegetation plugs in the mesocosms occurred in September 2021, in order to initially establish plants prior to the first wintry weather season. For the first 2 weeks, mesocosms were regularly watered with tapwater, to aid in plant establishment. At this point, simulated storm events began, in order to provide pollutant loading to the bioretention soils. The entire experiment was run until May 2023, including two winter seasons.

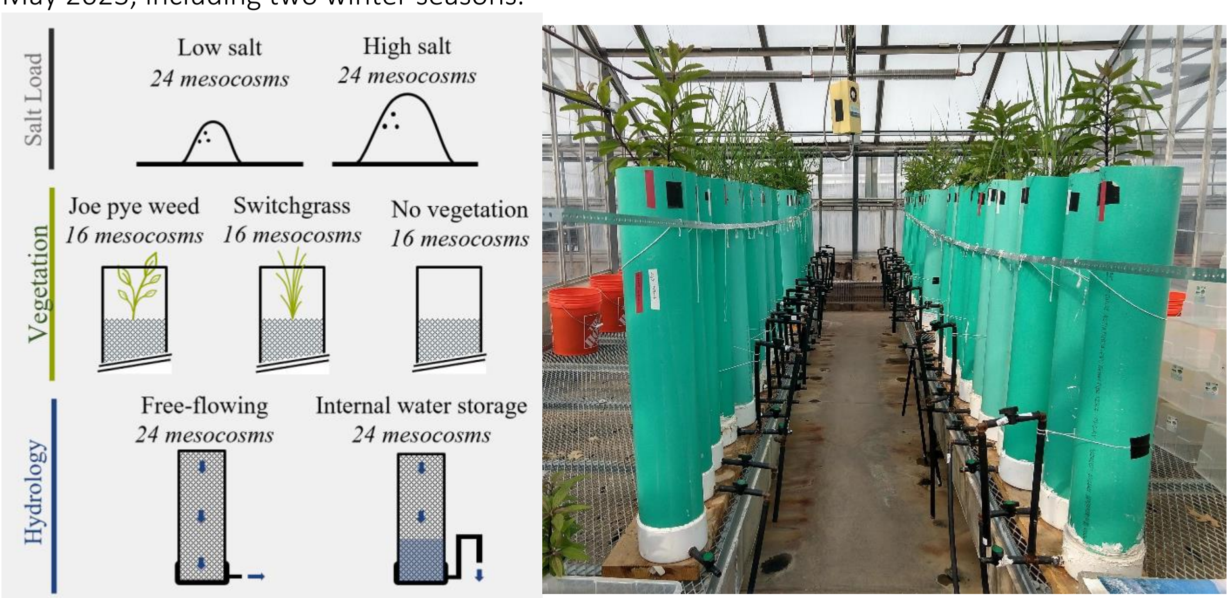

Figure 3. Schematic of bioretention mesocosm treatments (left) and photo of actual greenhouse setup with bioretention mesocosms (right) in late spring 2022

Storm events were sized based on mimicking typical precipitation regimes in the mid-Atlantic US. Annual average precipitation was divided into bi-weekly sampling events; while true precipitation varies widely in magnitude, here storm events were maintained at a consistent size in order to better isolate the effects of other variables on water quality outcomes. Runoff quantity was sized such that each mesocosm is receiving runoff from a fully impervious drainage area seven times larger than it, resulting in 1430 mL inflow volume. Runoff was delivered manually to the top of mesocosms and sourced from a larger reservoir of well-mixed semi-synthetic stormwater. Composition was based on previous studies of urban runoff in order to have representative concentrations of typical stormwater. The semi-synthetic stormwater was created using water harvested from the greenhouse office building roof, with additions of deionized water and laboratory salts to achieve typical stormwater concentrations (Davis et al., 2003; Payne et al., 2014). 100 mg/L sediment was added from dried and ground topsoil. This stormwater was used for storm events in mid spring through late fall. We switched to a winter semi-synthetic stormwater for in early spring (Feb and March), which contained elevated NaCl concentrations per the two salt treatments. NaCl was used, given that it remains the most commonly used de-icing salt. For the 2022 winter salty stormwater, concentrations of 500 mg Cl/L and 2000 mg Cl/L were used for the low and high salt treatments, respectively. After collecting data on water chemistry from the Lancaster field sites, and observing salt toxicity in some vegetation, concentrations were reduced to 1200 and 300 mg Cl/L in 2023 salty stormwater dosings. High salt mesocosms planted with *E. purpureum* had almost complete plant death after salty stormwater dosings in early 2022; these mesocosms had their plants replaced with new *E. purpureum* plugs in May 2022.

Table 1. Synthetic stormwater concentrations.

Constituent	Target Concentration (mg/L)	Average Concentration (mg/L)
Phosphate-P	0.5	0.49
Total phosphorus	-	0.63
Nitrate-N	1.5	1.61
Ammonium-N	0.5	-
Total nitrogen	-	2.92
Copper	0.15	0.12
Zinc	0.6	0.60
TSS	100	104.5
Sodium chloride-Cl, low	500[a]; 300[b]	523[a]; 331[b]
Sodium chloride-Cl, high	2,000[a]; 1,200[b]	2,058[a]; 1,291[b]

[a] Winter 1 concentrations
[b] Winter 2 concentrations

Throughout the experimental period, mesocosms were dosed with stormwater twice per week. Sampling occurred every four weeks. During the six weeks in early spring when salty stormwater was applied, sampling for water quality analysis occurred every two weeks. The mesocosms were not dosed with synthetic stormwater during winter, between approximately November and February. During this time, they were moved outside the greenhouse and surrounded with thin insulation, in order to induce senescence in plants, while not freezing the internal water storage zone.

For each sampled runoff event, total runoff volume was recorded after 3 hours of drainage. Samples were collected from a plastic bin receiving outflow, and immediately refrigerated in LDPE bottles. Three samples of synthetic stormwater influent were also taken for analysis. For effluent, one sample remained unfiltered and the other was filtered to 0.45 µm with cellulose acetate filters. A subsample of the unfiltered samples were acidified to pH<2 within 24 hours using sulfuric acid. Filtered water samples were analyzed for chloride, nitrate, nitrite, and total dissolved N, and unfiltered water samples were analyzed for environmentally available metals and phosphorus, as previously described. An additional unfiltered sample was retained for total suspended solids analysis via filtration. Water quality results are reported as removal efficiencies, where flow-weighted concentrations are compared for outflow to inflow.

Multiplying effluent volumes by concentrations enabled event load estimates to be calculated. Load data was analyzed alongside concentration data, but because effluent was collected only a few hours after watering, effluent volumes could be lower than total effluent; therefore, loads should be considered conservative estimates. Drainage after samples had been collected was also likely higher in concentration for at least some analytes because old water eventually flushed and was replaced by new water that had not spent as long in the mesocosms. Due to the resulting uncertainty in both load and concentration data, both should be considered conservative. On April 26th, effluent was collected for 24 hours for comparison with the scheduled April 28th sampling, which used the normal 2-hour period. This week was selected because the weather was consistently cloudy and cool. Many of the final volumes in the 24-hour drainage were greater or lower than what was recorded in the regular sampling on April 28, but differences were not attributable to the length of the drainage period.

Annual load estimates were calculated for 2022 from when the mesocosms were moved inside to when they were moved back outside. This required interpolation of concentrations and effluent volumes, both of which displayed temporal patterns. The interpolation was performed simply, by drawing a straight line between each pair of sampling dates and placing events between those dates on that line based on their distance in days from the sampling dates. Annual load values and efficiencies should be considered to be rough estimates. It should be noted that annual removal does not include much of the winter, which was compressed into a few weeks of salt application in March.

Removal efficiencies were determined as noted above. The result represents the effectiveness of each mesocosm at removing each analyte. Removal efficiencies are a common bioretention metric that this study uses to present much of the results, but it is important to recognize this metric's flaws and limitations, such as those outlined by McNett et al. (McNett et al., 2011). For example, removal efficiency does not account for background concentrations or concentrations considered to be irreducible. Removal of some low amount of nutrients or heavy metals may be impossible for any bioretention basin because of background concentrations in the soil; if the inflow concentration is already very low and near the same point as background concentrations, then a poor removal efficiency will be generated. This might lead to the incorrect assumption that this basin is performing poorly, when in reality the influent water is already very clean (McNett et al., 2011). Removal efficiency also assumes a relationship between influent and effluent concentrations, but the basin may actually be reducing the effluent to some background soil concentration regardless of influent concentration (McNett et al., 2011). In the case of the mesocosms, because influent concentration was controlled, it was relatively consistent in its concentrations.

For statistical analysis, independent variables were converted to binary variables indicating the presence of an IWS zone, the presence of P. virgatum, the presence of E. purpureum, and the presence of high NaCl. Multiple linear regression was performed with these independent variables against total nitrogen, nitrate, total phosphorus, TSS, copper, and zinc. Models were generated using automatic stepwise selection (forward, backwards, and both simultaneously) and manual selection with best subsets (using the adjusted R2, Mallows' Cp, and predicted residual error sum of squares). The best models were tested for linearity, independence/autocorrelation, constant variance/heteroskedasticity, multicollinearity, and normality with various tests and plots. Some corrections had to be made for constant variance and independence, which were done using transformations and the Cochrane-Orcutt estimation procedure. Models were analyzed using ANOVA and Student's t-test. A significance level of $\alpha = 0.05$ was generally used to help determine predictors for all statistical tests. The data was also analyzed visually, and data correlations were inspected individually.

Data from mesocosm #8 is not included in statistical analysis or figures from the time after reaching hydraulic failure in September 2022. The mesocosm cannot be considered to accurately represent a functioning bioretention basin after this time, though data was still collected. Several outlier data points (analyte concentrations and one effluent volume) were also removed due to known instrument or collection errors.

Samples of mesocosm vegetation and soils were taken for nutrient and metals analysis prior to the first sampled runoff event, and at the end the experiment in May 2023. Prior to the first runoff event, five unplanted vegetation plugs were used for the two vegetation types to analyze initial biomass and nutrient content. At the end of year two when the experiment is done, root tissue was also extracted from mesocosm soils. All sampled plant tissue was dried, weighed, and ground. Dried samples were analyzed for N and metals as previously described. Shoot biomass of plants was weighed in November 2022 and at the end of the experiment in May 2023. However, analysis was complicated by Joe Pye weed replacement of only high salt mesocosms in May 2022, and significant issues with plant re-emergence in spring 2023. Plant height was measured monthly for each mesocosm.

Results

Field study

Field study: soil moisture and salinity patterns

The average daily soil salinity over the entire study period at the Brandon Park high salt basin (BH) site was 0.39 mS/cm (Figure 4). The measured soil salinity ranged from 0.08 mS/cm to 12.24 mS/cm at 3-inch depth, while the value ranged from 0.064 mS/cm to 9.96 mS/cm at the 6-inch depth of soil at the BH site. The soil salinity at the Brandon Park low salt basin (BL) site was almost half of the BH site, with the average daily salinity of 0.21 mS/cm (Figure 5), which justified the selection criteria of the high and low salt basin. Similarly, the minimum and maximum soil salinity at the BL site was 0.035 mS/cm and 1.07 mS/cm at 3-inch depth of soil, 0.12 mS/cm and 1.46 mS/cm at 6-inch depth, respectively. The differences in the maximum soil salinity at the BH and the BL site suggested high salt entering the BH site compared to the BL site during winter. The soil moisture was measured as volumetric water content. The average daily and the average monthly soil moisture content at BH site was approximately 0.24 m^3/m^3 (Figure 6). Similarly, the BL site also had a similar average daily and average monthly soil moisture content of approximately 0.21 m^3/m^3 (Figure 7).

The salinity level at both BH and BL sites peaked right after winter storms, including several events in 2022 with known salt application (according to communications with City of Lancaster). It is very interesting to note that this sudden increase in the salinity level takes a while to get back to its original salinity level. In fact, in this study period ending in late spring 2023, the peak did not get back to its initial baseline level (Figures 4 and 5). A minor shift in the salinity level from its previous baseline value was seen after the salt application. This needs further exploration with continuous monitoring of salinity levels in the basin for few years.

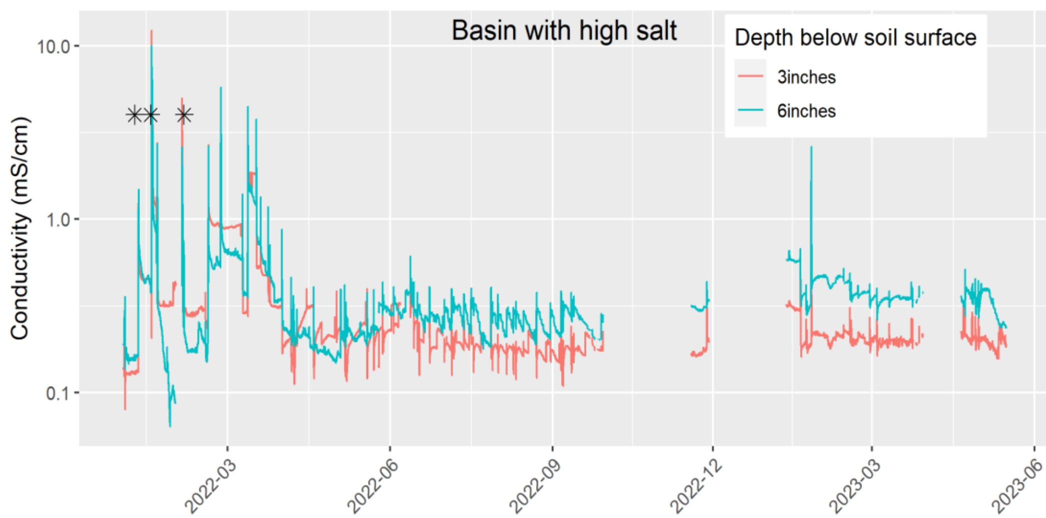

Figure **4**: Soil salinity at the high salt basin (BH). *Known deicing salt application. There are some gaps in soil sensor data due to battery issues.

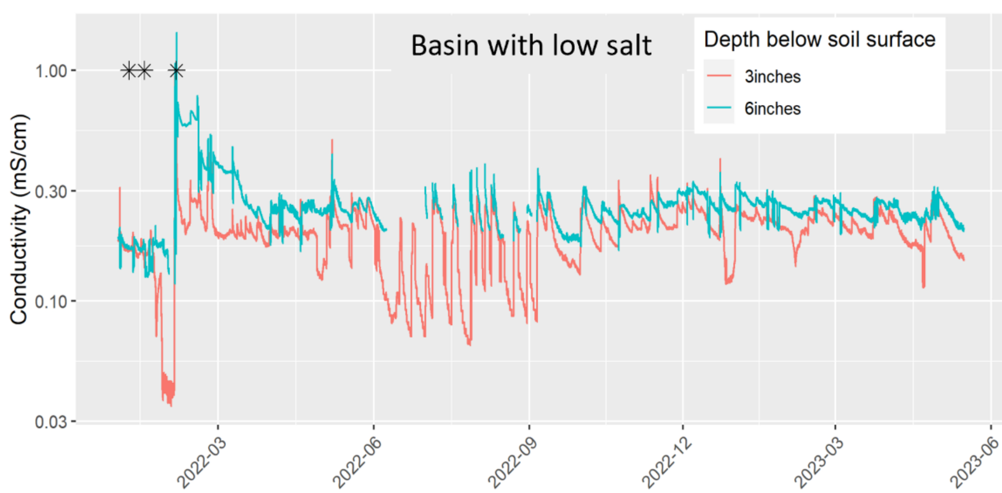

Figure **5**: Soil salinity at the low salt basin (BL). *Known deicing salt application.

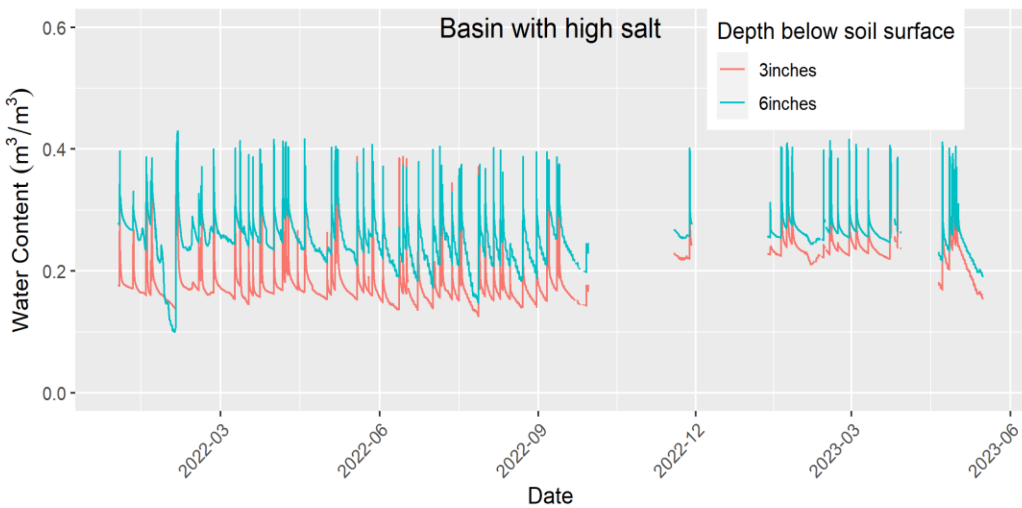

Figure 6: Soil moisture (volumetric water content) at high salt basin (BH). There are several gaps in data collection in fall-winter 2022 due to battery issues.

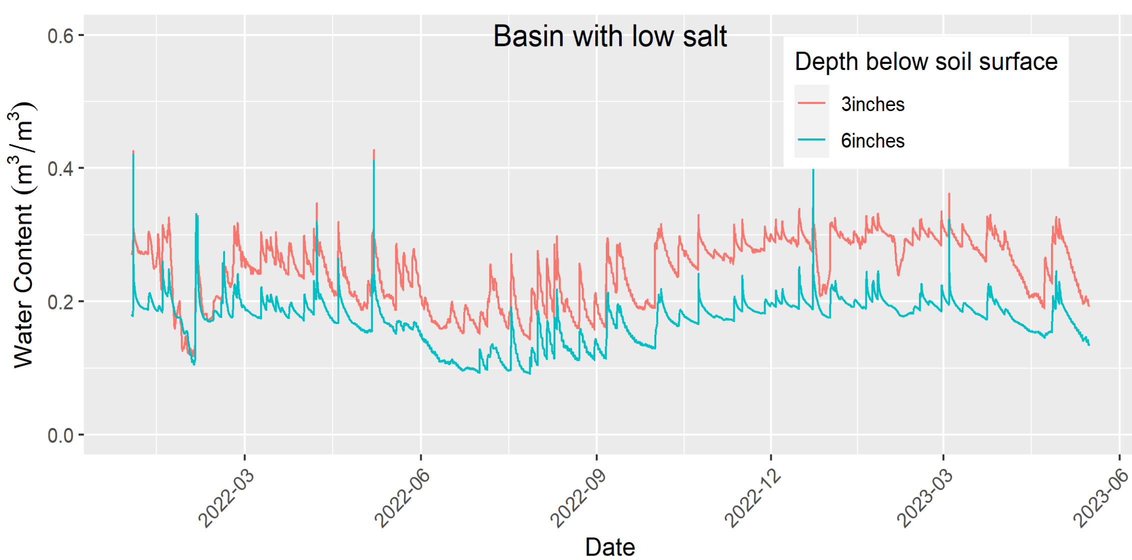

Figure 7: Soil moisture (volumetric water content) at low salt basin (BL)

Sixteen events were sampled at the BL basin, while 28 events were sampled at the BH basin. This was in part due to instrumentation challenges at the BL basin (e.g. events that generated flow into the basin, but did not trigger the automated sampler. Sampling adjustments were made to attempt to manage this issue). However, this was also in part due to far fewer events generating inflow in the BL basin, due to the size of its pre-treatment SCM. Sampled events were distributed through all seasons, and encompassed events with a precipitation magnitude of 1.5 mm to 52.3 mm.

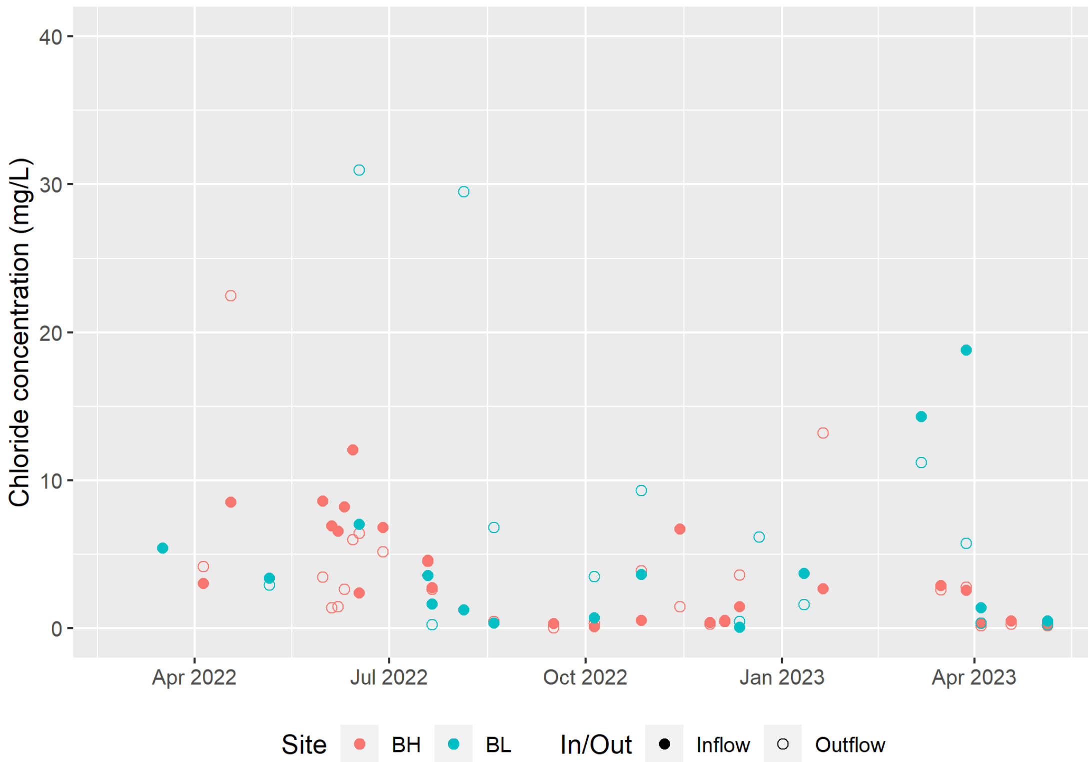

Figure **8**: Chloride concentration at the BH (high salt basin) and BL (low salt basin).

Field study: Chloride (Cl)

The average chloride concentration in the inflows of the BH site was 7.18 mg/L, and was 15.24 mg/L in the outflows (Figure 8). Chloride is able to interact with only a few anion adsorption sites compared to the sodium ions (Denich et al., 2013b; Kakuturu & Clark, 2015). This explains the flushing of chloride or the higher concentration in outflows compared to the inflows in the basin. The minimum measured influent chloride concentration at BH site was 0.12 mg/L while the maximum was 96.79 mg/L. The minimum and maximum effluent chloride concentrations, however, were 0.04 mg/L and 306.25 mg/L, respectively. The average effluent chloride concentration at BH site was almost twice its average influent concentration. These higher effluent concentrations suggest possible reduction in effluent volume compared to inflow, leading to increased concentration of salts, and possible temporary storage and eventual flushing of salts. All of the effluent concentrations were less than 25 mg/L, except for one event where the concentration was maximum at 306 mg/L. When individual storm behavior with chloride was considered, the rainfall events right after the salt application period caused increases in effluent chloride concentration suggesting higher first flush of chloride out of the system.

The average influent chloride concentration at the BL site was 9.81 mg/L and the effluent concentration was 30.63 mg/L. The minimum chloride concentration in the inflow was 0.05 mg/L, while the maximum was 91.23 mg/L. Similarly, the minimum and maximum chloride concentration in the outflow of BL were 0.23 mg/L and 297.75 mg/L, respectively. Surprisingly, the average measured chloride concentration in the BL site was higher compared to the BH site. Since the BL basin does not get as much inflow, the chloride in the basin may be temporarily stored by the soil for a longer time. When the basin next receives inflow, it flushes out more chloride from the soil. Additionally, these different patterns may be due to sampling timing or management differences. Due to instrumentation challenges, samples were not always collected from BL and BH for the same events; however, BL consistently has several events with higher chloride than BH for the same event in winter 2022-2023. This suggests some possible differences in management- BH receives runoff from a road that is salted via municipal truck, while BL receives runoff from a parking lot and sidewalks that may not always be salted simultaneously with BH.

It is valuable to note that chloride values observed in the obtained samples here were lower than expected, based on previous grab samples at this site and other field studies. This is likely due in part to sampling events that occurred in a milder winter season.

Field study: Nutrients

The average total nitrogen (TN) concentration observed in the inflow and outflow water samples at BH site were 2.36 and 1.63 mg/L, respectively (Figure 9). Similarly, the median TN concentrations at BH site were 2.15 mg/L for inflows and 1.31 mg/L for outflows. The average TN removal was 14% from the BH site, while the median TN removal was higher at 30%. However, there were numerous events with negative removal values, indicating export of nitrogen from the basin (Figure 10). Timing of negative removal values was inconsistent at the BH basin, with these export events occurring across all seasons. In 2023, the TN removal efficiency at BH site remained almost constant ranging from 22 to 46%, with a very slight declining trend.

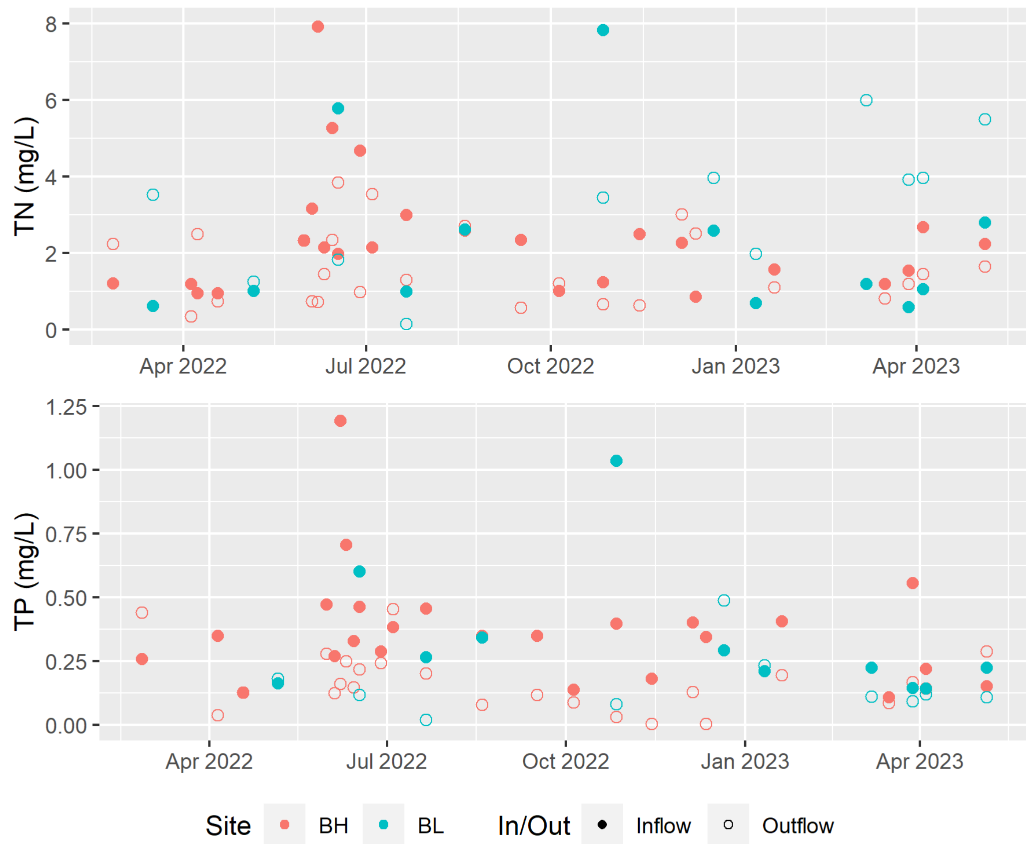

Figure 9: Nutrient (TN and TP) concentrations at BH (high salt basin) and BL (low salt basin)

The average TN concentrations at BL site were 2.32 mg/L for inflows and 9.78 mg/L for outflows (Figure 9). The median TN concentrations were found to be 1.13 mg/L for inflows and 3.73 mg/L for outflows. The higher average TN concentration in the outflows of BL site is due to one event where the TN was substantially higher (82 mg/L), which is considered an outlier and likely erroneous since all other outflow concentrations were below 6 mg/L. The average TN removal efficiency of the BL basin was -400%, while the median TN removal for the BL basin was found to be -96% (Figure 10). Thus, the basin is often exporting TN from the system. No distinct trend was seen in the removal efficiency during 2022. However, a decline in the removal efficiency can be seen in 2023 starting in the cold season from October 27, 2023, and it gets worse after increases in salinity in winter 2023. It further declines significantly from January 11, 2023 (-187%) to March 28, 2023 (-566%). The fact that there is consistently lower TN removal at BL basin compared to BH basin in early 2023 (Figure 10), along with consistently higher chloride concentrations at BL (Figure 8) implies a likely role of salinity in affecting nitrogen processing, rather than impacts of limited plant uptake of nitrogen at this time of the year.

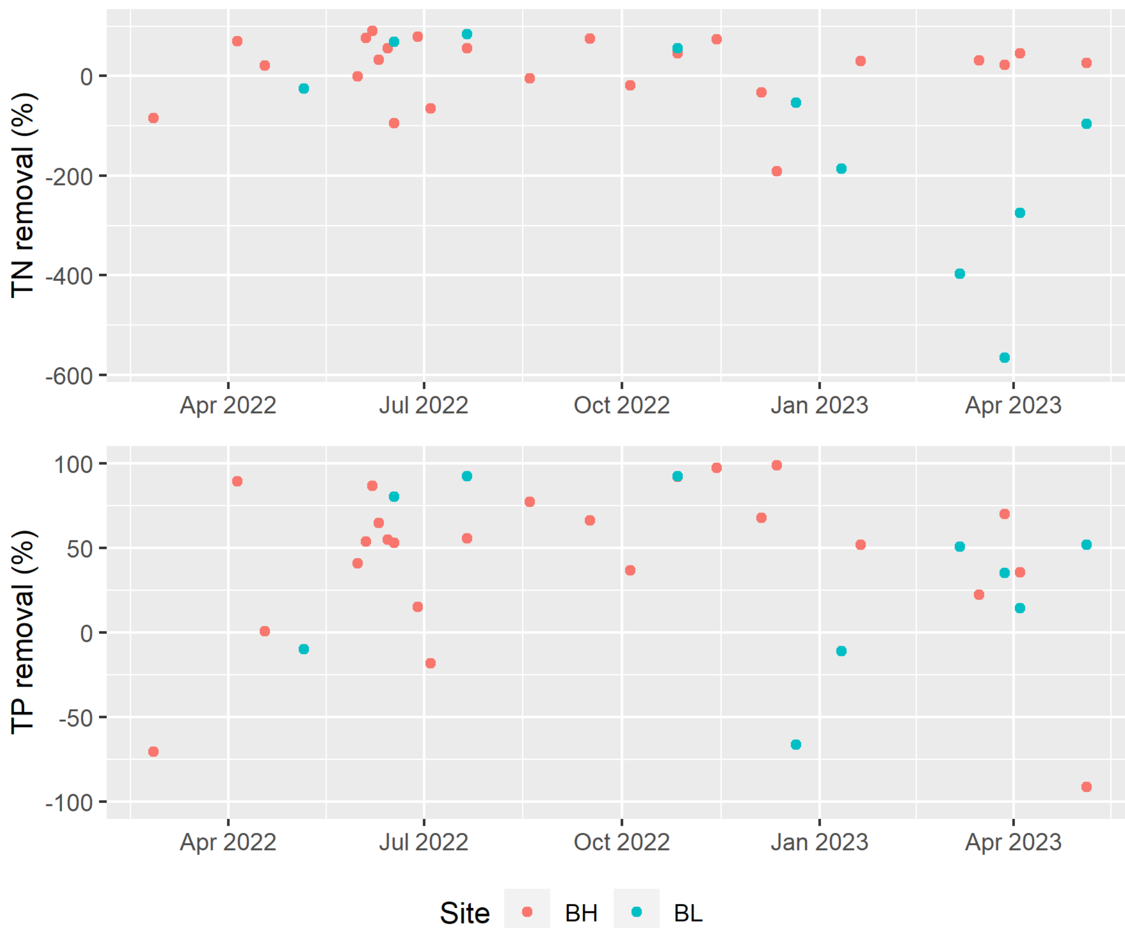

Figure 10: Nutrient (TN and TP) removal efficiency at BH (high salt basin) and BL (low salt basin)

The median TN concentrations observed in this study were higher compared to a collection of prior studies by International Stormwater BMP Database, where the median TN concentrations for inflow were 1.26 mg/L and 0.96 mg/L for outflow (Clary et al., 2020). One study evaluated three bioretention basins and observed the average TN concentration removal efficiency ranging from -196% to 48%, while the individual event's removal efficiency ranged from -426% to 100% (Lucke & Nichols, 2015), which were similar to the results obtained in this study. Other studies have also reported poor performance of bioretention basins in removing nitrogen, often due to leaching of N from organic material in soil media, as well as seasonal variability in biological N removal processes (Kakuturu & Clark, 2015; McManus & Davis, 2020a).

The average TP for the BH site was 0.37 mg/L for influent and 0.17 mg/L for effluent water samples. The median influent and effluent TP concentrations at BH site were 0.35 mg/L, and 0.15 mg/L, respectively (Figure 9). The average TP removal efficiency of the basin was 44%, while the median TP removal efficiency was quite high at 87%, demonstrating strong overall phosphorus removal (Figure 10). However, three events in spring or summer had negative removal efficiencies, indicating phosphorus export. The TP removal efficiency at BH site was -84% on February 25, 2022, which was much lower than its average and median removal efficiency suggesting the possible decline in TP removal efficiency due to the deicing salt applied on February 4, 2022. Similarly, a declining trend in the TP removal efficiency at BH site was seen in the year 2023 after the salt application in January, 2023. The TP removal efficiency was 99% during a December 12, 2023 rainfall event, and then it declined directly to 52% on January 20, 2023 and further to 22% during the March 16, 2023 event. It is unclear if this change is linked to de-icer application.

The average influent TP concentration at BL site was 0.33 mg/L with the median concentration of TP at the BL site was 0.23 mg/L, while the average effluent TP concentration was 0.49 mg/L with the median concentration of effluent was 0.12mg/L (Figure 9). The average TP removal was at BL site was -62%, with the median removal efficiency of TP was 35% at the BL site, which was lower than TP removal at the BH basin (Figure 10). Three events in winter or spring had negative removal efficiencies at the BL basin. However, these were not necessarily events with higher chloride concentrations.

Although there were a few events where leaching of phosphorus was observed in this study, the basins were able to reduce effluent TP concentrations in the majority of the sampled events. This study also supports the results of other prior studies in demonstrating good TP removal efficiency of bioretention basins (Davis et al., 2006; Liu & Davis, 2014; Randall & Bradford, 2013a).

Field study: Metals

The water samples were analyzed for various metals Cd, Cr, Cu, Ni, Pb, and Zn. The concentrations of Cd, Cr, Ni, and Pb were constantly lower than the detection limit (0.005 mg/L), and hence excluded from the analysis.

The average concentrations of Cu at the inflow and outflow of BH site were 39.46 µg/L and 18.83 µg/L (Figure 11). The average removal efficiency of Cu at BH site was estimated to be 28%, while the median removal was 45% (Figure 12). The removal efficiency of Cu at BH site ranged from -148% to 94%. A declining trend was seen in the removal efficiency of Cu from January, 2022 through early June, 2022. This could be linked to the effect of deicing salt that was applied twice in January and once in February. However, negative removal efficiencies were observed at a few points throughout the year, implying influence of factors beyond salt contributions.

The average concentrations at the BL site were 37.79 µg/L for the inflow and 55.34 µg/L for the outflow (Figure 11). The average removal efficiency of Cu at the BL site was found to be approximately -193%, while the median removal efficiency was 2% (Figure 12). There was one event in March, 2023 where the removal efficiency was incredibly low (over -2000%), which led to the lower average removal efficiency and should likely be considered an outlier. There were quite a few events seen where the removal efficiencies were negative meaning that Cu was leaching out from the system. In general, Cu retention was better at the BH basin than the BL basin, though it is not clear what the reason is. Although the export or leaching out of Cu in this study seems higher than desirable, it is still lower than one study in Washington that found the Cu export of around 600% from bioretention cells that had higher amount of compost (40%) as the media mix as reported in the International Stormwater BMP Database (Clary et al., 2020). The median inflow and outflow concentration of total Cu for a bioretention basin reported by International

Stormwater BMP Database was 13.1 and 7.13 µg/L, respectively, suggesting net removal of total Cu (Clary et al., 2020). However, it also reported that the inflow and outflow concentration for dissolved Cu were 6.85 and 7.54 µg/L, respectively, demonstrating net export of the dissolved Cu from the system (Clary et al., 2020).

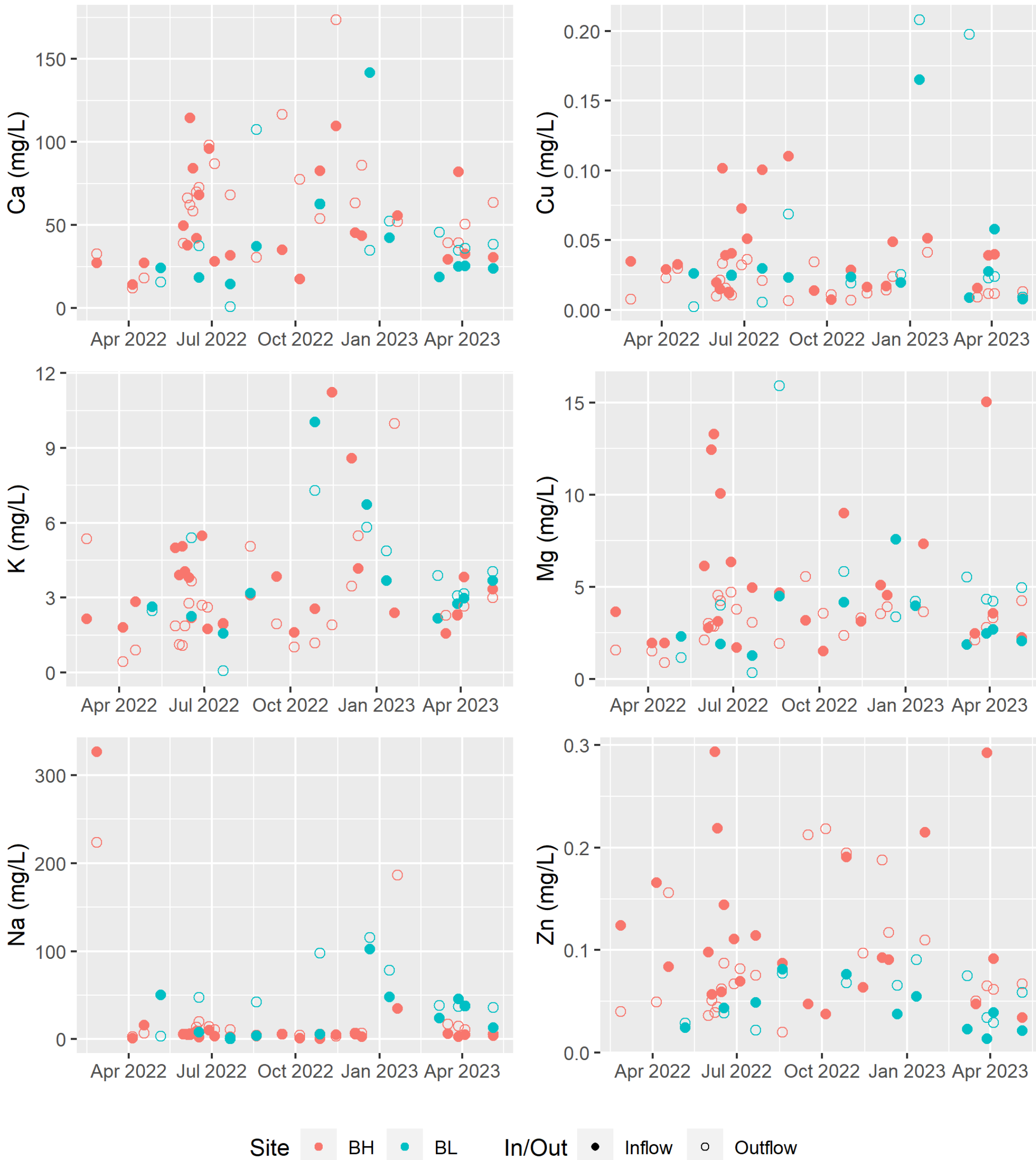

Figure **11**: Concentration of various metals and base cations at BH (high salt basin) and BL (low salt basin). One concentration of K (111.85 mg/L on 8/19/2022) was excluded from the figure for visualization purpose.

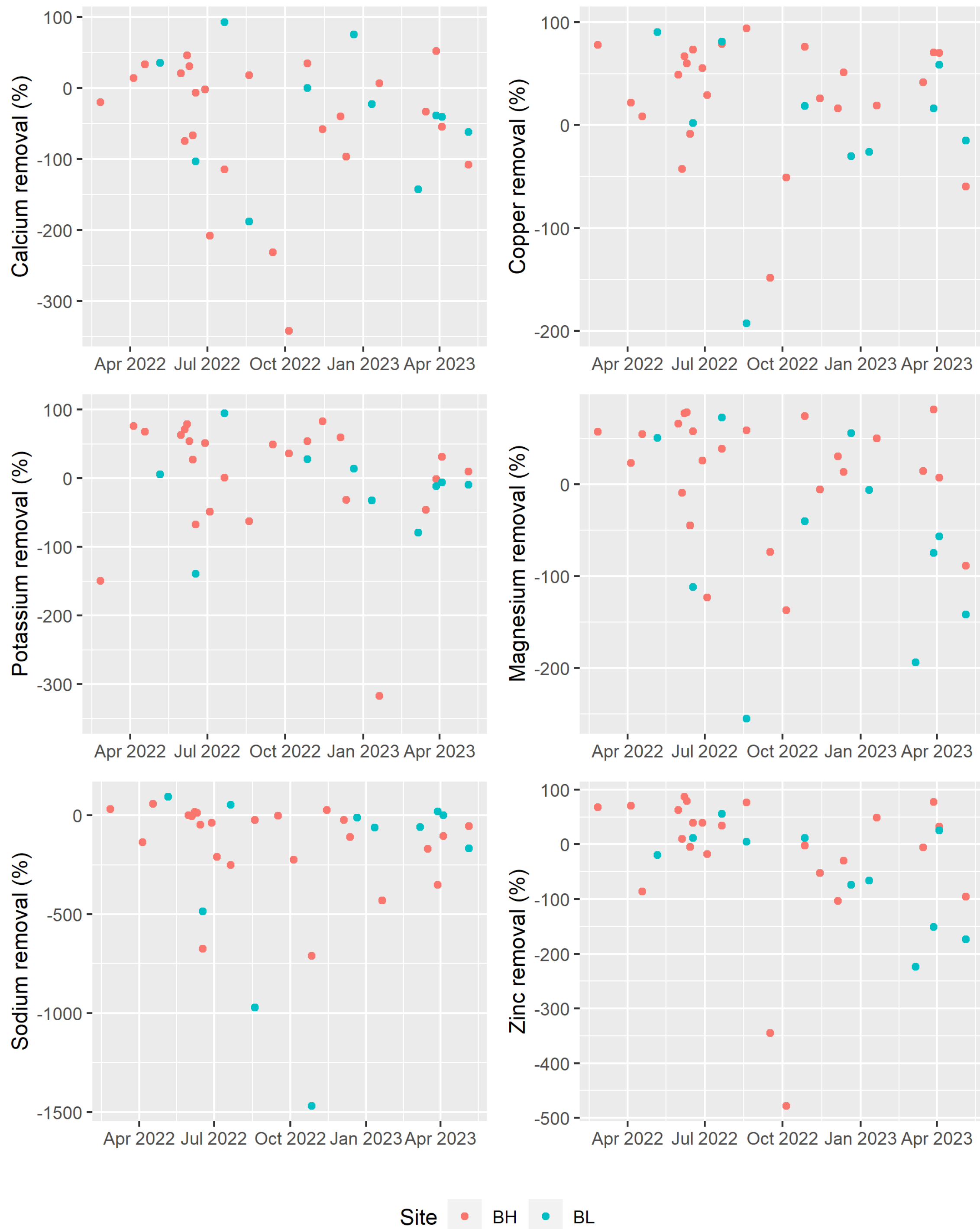

Figure 12: Removal efficiency of various metals and base cations at BH (high salt basin) and BL (low salt basin). Removal efficiency of Cu (-2214% on 3/7/2023) and K (-3415% on 8/19/2022) were excluded from the figure for visualization purpose.

The average Zn concentration in the outflows of BH site were found to be 0.09 mg/L which was 25% less than the average concentration in the inflows (0.12 mg/L) (Figure 11). On average, the removal efficiency of Zn was found to be -21%, while the median removal efficiency was 22%

(Figure 12). This removal efficiency was generally lower compared to the removal efficiency of Cu. While several low removal efficiencies occurred in winter and spring, the lowest values (indicating net export of Zn) actually occurred in fall 2022 at the BH basin. For the BL basin, the average inflow and outflow concentration of Zn were 0.04 and 0.05 mg/L, respectively (Figure 11). The average removal efficiency for Zn of -55% was worse than the BH basin, while the median removal efficiency was -20% (Figure 12). There was a distinct reduction in the removal efficiency in winter 2022-2023. The Zn removal efficiency at BL site decreased from -66% to -173% from January, 2023 to May, 2023. These reduced removal efficiencies occur during the same period as poorer water quality performance at BL for other constituents, as well as elevated chloride (Figure 8). The higher export of Zn from the bioretention basins compared to the Cu may be explained by their differences in sorption strength; similar patterns were also observed in the mesocosm study. Zn has higher sorption to metal oxides and is also considered to be more exchangeable compared to Cu, which may lead to the higher mobilization of Zn in the presence of salt in the basin (Doner, 1978; Karlsson et al., 2016; Kuo & Baker, 1980). One of the possible reasons behind the lower removal efficiency of Cu and Zn at the BL compared to the BH site may be that the soil in the BL site already has higher concentration of Cu and Zn which may have caused to leach out more metals from the system after the salt application, which needs further exploration through a separate soil assessment.

Field study: Base cations

The study also analyzed base cations (Ca, K, Mg, and Na). At BH site, the average influent concentration of Ca, K, Mg, and Na were 51.01, 3.69, 5.43, and 19.96 mg/L, respectively (Figure 11). Similarly, the average effluent concentration was observed to be 63.88, 2.78, 3.15, and 25.14 mg/L, respectively. The BH site was able to retain around 4% of K and 14% of Mg, while the basin exported 50% Ca and 143% of Na in the outflow (Figure 12). One of the possible reasons behind the higher export of calcium compared to potassium from the system could be the presence of calcium rich soil in the bioretention basin. Furthermore, this may also be caused by the presence of slightly acidic soil as well as vegetation uptake preferences. The flushing of Na from the BH site was quite evident, where Na is a typical component of de-icing salts.

For the BL site, the influent Ca, K, Mg, and Na concentrations were observed to be 39.62, 3.80, 3.16, and 31.26 mg/L, and effluent concentrations were 42.52, 13.82, 4.90, and 48.92 mg/L, respectively (Figure 11). All the base cations demonstrated net export patterns from the BL site, and the average export percentages were 36%, 322%, 64%, and 279% for Ca, K, Mg, and Na, respectively (Figure 12). The flushing of Ca and Mg were observed more after the salt application in 2023.

Field study: Total Suspended Solids (TSS)

At BH site, the average TSS concentration in the inflow was 198.76 mg/L and the outflow concentration was 10.58 mg/L. Similarly, the average influent TSS at BL site was 60.45 mg/L and the effluent TSS was 6.4 mg/L. The TSS was low in BL site compared to the BL site. Both basins showed great overall TSS removal with an average of 78% at BH site, and 77% at the BL site (Figure 4-12). Both sites were able to capture all of the TSS for some rainfall events with maximum removal efficiency of 100%. Most of the events showed >90% TSS removal (Figure 13). Samples for all events were not available for TSS analysis as it required more volume of water, and the ISCO automated samplers or lysimeters were not able to capture the required volume for certain events. Thus, it was challenging to draw any conclusions about variability in performance over time.

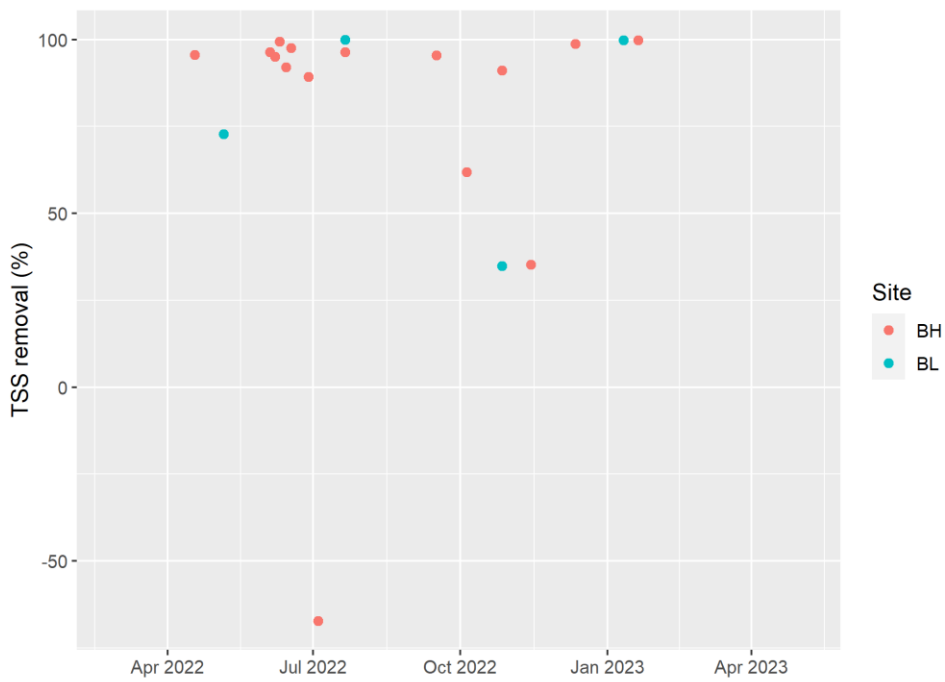

Figure **13**: Total suspended solids (TSS) removal efficiency of BH (high salt basin) and BL (low salt basin). Fewer samples had TSS data as compared to other analytes due to sample volume constraints.

Field study: Soils

Soil chemistry data from the two basins allows comparison between sites and in time. Soils at the BH basin demonstrate overall higher concentrations for all measured constituents (Table A1). These patterns can result from a combination of overall loading to the basin, as well as ability of basin soil and plant characteristics to support certain retention rates. Looking at samples taken at the start and end of the study (~1.5 years), concentrations of several pollutants of interest demonstrate an increase or net accumulation at the BH basin. Accumulating pollutants include zinc, copper, and phosphorus. However, at the BL basin, concentrations of zinc, copper, and phosphorus demonstrated no change after 1.5 years. While it is possible that we were unable to detect a change due to a relatively short time period and only five soil samples taken per basin, this overall pattern does align with what was observed in the water sampling- overall better pollutant removal and retention for the BH basin as compared to BL basin.

Field study: Statistical relationships

The statistical relationship of effluent concentrations and removal efficiencies with different parameters were tested using non-parametric spearman correlation coefficient (ρ) since the data did not follow normal distribution. For BH site, no significant correlation existed between concentrations of Cu and the base cations. Similarly, there was no significant correlation of Zn concentration with any of the base cations at the BH site, except for Ca and Mg. There was a positive correlation of Zn concentration with Ca (ρ = 0.52, p-value = 0.01) and Mg (ρ = 0.48, p-value = 0.019) at BH site. For BL site, there was no significant correlation of Cu concentration with Ca, K and Mg. However, there was a significant positive correlation of Cu with Na (ρ = 0.66, p-value = 0.031) at BL site. Similarly, at the BL site, Zn showed strong positive correlation with all of the base cations considered in the study – Ca (ρ = 0.88, p-value = 0.00067), K (ρ = 0.76, p-value = 0.0092), Mg (ρ = 0.71, p-value = 0.019), and Na (ρ = 0.71, p-value = 0.019). Furthermore, the metal concentration data were combined together for both sites to see if any correlation existed between effluent concentration of metals and any base cations. Statistical analysis showed significant positive correlation of Cu with Mg (ρ = 0.51, p-value = 0.002) and Na (ρ = 0.4, p-value = 0.017). Similarly, there was a significant positive relationship of Zn with Ca (ρ = 0.65, p-value = 3.98E-05) and Mg (ρ = 0.35, p-value = 0.041). This showed that the metal concentration in the effluent water sample increased with the higher concentration of base cations, when data from both sites were combined together.

The relationship of metals removal efficiency was also tested against soil salinity (averaged for one week prior to rainfall event), rainfall depth, TSS, and chloride. There was no relationship of Cu removal efficiency with any of these variables at the BH site. Similarly, no significant relationship of Zn removal efficiency was observed with soil salinity, TSS and chloride. However, there was a significant negative relationship of Zn removal efficiency with rainfall depth (ρ = -0.45, p-value = 0.027) at BH site (Figure 15). No significant relationships existed between Cu removal and other parameters (salinity, rainfall, TSS and chloride) at the BL site separately as well as when all the removal efficiencies from both sites were combined together. There was a significant negative relationship of Zn removal efficiency with rainfall depth at the BL site (ρ = -0.73, p-value = 0.015), as well as when the data from both sites were combined together (ρ = -0.51, p-value = 0.0018). Although not significant, there was a slight negative relationship of Zn removal with soil salinity (ρ = -0.59, p-value = 0.061) at the BL site (Figure 14). Thus, these relationships indicate best removal of Zn with smaller rain events, and poorer Zn removal (or more Zn flushing) at the BL site with high salinity. The poor removal of Zn due to high salinity could be attributed to its mobilization characteristics. Zn is generally more mobile compared to Cu, and is more likely to be flushed out with the high salinity and higher amount of rainfall.

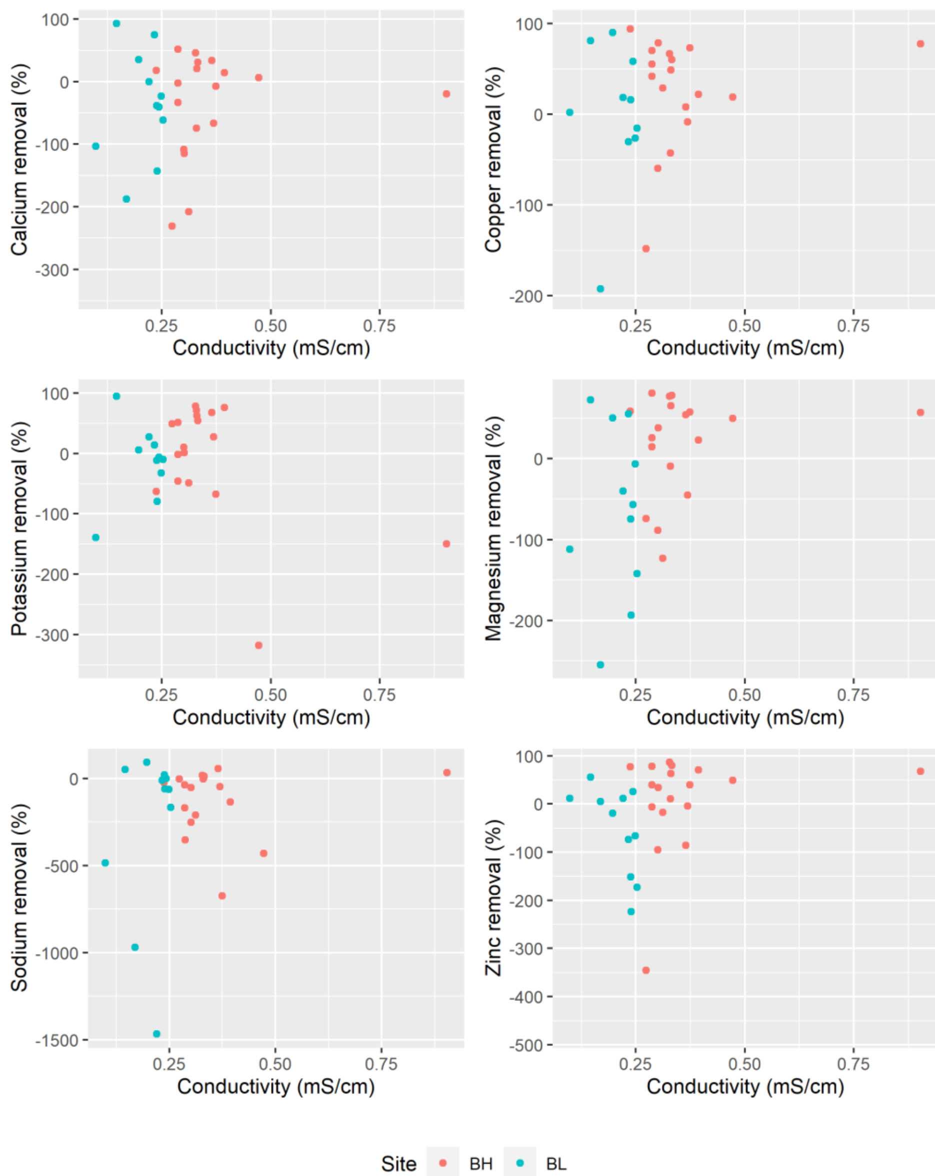

Figure **14:** Relationship of metals and base cations removal efficiency with soil salinity

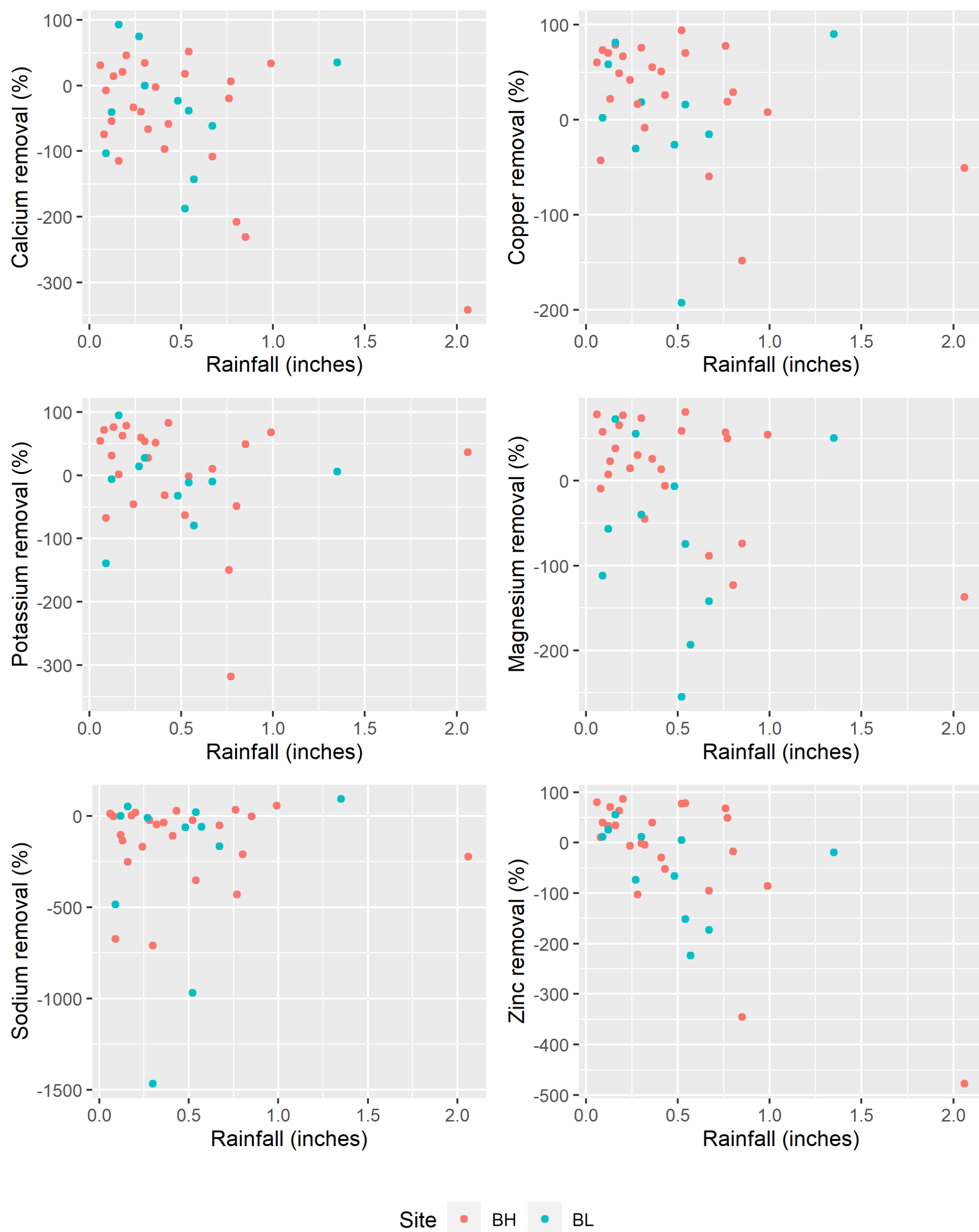

Figure **15**: Relationship of metals and base cations removal efficiency with rainfall

There was no significant relationship of effluent TN concentration with any of the base cations at BH site, except with K (ρ = 0.66, p-value = 6E-04). Similarly, there was a strong positive relationship of TN concentration with Mg (ρ = 0.74, p-value = 0.013) at the BL site, while no significant relationship existed with other base cations. Similarly, all the TN concentrations were grouped together from both sites and the statistical analysis showed significant strong positive correlation of TN concentration with three base cations – K (ρ = 0.73, p-value = 1.72E-06), Mg (ρ

= 0.55, p-value = 7E-03), and Na (ρ = 0.6, p-value = 2E-03). Furthermore, correlation of TN removal efficiency was also tested with salinity, rainfall, TSS, and chloride. There was a significant positive relationship of TN removal with chloride (ρ = 0.57, p-value = 0.007) at the BH site, while no significant relationship existed with soil salinity, rainfall and TSS. At BL site, no significant relationship of TN removal was observed with any of the parameters (soil salinity, rainfall, TSS and chloride). When all the TN removal efficiencies from both BH and BL sites were combined together, a significant relationship of TN removal was seen only with rainfall (ρ = -0.35, p-value = 0.039). No relationships were observed with soil salinity, TSS and chloride. The positive relationship of TN removal with chloride could be due to the possible complexation of ammonium nitrogen with chloride at soil exchange sites.

The effluent TP concentration was positively related with Na (ρ = 0.51, p-value = 0.01) at the BH site. However, it was not related to any other base cations at the BH site. Considering the BL site, no significant relationship of TP concentration was observed with any base cations. Furthermore, when all the TP concentration at both BH and BL sites were analyzed together, significant correlation was observed between TP and Na (ρ = 0.38, p-value = 0.024). This may indicate potential complexation of phosphorus with compounds containing these cations. The TP removal efficiency was not associated with soil salinity, rainfall, TSS and chloride at both BH and BL site. However, when the TP removal efficiencies from both sites were combined together, significant negative relationship was observed between TP removal and rainfall depth (ρ = -0.36, p-value 0.034). Other than with the rainfall depth, there was no association of TP removal with other parameters (soil salinity, TSS and chloride). Results showed that the performance of basins in TN and TP removal was better with smaller rainfall events (Figure 17). Although there was negative correlation of TN and TP removal with soil salinity, it was not statistically significant. The fact that there is both a negative relationship of nutrients with soil salinity and a positive relationship with chloride alludes the challenge of understanding the complex factors and lags in time that can affect water quality processes and their interpretation.

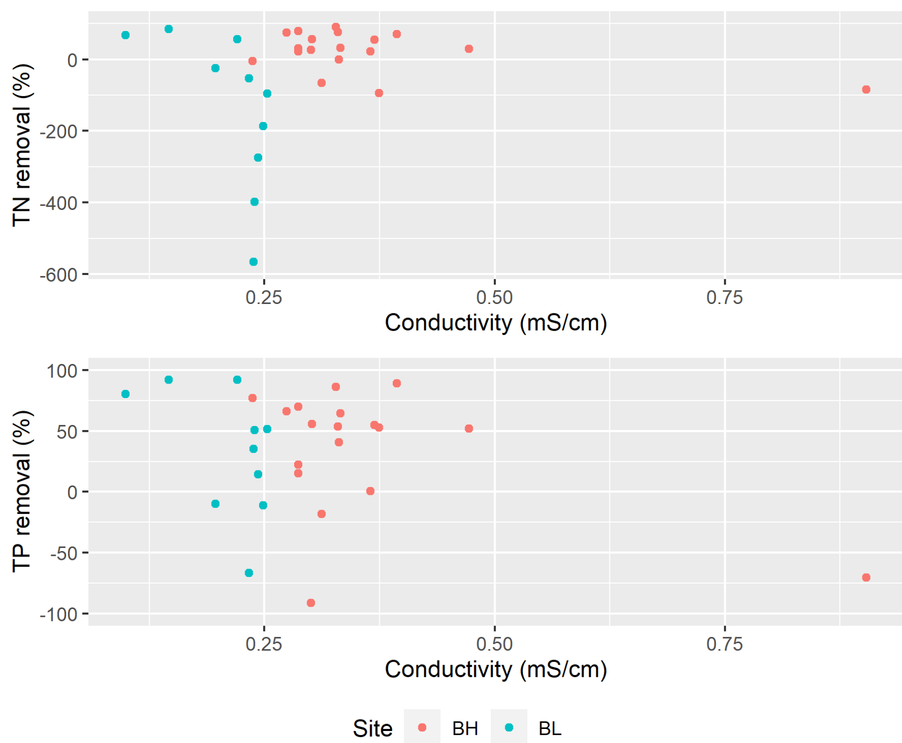

Figure 16: Relationship of nutrients (TN and TP) removal efficiency with soil salinity

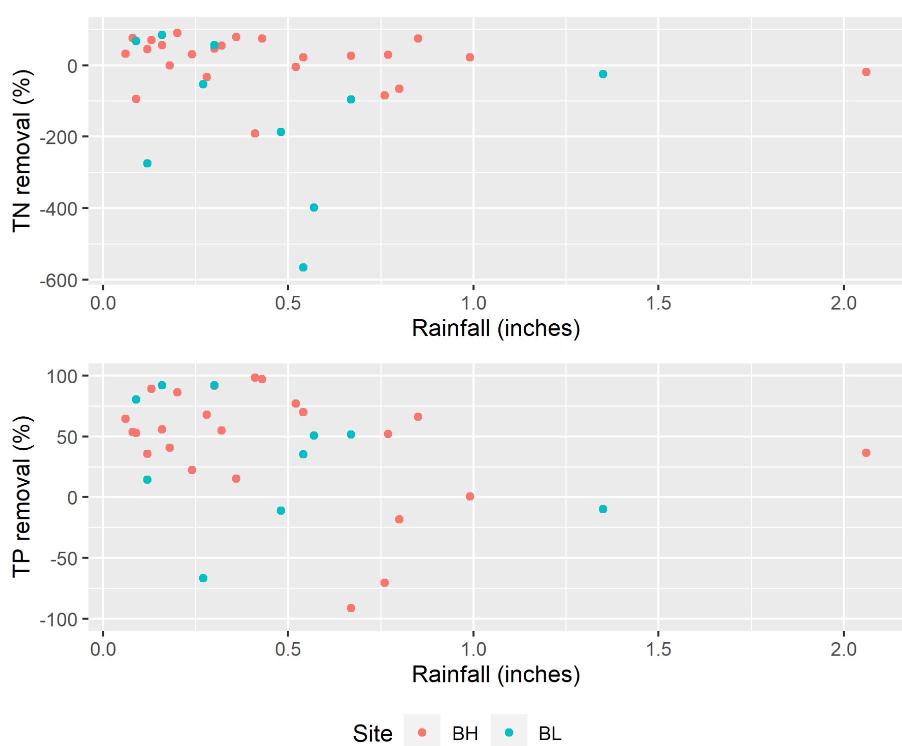

Figure 17: Relationship of nutrients (TN and TP) removal efficiency with rainfall

Mesocosm study

Mesocosm study: Chloride and sodium response

Chloride concentrations discussed below are shown in Figure 18. Initial chloride concentrations in the first mesocosm sampling in November 2021 (before the experiment had officially started and not shown in Figure 18) varied from 1-40 mg/L, with a median of about 16 mg/L. This was substantially higher than effluent concentrations in the late summer of 2022, indicating that the soil may have been previously exposed to salt.

As expected, chloride behaved conservatively throughout the experiment. Inflow samples of the nonsalt synthetic stormwater indicate that concentrations were generally less than 3 mg/L. Effluent concentrations during the salt applications in March 2022 and February 2023 came fairly close to their respective inflow concentrations before rapidly declining when the applications ended. The decline was fastest in the first 4 weeks after salt application in 2022 but leveled off over time. By 8 weeks, the effluent had mostly dropped to background concentrations (which were roughly equal to the nonsalt inflow concentrations). Some mesocosms remained very slightly elevated into the late summer and early fall. The 2023 data has been consistent with trends observed in 2022. Sodium concentrations discussed below are shown in Figure 19. While sodium data collection began only in August 2022, the few months of data collected at the end of the year's watering period indicated that sodium

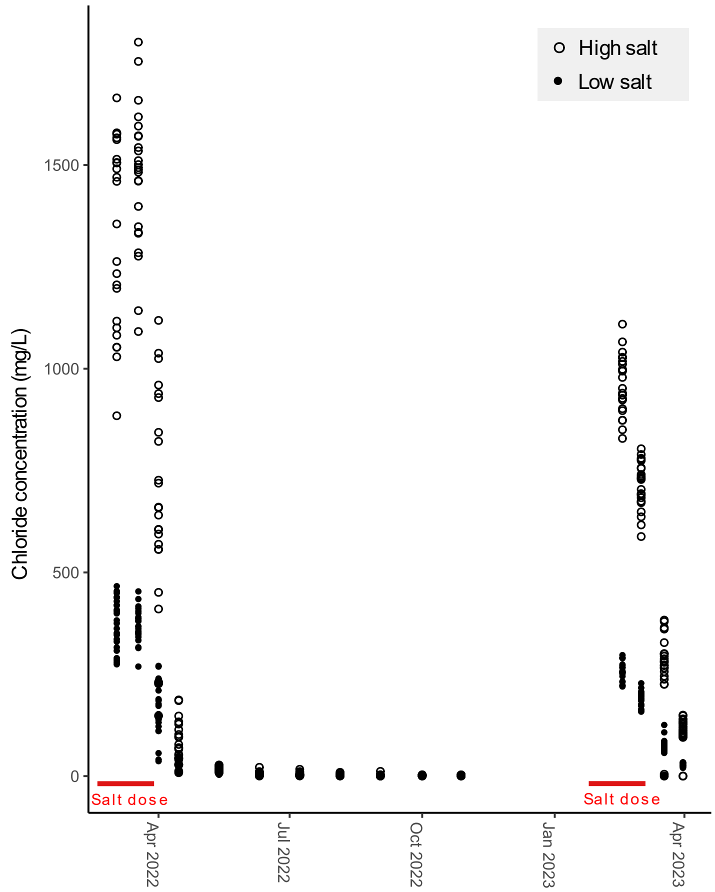

Figure 18: Chloride concentrations over the course of the experiment.

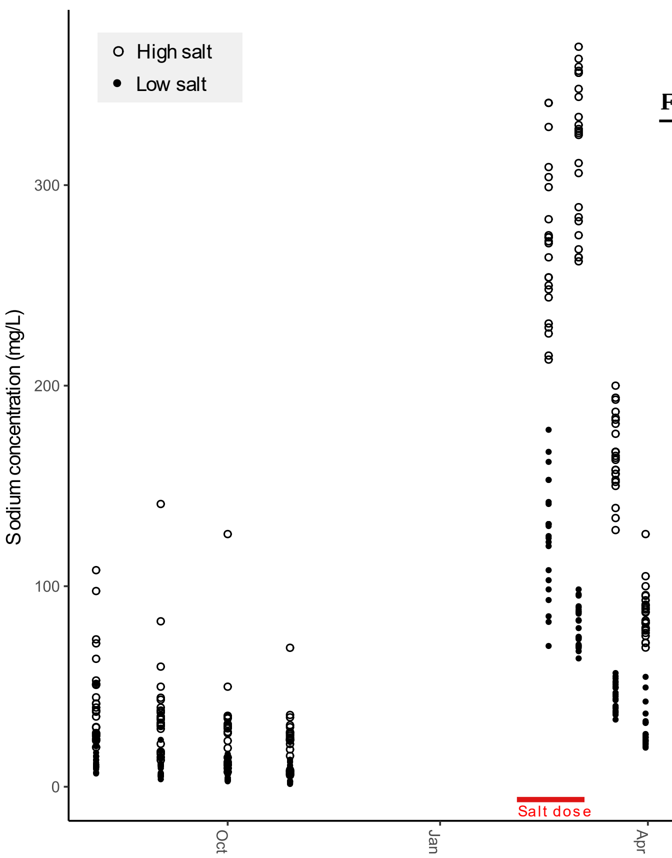

Figure 19: Sodium concentrations over the course of the experiment.

concentrations did not stabilize in all the mesocosms by late fall. Even in the mesocosms with the lowest concentrations, the concentrations were still slowly decreasing every month. Nonsalt inflow sodium concentrations were less than 2 mg/L and usually less than 0.5 mg/L. By the end of October, sodium in all mesocosms was still at least several times above the inflow concentrations, and some were an order of magnitude higher. The slower flush for sodium than for chloride could result in a slow buildup of sodium in the soil over years of salt application. In the spring of 2023, inflow sodium concentrations were calculated to be around 780 mg/L in the high-salt mesocosms and 195 mg/L in the low-salt mesocosms. The high salt concentrations spiked but did not approach these values. There was possible instrument error, potentially resulting in underreporting of sodium during the salt application period. Another explanation is sodium interaction with the media, with most of the sodium sorbed before the media's capacity was overwhelmed. Regardless, the overall trend for salt was similar to chloride, and effluent concentrations for both low- and high-salt mesocosms declined rapidly but appeared to be approaching one another and leveling off in spring 2023.

As discussed in Chapter 1, chloride is highly conservative, able to interact only with the few anion adsorption sites, while sodium sticks to the many cation exchange sites in the soil (Denich et al., 2013a; Kakuturu & Clark, 2015; Mason et al., 1999). This explains the rapid chloride flushing and slower sodium flushing. Denich et al. (2013) conducted a deicing salt mesocosm study that included a mass balance of sodium and chloride, and they found similar flushing rates in the first few months. While a full mass balance of sodium is not possible a mass balance for chloride is made uncertain by the variation in inflow concentrations and unmeasured outflow concentrations in this study, estimated mass balances indicated nearly full chloride flushing and much less complete sodium flushing. Denich et al. (2013) also found nearly full chloride flushing, but their mesocosms suffered from net losses of sodium, which does not appear to have occurred in this experiment. Field studies of infiltration-based green infrastructure like Burgis et al. (Burgis et al., 2020) and Mullins et al. (Mullins et al., 2020) have found short-term storage of sodium and chloride followed by chloride flushing by spring and summer and very limited long-term sodium storage. Studies of other forms of green infrastructure, such as the roadside retention/detention ponds studied by Barbier et al. (Barbier et al., 2018) and McPhillips & Walter (2014), have also found salt to flush back to baseline in spring and summer. Studies examining soils, especially those near roads, have found similar trends, as discussed by Robinson et al. (Robinson et al., 2017).

Kaushal et al. (Kaushal et al., 2005) documented stream salinization in response to road salt and recorded long-term increases attributed to new road construction; failure of short-term soil chloride storage to fully flush between winters; and chloride storage in groundwater, enabling a slow buildup over time. Year-round chloride persistence has been recorded by many studies, including in roadside drainage systems by Ostendorf et al. (Ostendorf et al., 2001), roadside soils by Czerniawska-Kusza (Czerniawska-Kusza et al., 2004), and green infrastructure and streams by Snodgrass et al. (Snodgrass et al., 2017). While chloride flushed from the bioretention mesocosms by the time of the next salt application, greater chloride loads or longer application periods could have influenced the results. These mesocosms replicated bioretention basins with an impermeable liner, but basins without a liner funneled chloride into groundwater, creating contaminated plumes, as studied by Burgis et al. (2020) and Snodgrass et al. (2017). Even if chloride flushes fully from the bioretention soil, the hydrologic connection between bioretention with free exfiltration to the subsoil and slow groundwater flowpaths could result in longer term impacts on nearby streams.

Mesocosm study: TSS response

TSS load removal efficiency over the experiment discussed below is shown in Figure **20**. Concentration removal efficiency trends were the same as load removal efficiency, so a graph of concentrations is not shown. The initial sampling in November did not include added influent TSS, so conclusions can not be drawn, but the recorded effluent TSS ranged mostly from 1 to 20 mg/L, with a few outliers ranging up to about 70 mg/L. Because the influent TSS was added using leftover bioretention topsoil, the particle sizes for the influent TSS were the same as for the bioretention media, and influent TSS was likely filtered very effectively. This, combined with the presence of TSS in the effluent even when none was added to the influent in November, indicates that much, if not all, of the effluent TSS consisted of filter media that washed out.

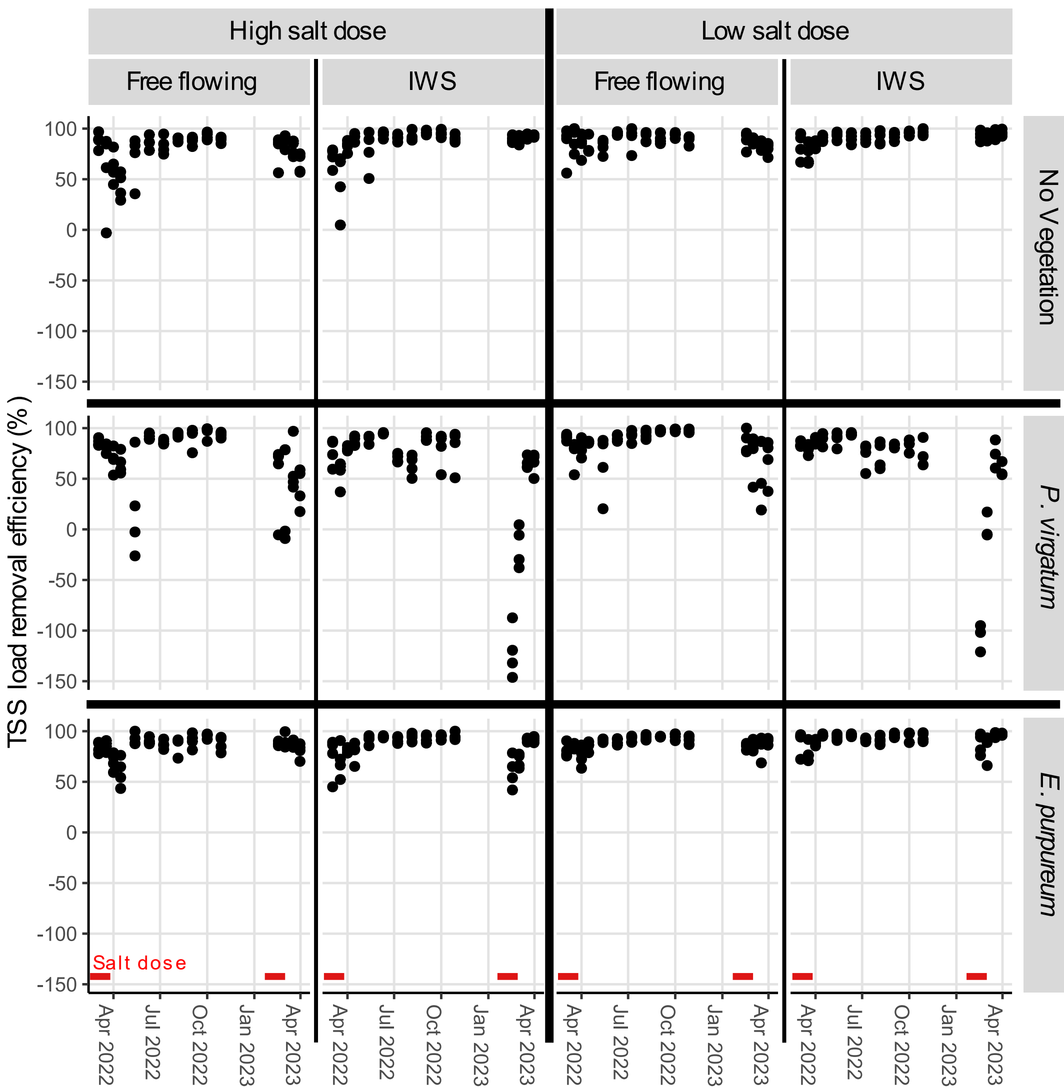

Figure 20: TSS load removal efficiency over the course of the experiment. Red bars indicate salt application.

Replicates in all treatment groups experienced some sort of dip or variability in load removal efficiency in the first 1-2 months of 2022, attributable to colloid dispersion induced by NaCl application. The dip could be fairly severe, almost wiping out removal in some mesocosms but not affecting it much in others. The effect often appeared to be worse in the high-salt treatments, and the worst removal was delayed by 2 to 8 weeks after salt dosing ended. This delay was likely influenced by the time it took for sodium to flush and background electrolyte concentrations to dip low enough for colloid dispersion to occur. Nevertheless, there was little to no difference in the timing between high and low NaCl treatments. This may be explained by high sodium concentrations flushing much more rapidly than low ones, so sodium concentrations for high- and low-salt mesocosms approached one another after just 4 weeks. The initial dip in TSS removal efficiency did not appear to be influenced by the presence of IWS or the presence or type of vegetation. The dip eventually returned to very high (almost always over 75%) load removal efficiency in nearly all mesocosms for the remainder of 2022. The return was mostly regardless of vegetation, IWS, or salt treatment. The exception was for the IWS *P. virgatum* replicates, both high- and low-salt. In early July, these mesocosms began showing large variability in TSS removal performance, varying from 50% to nearly 100%. The source of the variability is unclear. It occurred in both high- and low-salt treatment groups, so concentration appears to have had little or no effect. By the end of the year, even by July, most sodium flushing was complete, yet the variability continued, potentially caused or contributed to by an interaction between *P. virgatum* and IWS.

In the second spring (up to the current sampling date), most *E. purpureum* and unvegetated replicates showed good removal efficiency, generally regardless of salt concentration or IWS presence. Surprisingly, the *E. purpureum* free-flowing and unvegetated IWS mesocosms showed little signs of colloid dispersion. However, other replicates did show signs of variability or declining removal efficiency, and the *E. purpureum* IWS replicates showed an immediate drop. The drop, not observed in the first spring, could have resulted from increased vulnerability to colloid dispersion after the first year of salt application, yet it was surprising, considering the decreased salt dose overall. The *P. virgatum* replicates all showed significantly increased variability, but those with IWS were by far the most affected, with a significant immediate drop (as with *E. purpureum*) that improved over subsequent events. Some *P. virgatum* replicates were even the first in the experiment to net-release TSS. Again, salt concentration appeared to have little effect on the trend, but the timing implies that this poor performance could have been the result of salt-induced colloid dispersion. However, it is surprising that colloid dispersion would occur when the background sodium concentrations were still so high, and other studies of NaCl in bioretention and soil have found flocculation or very limited effects on TSS at high sodium concentrations (Amrhein et al., 1992, 1993; Kakuturu & Clark, 2015; Szota et al., 2015). Perhaps the second year's lower sodium inflow concentration helped enable dispersion. The performance drop could also be attributable to the effects of freeze-thaw before the mesocosms were brought inside, although it would also be surprising that the stabilization time was so long. Studies like Kratky et al. (Kratky et al., 2017), Khan et al. (Khan et al., 2012), Muthanna, Viklander, Blecken, & Thorolfsson (Muthanna et al., 2007), Roseen et al. (Roseen et al., 2009), Søberg et al. (Soberg et al., 2020), and Géhéniau et al. (Geheniau et al., 2015) have shown that bioretention performs well for TSS removal even in the winter.

These results suggest that *P. virgatum* somehow destabilized the filter media or caused a release of TSS greater than the other vegetation treatments and that the release was amplified by the presence of an IWS zone. The spring 2023 performance could also be linked to the variability that the *P. virgatum* IWS mesocosms showed the previous fall. Perhaps the destabilization amplified the effects of or increased vulnerability to colloid dispersion caused by sodium or freeze-thaw. The previous year's salt application could also have contributed to increased vulnerability to subsequent dispersion events. Destabilization could also have been linked to the immediate drop in *E. purpureum* IWS mesocosms; perhaps vegetation in general interacted with IWS in a way that affected TSS output.

After statistical analysis, *P. virgatum* and salt concentration were found to be the best statistically significant predictors of TSS (p-values in Table **3**). The results were the same for concentration, load, concentration removal efficiency, and load removal efficiency. *P. virgatum* and high-salt treatments were negatively correlated with TSS removal efficiency, so *P. virgatum* and high salt concentrations resulted in lower removal efficiencies. Both variables were very weak predictors of TSS removal, with a combined adjusted R^2 of 0.11 for load removal efficiency. This is unsurprising for salt, which generally influenced removal only within the first 2 months after application, while trends over the remainder of the year were determined by other variables. Both high- and low-salt mesocosms also flushed quickly, eventually approaching the same values at similar times despite starting at different concentrations, so the difference between them diminished rapidly after the first month or two of flushing. *P. virgatum* began to perform significantly differently from the other mesocosms only in July 2022, limiting its usefulness as a predictor.

In the literature, the interactions between TSS and IWS or vegetation have been somewhat varied. Some bioretention studies, such as Li et al. (Li et al., 2014), Subramaniam et al. (Subramaniam et al., 2015), and Søberg et al. (2020), have found IWS to improve the consistency of bioretention and its overall TSS removal performance. The improvements have been attributed to increased retention time. Other studies, such as Barrett et al. (Barrett et al., 2013) and Blecken et al. (Blecken et al., 2009), have found IWS to have no noticeable effect on TSS performance. It is therefore surprising that, in this experiment, the *P. virgatum* IWS mesocosms showed such poor removal. The reason for this trend is unclear. However, across most of the data in this study, IWS had little to no effect on TSS performance, which fits results in the existing literature. Perhaps IWS interacts negatively with TSS removal performance only under very specific circumstances. Studies such as Shrestha et al. (Shrestha et al., 2018) and Read et al. (Read et al., 2008) have found different vegetation species to vary in their removal of TSS but to generally perform well. The poor performance of some *P. virgatum* replicates in this study is surprising in view of such studies.

Several studies of bioretention and roadside soils have linked NaCl with decreased TSS removal performance, soil clogging, and increased particulate outflow, such as McManus & Davis (2020), Denich et al. (2013), Amrhein et al. (1993), Amrhein et al. (1992),and Kakuturu & Clark (2015). These studies have attributed such effects to colloid dispersion and have variously found the effects of deicing salt on TSS to lag or last longer than the period of dosing. They have also observed clogging of filter media, which in this study was observed in only one low-salt *P. virgatum* IWS mesocosm, although infiltration rates were anecdotally low in many of the *P. virgatum* mesocosms. Some studies, such as Amrhein et al. (1992), Amrhein et al. (1993), Kakuturu & Clark, (2015), and Szota et al. (2015), did not find TSS removal or related media effects like clogging to worsen with increasing salt concentration, and they attributed this to the need for electrolyte concentrations to be low enough for colloid dispersion and to extremely high sodium concentrations favoring flocculation of soil particles. The lack of effect of high sodium concentration on TSS has also been attributed to overwhelmed exchange capacity of the soil, resulting in much of the sodium flushing before it is able to contribute to effects like dispersion. While this study showed high concentrations of sodium to have a slightly greater effect on TSS removal performance, the difference was very minor and could have been caused by a slightly increased duration of sufficiently high sodium to favor dispersion.

Across all mesocosms and events, TSS concentration removal efficiencies were 67% on average, with a median of 79%. The average effluent concentration was 34.5 mg/L, with a median of 22.5 mg/L, but high concentrations ranged into the low hundreds. TSS load removal efficiencies were 81%, with a median of 88%. TSS performance by treatment (Table 2) indicates similar trends to those discussed above. Free-flowing and IWS averages and medians were similar, but low-salt mesocosms performed better than their high-salt counterparts overall.

There was also a notable difference in vegetation treatment, with *P. virgatum* performing worse than *E. purpureum* and unvegetated mesocosms and dragging down the overall performance of vegetation. TSS removal efficiencies and effluent concentrations in this experiment were decent and generally lined up with what previous studies have demonstrated but were a little poorer than most previous results (Clary et al., 2020; Hunt et al., 2006; Shrestha et al., 2018). Poorer performance is not surprising, considering the effects of salt application; in the summer and fall removal was often excellent.

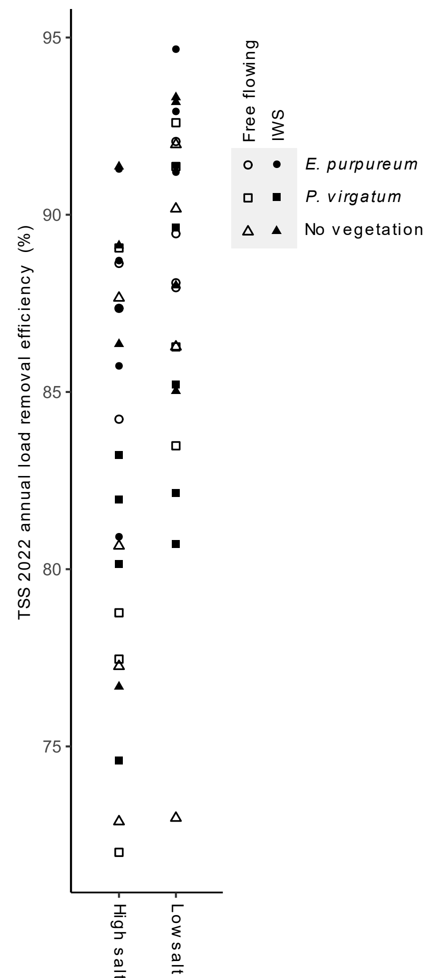

Figure 20: Total annual 2022 TSS load removal efficiency.

The overall average annual load removal efficiency was 86% and the median was 87%. There was a noticeable difference between high- and low-salt performance, and low-salt mesocosms performed well more consistently than mesocosms that received the higher salt

Table 2. TSS load and annual load removal efficiencies by treatment.

Treatment	Average removal (%)	Median removal (%)	Annual average removal (%)	Annual median removal (%)
Vegetation	78.6	87.5	85.8	87.3
No vegetation	85.4	89.2	85.2	87.0
E. purpureum	87.4	90.4	88.9	88.7
P. virgatum	69.5	83.8	82.6	82.2
IWS	79.7	89.3	86.7	87.4
Free flowing	82.1	87.1	84.6	86.8
Low salt	84.9	90.0	88.3	89.5
High salt	76.9	86.7	83.1	83.8

concentration, as shown in Figure 20. This was confirmed statistically with an adjusted R^2 of 0.33 and the good statistically significant predictors of salt concentration and *P. virgatum* (p-values in Table 3, *E. purpureum* not included because it failed the). Without the dip in *P. virgatum* performance in early 2023, the vegetated and unvegetated mesocosms were similar in annual performance, as shown in Table 2. Salt concentration was the only treatment that varied significantly, with low performing better than high, as expected.

Table 3. P-value significance levels of tests for load removal efficiency and annual load removal efficiency.

	Treatment	TSS	TN	TP	Cu	Zn
Event removal efficiency:	Vegetation	0.01*†	<0.001	<0.001	0.001	n.s.
	E. purpureum	<0.001†	0.01†	0.1†	n.s.	n.s.
	P. virgatum	<0.001*	<0.001†	0.01†	0.01†	n.s.
	Low/High Salt	<0.001*	n.s.	<0.001*	0.01*	0.05*
	Free-flowing/IWS	n.s.	<0.001	<0.001	<0.001	0.1
Annual Removal Efficiency:	Vegetation	n.s.	<0.001	0.05	n.s.	n.s.
	E. purpureum	0.01	0.05†	n.s.	n.s.	n.s.
	P. virgatum	0.1*	0.05†	n.s.	n.s.	n.s.
	Low/High Salt	0.01*	n.s.	0.01*	n.s.	0.05*
	Free-flowing/IWS	n.s.	0.001	<0.001	0.1	0.1

n.s Not significant
* Negative effect on removal efficiency
† Very poor or redundant predictor

Mesocosm Study: Nitrogen response

The pre-experiment samples collected in November of 2021 had very high nitrate-N and total nitrogen. The results of those samples revealed significant nitrogen load flushing for nearly all the mesocosms, among the worst load and concentration performances during the experiment. The unvegetated free-flowing mesocosms performed the worst, with an average load removal efficiency of about -480%. The unvegetated IWS mesocosms also performed poorly but much better than the free-flowing mesocosm replicates, with an average of nearly -190%, though performance was highly variable across the group. Vegetated free-flowing mesocosms performed even better, and both species were similar (-65% for *E. purpureum* and -43% for *P. virgatum*). Performance remained variable, but a few replicates did manage slight positive removal. The best group of replicates had both vegetation and IWS, with mostly positive load removal efficiencies (though with high variability). *E. purpureum* removed 5% of the total nitrogen load on average, and *P. virgatum* removed 1%.

This first collection point hinted at trends that would become clearer as the experiment continued. While IWS and vegetation both improved nitrogen removal, combining them yielded the best results, maximizing performance and reducing variability. The massive nitrogen export could be attributed to a first-flush effect, but – as will be seen – this flushing did repeat later in the experiment. The soil had a fairly high organic-matter (5-6%, a figure that does not reflect the sieved-out larger woody debris, as noted in the methods, or the added woodchips) content for bioretention media when compared with values discussed in Chapter 1. Mineralization of soil organic matter, as well as the wood chips added in the sand layer, could explain the nitrogen

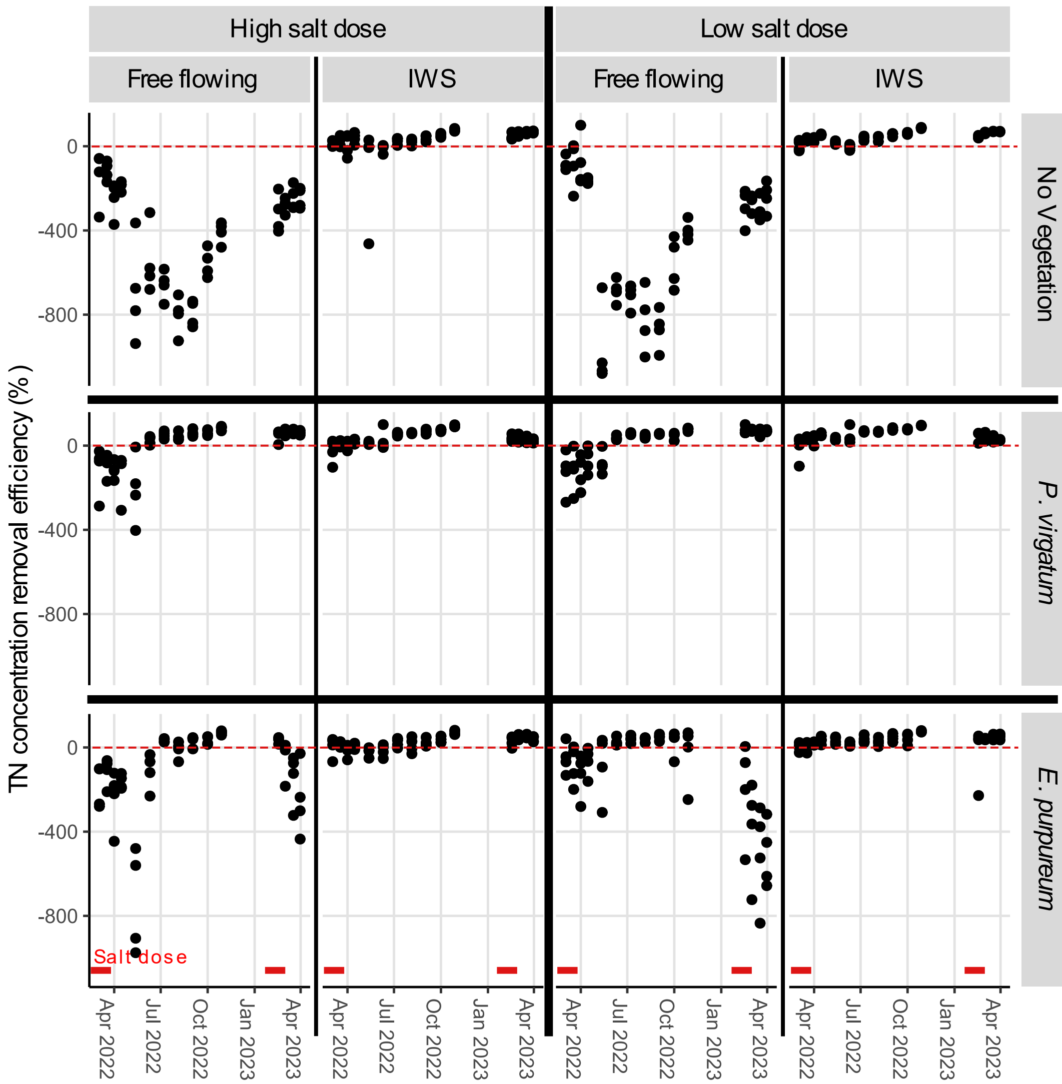

Figure 21: TN (total nitrogen) concentration removal efficiency over the course of the experiment. Dashed red line shows 0% removal efficiency. Red bars indicate salt application.

export. The variability and somewhat poor performance of IWS and vegetation indicated that the plants and denitrifying microbial communities were not yet fully established at the time the samples were collected.

Total nitrogen concentration and load removal efficiencies discussed below are shown in figures **21** and **22**, respectively. Overall trends were very similar, but nitrogen loads indicated generally better performance overall than concentrations. The mesocosms reduced outflow volumes fairly substantially, depending on the season; the volume reduction resulted in load reduction even when concentration removal efficiency might be negative. The same trend was observable in other analytes (TSS, phosphorus, copper, and zinc).

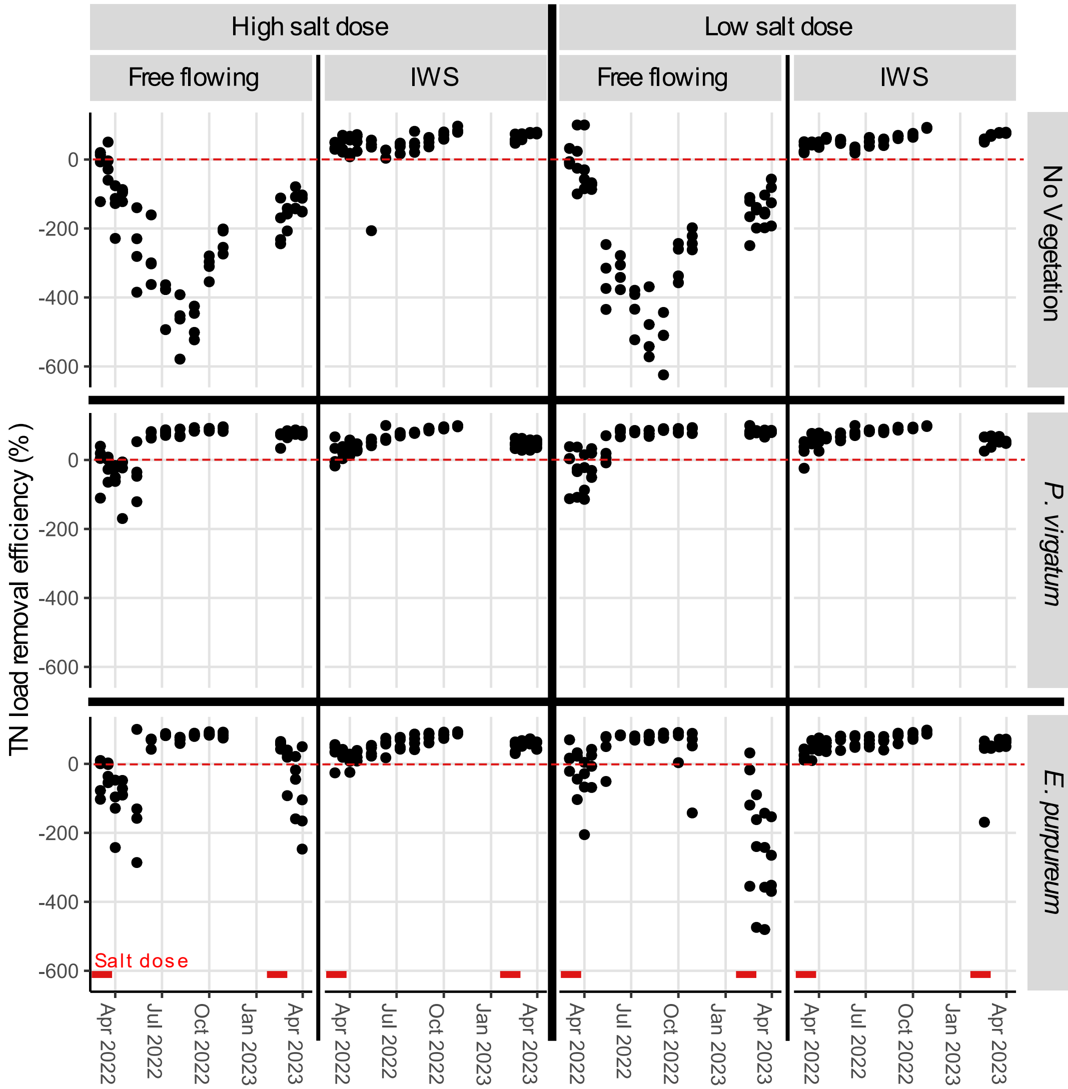

Figure 22: TN (total nitrogen) load removal efficiency over the course of the experiment. Dashed red line shows 0% removal efficiency. Red bars indicate salt application.

The unvegetated free-flowing mesocosms in both figures showed poor removal year-round, with the worst performance in late summer. At the beginning of 2023, concentrations and loads generally lined up with where they had been the previous year (but were slightly better). There was no difference between salt concentration for these replicates or for any total nitrogen treatments throughout the experiment. The timing of the downward trend did not line up with the peak April/May impacts of salt observed for the other analytes, such as TSS and phosphorus. It is possible that the trend was not influenced by salt at all but rather by seasonal changes. As in the pre-experiment sampling in 2021, nitrogen must have leached from organic matter and wood chips in the mesocosms. Mineralization rates and microbial activity might have increased in summer as the mesocosms received more sunlight and heat, which peaked in June or August—that is, when removal reached its lowest point. As noted in the methods, while the greenhouse temperature was controlled, the mesocosms sat in the sun and could still have gotten quite warm. It is also possible that seasonal trends masked any effect that salt had or that salt had indirect effects, such as dispersion increasing the availability of organic nitrogen for mineralization and thereby amplifying normal trends. Export should eventually deplete soil nitrogen, which could result in better long-term performance; improvement might be visible in the second year if the replicates continue to trend up.

The free-flowing *E. purpureum* and *P. virgatum* mesocosms performed very similarly throughout 2022. They both initially had high variability, and their performance often worsened over the first few sampling dates, roughly following the performance of the unvegetated mesocosms. The vegetated replicates could have been following the same seasonal trend as the unvegetated ones as microbial communities recovered from the winter and mineralization increased without a means of nitrate removal. The observable dispersion effects on TSS occurred in the first 2-3 months, so variability in total nitrogen in free-flowing mesocosms during this time could be attributed to organic colloid dispersion. Total suspended solids generally did not correlate well with total nitrogen, which is not surprising; most nitrogen export occurred as nitrate, and dispersed organic nitrogen is not necessarily captured as TSS. Performance rapidly improved between May and July, and the vegetated free-flowing replicates mostly performed well (greater than 60%) nearly all of the time for the remainder of the year. Good performance likely resulted from nitrogen assimilation and plant-enhanced microbial activity catching up with and suppressing the effects of season or salt in unvegetated mesocosms. While growth started as early as March, vegetation did not improve concentrations more than did unvegetated columns until the plants were approaching maturity in May. Even after the vegetation had reached maturity, many of the mesocosms continued to improve. It is still possible that other seasonal and plant-related trends masked salt-induced changes and that salt influenced concentrations indirectly by inhibiting early-season growth and by affecting root nutrient uptake.

In 2023, trends in free-flowing vegetated mesocosms changed. Despite many plants not surviving the winter (and the plants that survived not growing substantially until late March), *P. virgatum* continued to perform well, near prewinter levels. These mesocosms are known to have suffered from dispersion and soil structure-related issues, and it is possible that dispersion reduced drainage so the mesocosms held more water. The additional water could have improved denitrification and removal performance.

E. purpureum experienced an extreme dip in performance. This could be attributed to dead and decaying organic matter, perhaps increased by organic colloid dispersion and primed by freeze-thaw and the previous year's salt application. If dispersion is at play, then it is surprising that the worst TSS dispersion effects occurred with *P. virgatum* but the worst total nitrogen export occurred with *E. purpureum*; however, as noted, TSS and total nitrogen do not

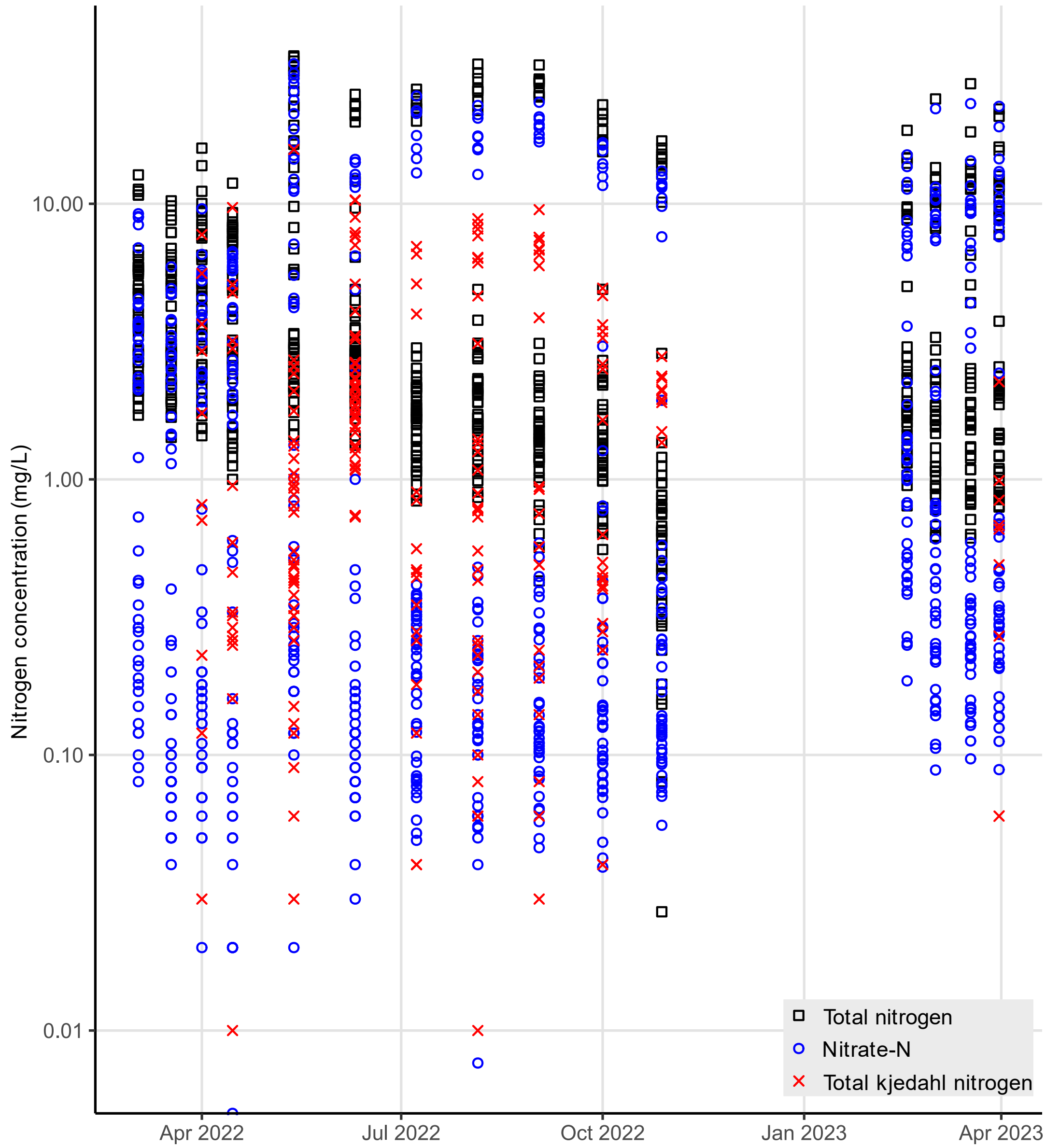

Figure 23: Effluent concentration of nitrogen species over the course of the experiment. Not the logarithmic y-axis.

necessarily correlate. Regardless, plants were mostly inactive during this time, so no conclusions can be drawn from 2023 regarding their performance.

Mesocosms with internal water storage performed generally the same regardless of salt concentration and presence or species of vegetation. For these mesocosms, performance was positive nearly year-round, though some variability existed in the early spring in both years; removal was relatively low but improved to nearly 100% after a few months. Good performance was attributable to increased denitrification, and poor early performance could just have been microbial communities recovering from the winter. The early variability and slight downward trends in concentration or load that some groups showed in April and May could have resulted from salt-induced dispersion of organic colloids, effects of salt on microbial populations, or reduction in CEC affecting ammonium removal, coinciding with TSS dispersion and peaks in TSS, phosphorus, and total organic carbon (TOC). If so, the dispersion was not influenced by salt concentration, and the impact was minor compared to seasonal trends in unvegetated free-flowing mesocosms. The improvement over the spring could also be supported by the growth of plants in vegetated replicates. 2023 appears to be performing slightly better than early 2022, possibly because microbial communities have adapted to become more salt tolerant.

One notable set of outliers occurred in the May 2022 sampling, the fifth of the year. Shortly before sampling, the *E. purpureum* in all high-salt mesocosms were replaced and a few inches of topsoil added to all unvegetated mesocosms. In the May 2022 sampling, the free-flowing unvegetated and *E. purpureum* mesocosms showed a rapid spike in concentration inconsistent with existing trends (Figure 21). The spike is attributable to soil disturbance; a nitrogen spike after replacement of another species of joe pye weed was also observed by Muerdter et al. (C. P. Muerdter et al., 2019). Interestingly, this trend is much harder to distinguish in the load data (Figure 22). Regardless, the trend does not appear at all in any of the unvegetated IWS or high-salt *E. purpureum* IWS mesocosms, indicating that IWS offered protection against the effects of soil disturbance. Some disturbance would be expected in a normal bioretention basin with yearly maintenance, so IWS offers another advantage here.

Nitrite-N (not shown in Figure 23) was consistently around 0.5-1.5 mg/L for all mesocosms. Nitrite-N concentrations could not be collected during and for a short period after salt dosing because the data was collected via ion chromatography and chloride and nitrite peaks are adjacent, so the large chloride peaks interfered with nitrite-N. TKN was calculated by subtracting nitrate-N and nitrite-N from total nitrogen, so this also prohibited TKN calculation during these periods. Sometimes nitrite-N and nitrate-N combined were greater than total nitrogen. In these cases, no TKN value could be calculated. While nitrite-N was stable, certain sampling dates were seemingly randomly higher or lower, and it’s possible that there was instrument error. Nitrite-N could have been overestimated, and there’s a lack of TKN values in the 0 to 1 mg/L range. The TKN values present in Figure 23 therefore represent a fraction of the mesocosms.

Nitrate-N (Figure 23) often correlated with total nitrogen, as shown by Figure 23 and Table 5, though not always. The nitrate-N data generally fell into one of two categories. In one group of mesocosms, the nitrate-N closely followed total nitrogen, and most total nitrogen was nitrate-N. In the second group, nitrate-N made up only a small fraction of total nitrogen.

TKN (Figure 23), which often made up much of the difference between nitrate-N and total nitrogen, varied a great deal but fell into two categories paralleling the categories for nitrate-N. For mesocosms with high nitrate-N relative to total nitrogen, TKN made up a much smaller proportion of the total nitrogen quantity. These mesocosms were mostly free flowing. It is likely that most TKN was quickly ammonified and nitrified into nitrate-N in the aerobic environment these mesocosms provided. For mesocosms with low nitrate-N relative to total nitrogen, TKN made up a greater proportion. These mesocosms usually had IWS, with an anoxic environment that limited nitrification but enhanced denitrification. This removed most of the nitrate but left TKN generated in or near the IWS zone with limited removal pathways, resulting in its loss to effluent (most likely from the wood chips in the IWS zone or organic material just above it). The variability in IWS mesocosms was almost entirely attributable to TKN, and nitrate-N was consistently very low. TKN variability could be attributed to organic colloid dispersion.

Vegetated mesocosms also appeared to decrease the concentration of nitrate-N relative to total nitrogen, potentially by releasing TKN in root exudates and assimilating nitrate-N.

Table 4. Total nitrogen load and annual load removal efficiencies by treatment.

Treatment	Average removal (%)	Median removal (%)	Annual average removal (%)	Annual median removal (%)
Vegetation	-15.3	28.5	53.3	56.8
No vegetation	-194.5	-29.3	-117.4	-111.4
E. purpureum	-48.6	18.2	47.8	53.3
P. virgatum	19.0	44.0	54.8	60.2
IWS	33.5	37.2	57.6	57.8
Free flowing	-182.6	-93.6	-67.4	23.1
Low salt	-74.4	28.4	-1.5	55.6
High salt	-76.8	13.1	-8.3	43.7

Statistical analysis confirms the trends observed in Figures **21** and **22**. Vegetation and IWS were good, statistically significant predictors of nitrogen concentration and load removal efficiency (see Table **3**). Both increased nitrogen removal efficiency. The adjusted R^2 for these two predictors and total nitrogen load removal was 0.37. This was low but unsurprising, considering the seasonal trends in performance (especially affecting free-flowing vegetated or unvegetated mesocosms) and the potential effects of salt not captured in this model. Statistical analysis of the 2022 annual load had the same results, but with an adjusted R^2 of 0.65, much higher now that seasonal changes were excluded.

While the performance of *E. purpureum* is significantly worse than that of *P. virgatum* for event removal efficiency, mesocosms with vegetation still performed much better overall. The 2022 annual load removal statistics (Table **3**), which do not include the massive nitrogen export that *E. purpureum* mesocosms suffered at the beginning of 2023, show the two species being much closer in removal. Mesocosms with IWS performed much better than free-flowing mesocosms in both event and annual removal. There was little difference between high- and low-salt results, indicating that if salt is affecting nitrogen removal, its concentration is not. This does not mean that salt is having no effect at all; it could be that the effects are masked, effectively remediated by vegetation and IWS; or that the columns were saturated with salt and that added salt past some point less than 500 mg/L Cl had little effect on performance.

Table 5. Overall effluent results for TN (total nitrogen) and nitrate-N.

Statistic	TN	Nitrate-N
Average concentration (mg/L-N)	5.15	3.05
Median concentration (mg/L-N)	2.28	0.32
Concentration range (mg/L-N)	0.03 - 34.40	0.01 - 32.23
Average concentration removal efficiency (%)	-76.6	-89.5
Median concentration removal efficiency (%)	21.8	80.1
Average load removal efficiency (%)	-5.6	-13.8
Median load removal efficiency (%)	51.0	88.7

These results may also be viewed in Figure **24,** showing the annual load removal efficiency for each replicate in 2022. The IWS mesocosms performed more consistently and better overall than the free-flowing replicates. Vegetated replicates were able to achieve positive removal even without IWS, but the best results were generally achieved with both treatments combined. Salt concentration had no visible effect. The average annual nitrogen removal efficiency was -6.8%, and the median annual nitrogen removal efficiency was 48%. Average and median concentrations and removal efficiencies and concentration ranges for total nitrogen and nitrate-N (Table **5**) were not great. These overall and annual results would be much better but for the massive leaching shown by the free-flowing unvegetated mesocosms.

The nitrogen effluent concentrations and removal efficiencies that some replicates showed in this study were much worse than normal removal in the literature, although significant export of nitrate (sometimes also resulting in total nitrogen loss) was observed in some studies (This literature includes (BIRCH et al., 2005; Brown et al., 2013; Clary et al., 2020; Hatt et al., 2009; LeFevre et al., 2015; Passeport et al., 2009).This was likely the result of the soil organic matter and wood chips discussed previously. It is possible that salt directly or indirectly contributed to nitrogen leaching by. It is also possible that the media was too sandy, hindering the formation of denitrifying microsites observed by others, though dispersion may have actually corrected this in some *P. virgatum* mesocosms (Lucas & Greenway, 2008; Parkin, 1987; Strong & Fillery, 2002).

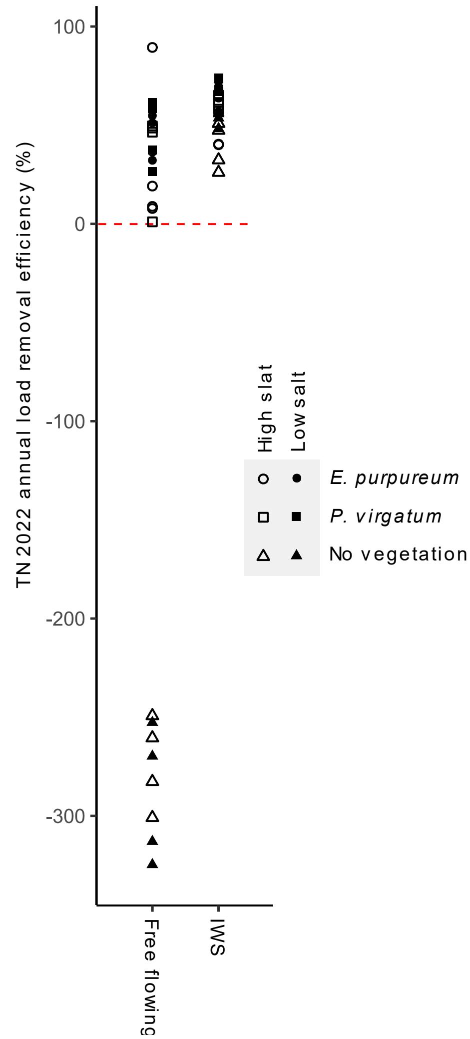

Figure 24: Annual 2022 TN (total nitrogen) load removal efficiency. The red dashed line indicates 0% removal efficiency.

This study highlights the benefits of vegetation for nitrogen performance. Although the overall removal statistics in Table **4** were negatively affected by poorer winter and early-spring performance, under ideal conditions (mature well-watered vegetation in the summer), both *E. purpureum* and *P. virgatum* consistently removed more than 70% of the total nitrogen load and often more. This was attributable to nitrogen assimilation into biomass and plant-enhanced microbial activity. The performance of vegetated mesocosms in this study compared well with the literature (for example, (Dagenais et al., 2018; Glaister et al., 2014; Huang et al., 2022; Morse et al., 2018; C. P. Muerdter et al., 2019; Rycewicz-Borecki et al., 2017; Skorobogatov et al., 2020; Zinger et al., 2013).

IWS was found to be fairly effective year-round and extremely effective when combined with vegetation, with performance often exceeding 80% under ideal conditions (as opposed to the lower overall concentrations in Table **4**). Its performance was attributable to anoxia and increased activity of denitrifying bacteria. This study's data reflects data in other studies of IWS in the literature, many of which have also found substantial improvement and similar performance (Glaister et al., 2014; Huang et al., 2022; Morse et al., 2018; Sharkey & Hunt, 2012; Wang et al., 2018; Yaron et al., 2007; Zinger et al., 2013). Several other studies also observed TKN export or dips in removal in IWS bioretention, attributed to leaching of nitrogen from carbon amendments and inhibited nitrification due to anoxia, and in this case possibly organic colloid dispersion (Hunt et al., 2006; Randall & Bradford, 2013b; Sharkey & Hunt, 2012; Yaron et al., 2007; Zinger et al., 2013).

Salt concentration had no discernible direct effect on nitrogen in this study. It could be that salt concentration has increasing effects up to a point, and that this point was lower than 500 mg/L Cl. Trends are perhaps masked by the good performance of IWS and vegetation; attributable to other factors, such as temperature and season; or amplified existing trends (inhibiting plant growth or denitrifier activity, dispersion increasing substrate accessible to mineralizing microbes, etc.) without a clear way to distinguish differences. The literature on salt and nitrogen is somewhat mixed. Denich et al. (2013) and Valtanen et al. (Valtanen et al., 2017)(2017) did not link deicing salt with poor nitrogen performance, while Szota et al. (2015) confirmed that salt-tolerant species could effectively remediate nitrogen despite deicing salt but found performance to decline with increased salt exposure, attributing poor performance in part to plant death. Endreny et al. (Endreny et al., 2012)(2012) observed that deicing salt increased nitrogen in effluent and altered microbial community structure, affecting nitrogen cycling. McManus & Davis (2020) also observed deicing salt to increase nitrogen in effluent. Amrhein et al. (1992) observed the loss of organic matter in the presence of deicing salt, and Kakuturu & Clark (2015) recorded the loss of nitrogen from soil exposed to salt.

Mesocosm study: Phosphorus response

Total phosphorus data was not collected in the November 2021 pre-experiment sampling. Phosphate data throughout the experiment was inconclusive, and the ion chromatograph generally yielded no result. The instrument's ability to detect small phosphate concentrations was observed to be poor, and it is likely that mesocosms generally had very low phosphate concentrations, which were below the detection limit of the instrument. Much of the total phosphorus exiting the mesocosms was therefore in organic or sorbed forms. Nevertheless, TSS and total phosphorus were only poorly positively correlated throughout the experiment. Treatment type might be part of the reason; total phosphorus and TSS outflow in IWS mesocosms were not correlated at all, while free-flowing mesocosms generally had slightly stronger positive correlations. Most total phosphorus appeared to be in dissolved organic or colloidal form not captured as TSS or phosphate, and IWS appeared to enhance this trend. When mesocosms performed well, total phosphorus was frequently below the ICP-OES detection limit of 0.01 mg/L. For the purposes of statistical analysis and graphics, the detection limit was used for these events. Actual performance may have been slightly better than the statistics provided below.

Total phosphorus load removal efficiency trends (Figure 25) were very similar to concentration removal efficiency. All groups showed good initial performance in early 2022, followed by a rapid decline that reached its worst in about April. The size of the decline depended on salt concentration and mesocosm hydrology. It could be severe, falling to 20-40% in some mesocosms while barely affecting removal in others. The high-salt treatments performed worse than their low-salt counterparts, and the IWS mesocosms performed better than free-flowing mesocosms. The salt-induced decline in performance was best mitigated by lower salt exposure and the presence of IWS.

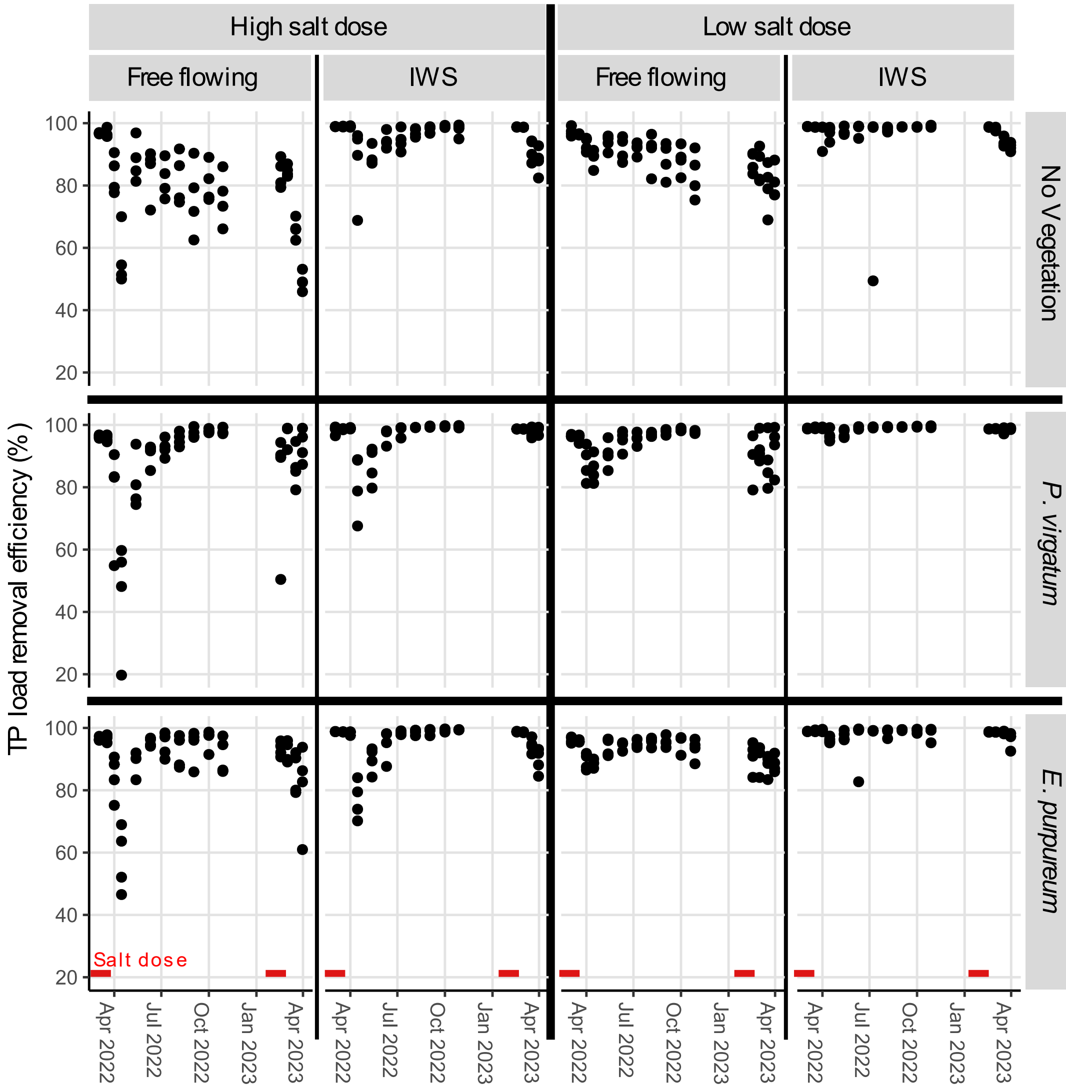

Figure 25: TP (total phosphorus) load removal efficiency over the course of the experiment. Red bars indicate salt application.

The decline gradually improved over the following months, and concentrations returned to 0.04 mg/L or less, which seemed to constitute the background removal ability of these mesocosms. The time it took to return to baseline depended on the severity of the drop in performance; the return occurred anywhere between early spring and late fall. Toward late summer and fall, unvegetated and *E. purpureum* mesocosms began suffering from dropping and variable performance. It is not clear what caused this, but it could have been a seasonal trend. Salt concentration also appeared to influence the severity of the performance drop, though given the delay after dosing, the mechanism is unclear. It is unlikely that the media was approaching phosphorus saturation. Regardless, the same effect was not present in IWS mesocosms, and *E. purpureum* seems to have suppressed it somewhat, while *P. virgatum* suppressed it completely.

In 2023, many of the mesocosms experienced a decline in phosphorus performance similar to that in the previous year. Again, phosphorus performance appeared to have been made worse by increased salt concentration and the absence of IWS. Surprisingly, the lower salt concentrations used in 2023 appeared to have had little to no effect on performance. It is possible that this was partially the result of increased variability in the previous fall, as well as the accumulation of phosphorus and previous year's salt application increasing the soil's vulnerability to phosphorus loss.

The average event effluent total phosphorus concentration was 0.08 mg/L and the median was 0.04 mg/L. Concentrations ranged from below the detection limit (0.01 mg/L) up to 0.81 mg/L. The average and median concentration removal efficiencies were 87.4% and 93.0%, respectively, and the average and median load removal efficiencies were 92.7% and 96.4%, respectively. Overall performance was quite good despite the salt application. Table 6 shows overall results for each treatment. IWS and low-salt mesocosms performed noticeably better in event load removal efficiency. Vegetation followed the trends shown in Figure 25, with *P. virgatum* performing the best, followed by *E. purpureum* and then the unvegetated mesocosms.

These trends were confirmed with statistical analysis (see Table 3). Vegetation, salt concentration, and IWS were statistically significant and good predictors of total phosphorus, with vegetation (the presence of *E. purpureum* and/or *P. virgatum*) and IWS associated with improved performance, while high salt concentrations were associated with poor performance. The adjusted R^2 was 0.31 (low for the same reasons outlined in the nitrogen discussion).

Annual 2022 total phosphorus performance (Figure 26) and statistics (Table 6) indicate that performance generally followed the established trends, with IWS and low salt concentrations performing best, while vegetation treatments performed similarly but unvegetated mesocosms often performed the worst. This was confirmed statistically (see Table 3), and low salt concentration, IWS, and vegetation were good, statistically significant predictors of lower or higher total phosphorus load removal efficiency, with an adjusted R^2 of 0.65, higher than that of event load removal (thanks to the removal of temporal trends).

With average load removal efficiencies often above of 90% and effluent concentrations below 0.05 mg/L, overall performance of the mesocosms in this experiment was equal to or greater than what much of the literature found. While some studies have demonstrated good phosphorus performance (greater than 70% removal), phosphorus leaching is a serious problem in field studies, many of which have recorded net phosphorus loss (this literature includes (BIRCH et al., 2005; Bratieres et al., 2008; Clary et al., 2020; Dietz & Clausen, 2006; Houdeshel et al., 2015; Komlos & Traver, 2012; LeFevre et al., 2015; Passeport et al., 2009; Rycewicz-Borecki et al., 2017). The high level of removal in this study occurred despite the soil's high organic matter content and the presence of wood chips.

The positive effects of IWS, generally improving removal/variability and mitigating the effects of salt, were somewhat unexpected. Some existing literature has indicated that anoxic conditions would increase the solubility and mobility of phosphorus, leading to its loss from the media (Clary et al., 2020; Palmer et al., 2013; Zinger et al., 2013). However, a variety of other studies have found IWS to have no effect or to improve phosphorus removal in bioretention media (Clark & Pitt, 2009; Dietz & Clausen, 2006; Glaister et al., 2014; Soberg et al., 2020; Wu et al., 2017; Zhang et al., 2011).The results of this study fit the findings of the latter group. It is likely that increased retention time, slightly increased sorption capacity, or increased availability of soluble iron enabled higher performance (Blecken et al., 2009; Glaister et al., 2014; Phillips, 1999).

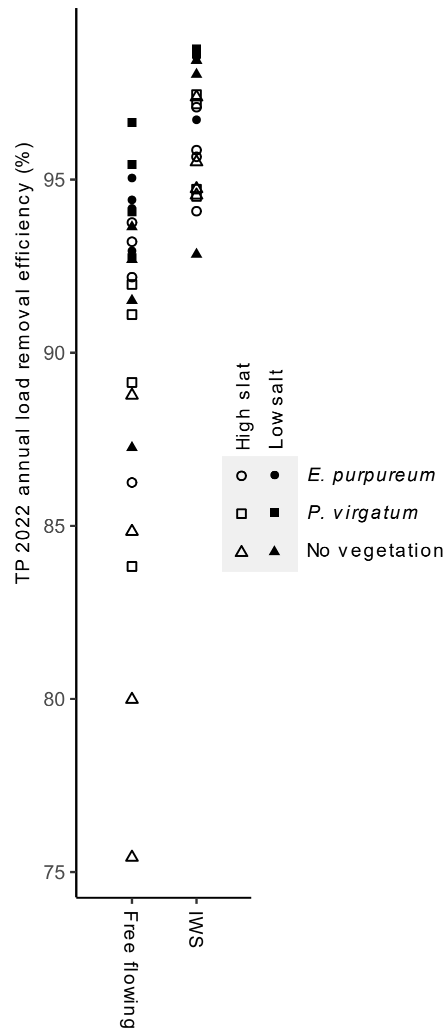

Figure 26: Annual 2022 TP (total phosphorus) load removal efficiency.

Hatt et al. (2008)(Hatt et al., 2008), Komlos & Traver (2012), Muerdter et al. (2016)(C. Muerdter et al., 2016), and Passeport et al. (2009) found most phosphorus to be retained in the top few centimeters of soil early on in bioretention cell operation. IWS should be kept away from the top of a bioretention cell for this reason, although saturation and downward migration of phosphorus do occur over time and phosphorus would

Table 6. Total phosphorus load and annual load removal efficiencies by treatment.

Treatment	Average removal (%)	Median removal (%)	Annual average removal (%)	Annual median removal (%)
Vegetation	94.3	97.2	94.6	94.7
No vegetation	90.1	94.0	91.5	93.2
E. purpureum	93.8	96.4	94.8	94.7
P. virgatum	94.2	97.8	94.3	94.7
IWS	96.8	98.7	96.7	97.2
Free flowing	88.8	92.1	90.5	92.4
Low salt	94.8	96.7	95.5	95.4
High salt	90.8	96.0	91.6	93.9

eventually approach the IWS layer (Davis et al., 2001; Komlos & Traver, 2012; Lucas & Greenway, 2008; Tedoldi et al., 2016; Wu et al., 2017). In this study's relatively new mesocosms, it is possible that influent phosphorus was intercepted by the media surface and that most effluent phosphorus was leaching from the media. IWS then would have had little effect on reduction of influent phosphorus but would have reduced phosphorus loss from the media, either by decreasing mineralization of organic phosphorus or by increasing the sorption capacity of the lower media layer.

The good performance of IWS for phosphorus may also be explained by considering the system's stability. If anoxic sediment becomes oxidized or oxidized sediment is reduced, phosphorus and heavy metals may be mobilized (Blecken et al., 2010; Calmano et al., 1992; Clary et al., 2020; Scholz et al., 2002; Stephens et al., 2001). While rain events do introduce dissolved oxygen to the IWS zone and limit oxygen movement in the upper layers temporarily, as long as the bioretention mesocosms are stable long-term, the upper layers should remain aerobic and the IWS zones anoxic. In this experiment, with regular watering, the same stability would have been achieved, limiting the ability of phosphorus in either part of the mesocosms to encounter a different redox potential and potentially be mobilized. Phosphorus could migrate down into the IWS zone over time, but in the field as long as physical disturbance (and salt application) are minimized and steps are taken to maintain the upper media's phosphorus sorption capacity, any potential harm caused by IWS should be reduced.

While redox changes with long-term flooding during lengthy periods of rain may be of concern regardless of IWS presence, drying of the IWS zone during drought could become an issue for bioretention with IWS. IWS is also believed to increase the stability of bioretention moisture regimes, enabling plant survival during drought (Blecken et al., 2010; Glaister et al., 2017; Zhang et al., 2011). The drying of the IWS zone therefore is likely not of major concern. In this study, even after spending months outside in the winter receiving relatively little rainfall, mesocosm IWS zones were still observed to be saturated.

Phosphorus removal benefited from the presence of vegetation, which reduced variability and slightly improved summer/fall performance but failed to mitigate salt-induced performance declines. Many other studies have found vegetation to improve bioretention effectiveness (Glaister et al., 2017; Houdeshel et al., 2015; Lucas & Greenway, 2008; Rycewicz-Borecki et al., 2017; Turk et al., 2017; Wu et al., 2017). Studies including Glaister et al. (2014), Palmer et al. (2013), Szota et al., 2015 have found sorption to be the primary removal pathway, which did seem to be the case for the mesocosms in this study, with unvegetated mesocosms performing nearly as well as vegetated ones. The vegetation did not improve salt-induced phosphorus flushing, likely because it was still dormant or had only just begun to grow. The degree to which vegetation improves phosphorus performance depends upon species, which has also been observed by Glaister et al. (2017), Lucas & Greenway (2008), Read et al. (2008), and Turk et al. (2017).

This study found a clear negative link between salt and phosphorus removal, likely the result of some combination of desorption from the soil (spurred by effects on phosphorus complexes and precipitates, as well as competition with chloride for exchange sites) and dispersion of organic colloids or mineral colloids with sorbed phosphorus, as well as indirect effects, such as on vegetation. Several other studies have had similar results. McManus & Davis (2020) found salt to cause a slightly delayed decrease in phosphorus performance, which became net export at higher concentrations (2000+ mg/L NaCl). Søberg et al. (2020) found that salt negatively affected phosphorus removal, especially when combined with high temperatures, although IWS did little to improve phosphorus performance. Goor et al. (2021)(Goor et al., 2021) found a delayed increase in phosphorus effluent concentrations in spring, linked with winter deicing salt application. However, Valtanen et al. (2017)(Valtanen et al., 2017) found salt to have no effect on phosphorus, and Szota et al. (2015) found total phosphorus retention to actually increase with greater salt concentrations. This was attributed to salt turning dissolved influent phosphorus into particulate form, which was filtered effectively. They did find a net loss of dissolved phosphorus, which was attributed to desorption from the media.

Mesocosm study: Copper response

Initial copper concentrations in November 2021 were not influenced by the vegetation or IWS treatments, generally hovering just over 0.021 mg/L, with loads around 0.018 mg. This translated into an average load removal efficiency of 89.2%, excellent performance. All copper concentrations were measured as total copper, and actual bioavailable copper may be less than what is shown in these results. The detection limit of ICP-OES was 0.005 mg/L, and values below this were replaced with 0.005 for statistical analysis and visual representation, so the results presented below slightly overestimate actual copper effluent concentrations and underestimate removal.

Trends in copper load removal efficiency (Figure 27) were very similar to concentration trends. While copper was generally fairly variable and frequent outliers make trends hard to distinguish, load removal was nearly exclusively better than 70% and often above 90%. All three high-salt free-flowing groups of replicates showed a similar rapid decline in copper load removal efficiency, reaching their lowest level in April before returning to prewinter removal levels over the next few months. The decline, though still detectable despite the noise, was much smaller in the low-salt free-flowing mesocosms. The drop was attributable to the effects of salt, and concentration played a role in its severity. It is likely that salt-induced processes like dispersion of inorganic or organic colloids containing sorbed copper, desorption spurred by factors like

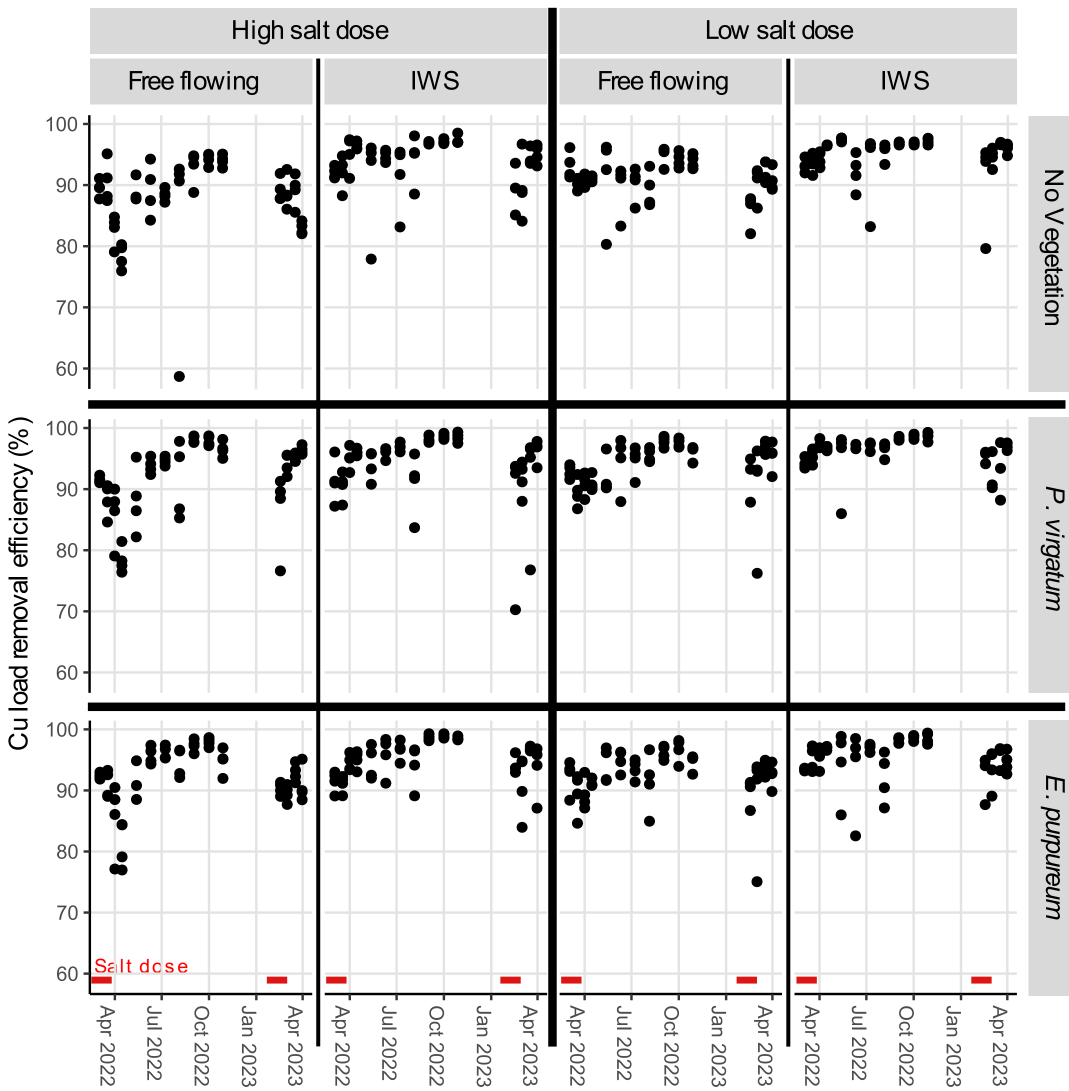

Figure 27: Total copper load removal efficiency over the course of the experiment. Red bars indicate salt application.

acidification, competition for exchange sites, the effects of salt on copper complexes, and the death of copper-containing organisms decreased performance at higher concentrations. With that being said, even at 2,000 mg/L Cl, removal still surpassed 70% at worst; at 500 mg/L Cl, the effect was almost insignificant.

The early performance of the high-salt IWS mesocosms appeared similar to the low-salt free-flowing ones, and the low-salt IWS replicates appeared slightly better. Internal water storage had a beneficial impact on copper removal, almost mitigating its effects entirely at low to medium salt concentrations. Vegetation, on the other hand, appeared to be have little effect on load performance, though there is a very slight positive effect of both *E. purpureum* and *P. virgatum*, especially later in the year.

Copper performance in the summer and fall was generally good regardless of treatment, but relatively large variability existed. It is important to keep in mind that variability appeared more amplified than for the other analytes because performance was nearly always excellent, making the y-axis scale quite small. Regardless, some mesocosms appeared to dip in performance before improving over several months (possible due to the delayed effects of salt) or to rapidly bounce in removal. Some of these dips were significant.

The 2023 data seemed to show trends similar to the 2022 trends. Another decline was in progress across treatments, which seemed to be mitigated again by lower salt concentration and the presence of IWS. Nevertheless, there was less difference between free-flowing and IWS columns and many more outliers, making trends more difficult to distinguish. The decline in 2023 appeared to be less severe than the previous year's decline across both salt concentrations, likely caused by the lower concentrations used in 2023. The increasingly muddled trends and frequent outliers could be caused by increased vulnerability to copper after a full year of copper loading and the previous winter's salt application.

The overall average and median effluent concentration was 0.015 mg/L and 0.012 mg/L, respectively, with a concentration range of <0.005 to 0.076 mg/L. When combined with the concentration removal efficiency average and median (88.1% and 90.2%, respectively) and the load removal efficiency average and median (93.1% and 94.4%, respectively), copper removal was excellent overall. This is further supported by the statistics in Table 7, which show load averages and medians by treatment.

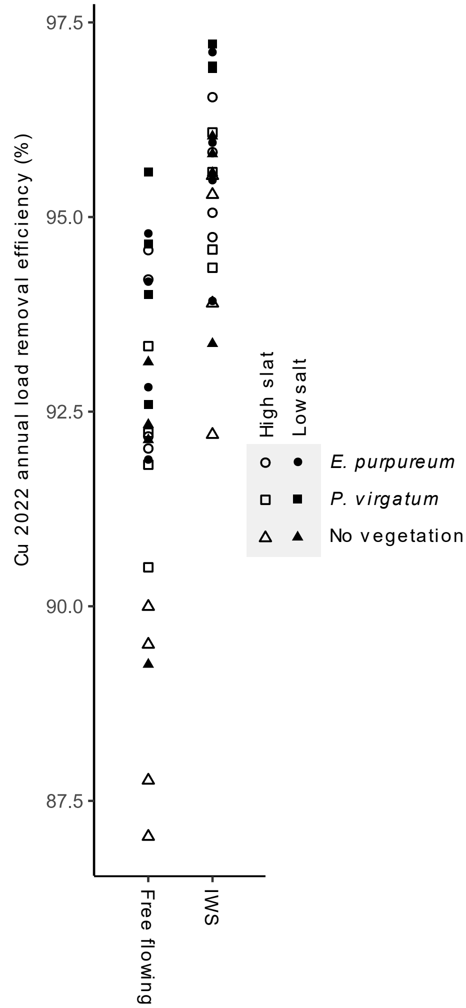

Figure 28: Annual 2022 total copper load removal efficiency.

There was only a slight increase in load average and median removal in vegetated mesocosms relative to unvegetated mesocosms. *E. purpureum* and *P. virgatum* performed almost identically. It seems that vegetation plays little role in bioretention performance for copper and that soil sorption is the primary removal pathway. There was a slightly more noticeable difference between IWS and free-flowing mesocosms, although the improvement provided by IWS was nearly negligible overall and likely mostly stemmed from mitigating the effects of the salt-

Table 7. Total copper load and annual load removal efficiencies by treatment.

Treatment	Average removal (%)	Median removal (%)	Annual average removal (%)	Annual median removal (%)
Vegetation	93.9	95.1	94.4	94.6
No vegetation	92.1	93.2	92.4	92.7
E. purpureum	93.8	94.6	94.5	94.7
P. virgatum	94.0	95.7	94.4	94.6
IWS	94.9	96.1	95.4	95.6
Free flowing	91.7	92.4	92.2	92.3
Low salt	94.0	95.0	94.4	94.7
High salt	92.6	93.8	93.1	94.0

induced decline in early spring. The difference between high and low salt concentrations was also small, probably because the effects of salt were limited to a brief period after salt application ended. This is confirmed by statistical analysis, with good, statistically significant relationships between copper load removal and salt concentration, vegetation, and IWS (see Table **3**). Salt concentration had a minor negative effect on copper, IWS had a minor positive effect, and vegetation had a very minor positive effect. The adjusted R^2 for these predictors was 0.11, unsurprising given their minor (and for salt, short-term) effects. Outside factors clearly caused more significant variation in the data.

Annual load removal averages (Table **7** and Figure **28**) line up with established trends from event load removal efficiencies. Internal water storage slightly improved removal, while high salt slightly decreased removal efficiency and vegetation had no clear effect. Only IWS was found to be statistically significant at this level as shown in Table **3**, though IWS only passed at $\alpha = 0.1$. The resulting model had an adjusted R^2 of 0.06. There was very little influence of any of the predictors on annual copper performance.

Overall, copper removal efficiencies were at the upper end of what is recorded in the literature. Effluent concentrations generally fell within the normal range, although it significantly exceeded it after salt application (BIRCH et al., 2005; Clary et al., 2020; Davis et al., 2001; Hatt et al., 2009). Although a removal rate of 80-90% or more is not uncommon in laboratory studies, extremely high copper removal occurred in the experiment despite the salt application. Other studies involving deicing salt or replicating winter had similar results (McManus & Davis, 2020a; Muthanna et al., 2007; Paus et al., 2014). This suggests that winter salt application does not compromise the annual removal capabilities of bioretention for copper, though vulnerability might increase after years of operation and copper buildup in the soil.

As was the case with phosphorus, the positive effects of IWS were somewhat unanticipated. Concerns regarding metal and complex solubility would suggest that copper should respond negatively to the introduction of IWS. However, the results of this study are supported by a variety of other studies that have found no effect of IWS on copper, a slight positive but insignificant effect, or a substantial positive effect (Blecken et al., 2009; Dietz & Clausen, 2006; Fierer & Schimel, 2002; Søberg et al., 2017). This has been attributed to factors such as increased retention time and sorption to organic amendments in the IWS zone. The saturated soil may also have slightly increased sorption capacity (Blecken et al., 2009, 2010; Phillips, 1999).

Studies have shown that most heavy metals, like phosphorus, are intercepted by the surface of bioretention basins early in their operation but that saturation creeps downward over time (Davis et al., 2001; Tedoldi et al., 2016). As in these other studies, the columns here were early in their operation, and the surface was likely where most copper sorption occurred. Therefore, there was probably minimal interaction between the most active areas of copper removal and the IWS zone. However, after years of operation and saturation or downward migration, the IWS may interact more with influent copper than could occur in this study. Norrström & Jacks (1998)(Norrström & Jacks, 1998) showed downward migration in soil receiving deicing salt, and it is known that salt increases the mobility of copper (Acosta et al., 2011; C. Amrhein et al., 1993; Christopher Amrhein & Strong, 1990; Calmano et al., 1992; Nelson et al., 2009). It is possible that salt could lead to greater or premature interaction between the IWS zone and copper. While increased copper mobility in response to deicing salt was observed in this study, IWS actually mitigated these effects, suggesting that IWS reduces copper mobilized by salt and may benefit copper removal even in the long term as the media is saturated.

As with phosphorus, good IWS performance may be attributed to the improved stability of the columns' moisture regime created with IWS and regular watering. IWS is expected to improve long-term stability in bioretention more than free-flowing. The real concern may not be the IWS itself, but oxidized or reduced soil changing back and forth during droughts and floods, thereby mobilizing metals (Blecken et al., 2010; Calmano et al., 1992; Clary et al., 2020; Scholz et al., 2002; Stephens et al., 2001). In this study, the IWS layer was observed to retain significant quantities of water after months of receiving relatively little precipitation in the winter, though summer droughts may be more significant.

The limited (and generally insignificant) effects of vegetation on copper present in this study correspond with other findings in the literature. Studies including (Muthanna et al., 2007; Read et al., 2008, 2009; Rycewicz-Borecki et al., 2017; Sun & Davis, 2007) have found similar results. This suggests that sorption is the primary removal pathway for copper in bioretention, though it is possible that plants may be more significant in the long term. While copper in mesocosms with *E. purpureum* and *P. virgatum* behaved similarly, it is possible that other species might have different effects, such as increased copper assimilation or more preferential flowpaths. It is also important to note that plants have beneficial effects on bioretention other than direct improvement of heavy metals retention, as outlined in Chapter 1.

The negative effect of salt application on copper was minor but unsurprising. Similar results have been observed in various soil and bioretention studies, mostly with minor effects of salt on copper mobility, though some studies found greater loss (Acosta et al., 2011; Amrhein et al., 1993; Backstrom et al., 2004; Endreny et al., 2012; Kakuturu & Clark, 2015; Paus et al., 2014). These studies attribute mobility to effects of NaCl on soil pH, competition between Cu and Na for ion exchange sites, complexation with chloride, and dispersion, especially of organic colloids. Variation in the literature is at least partially attributable to different soil initial copper concentrations and properties (CEC, organic matter concentration, texture, etc.).

It is likely that copper buildup after years of loading could increase the vulnerability of these mesocosms to salt-induced mobility, but this study supports the general consensus, which seems to be that while NaCl does increase the short-term mobility of copper in bioretention, it does not compromise bioretention's annual effectiveness. Copper's affinity for forming strong complexes with organic matter has been credited with helping to protect it from chloride complexes. However, several studies have linked copper mobility with organic colloid dispersion, making colloid-assisted transport a major pathway for copper loss in the presence of sodium (C. Amrhein et al., 1993; Christopher Amrhein et al., 1992; McManus & Davis, 2020a; Nelson et al., 2009; Norrström & Jacks, 1998). In this study, there were only weak correlations between Cu and TOC or TSS, although salt-induced peaks of these variables occurred roughly simultaneously, implying that dispersion could be contributing to copper mobility. Paus et al. (2014) linked high temperatures with the amplified effects of salt, and it should be noted that because the greenhouse was much warmer than normal winter conditions, actual copper mobility might be less than what occurred in this study.

Mesocosm study: Zinc response

Initial zinc performance in pre-experimental data from November 2021 was good, with effluent concentrations ranging from about 0.005 to 0.05 mg/L. There were no discernible trends based on treatment. The average effluent concentrati on was about 0.015 mg/L, which translates into a load removal efficiency of 98.3%. This excellent performance was maintained fairly well throughout the experiment. Zinc was measured as total zinc throughout the experiment, and actual bioavailable zinc was likely lower than what is presented below. The detection limit of ICP-OES was 0.005 mg/L, but measured concentrations were never lower than this.

Zinc load removal efficiency (Figures 29 and 30) in early 2022 was nearly complete, almost always over 95%. This rapidly declined after salt application, and a major flushing event happened in several columns in May, dropping into the negative hundreds of percent. These outliers, visible in Figure 29, obscure the finer trends in the rest of the data. Note that Figure 30 has a logarithmic y-axis, but the data has been reflected and translated such that the axis is oriented around 100 and gets increasingly negative. These reveals rapid increase across all mesocosms, peaking in May (though most do not exhibit flushing) before declining back to presalt levels. Note that because the flush was so rapid, it is possible that other mesocosms experienced a flush as well, but data resolution and sampling intervals were too coarse for this to be captured. There could have been an underestimation of the true extent of flushing. The initial decline was extremely rapid, and nearly all columns were above 90% by June, but improvement slowed after that, and it took until early fall for the columns to fully return to normal.

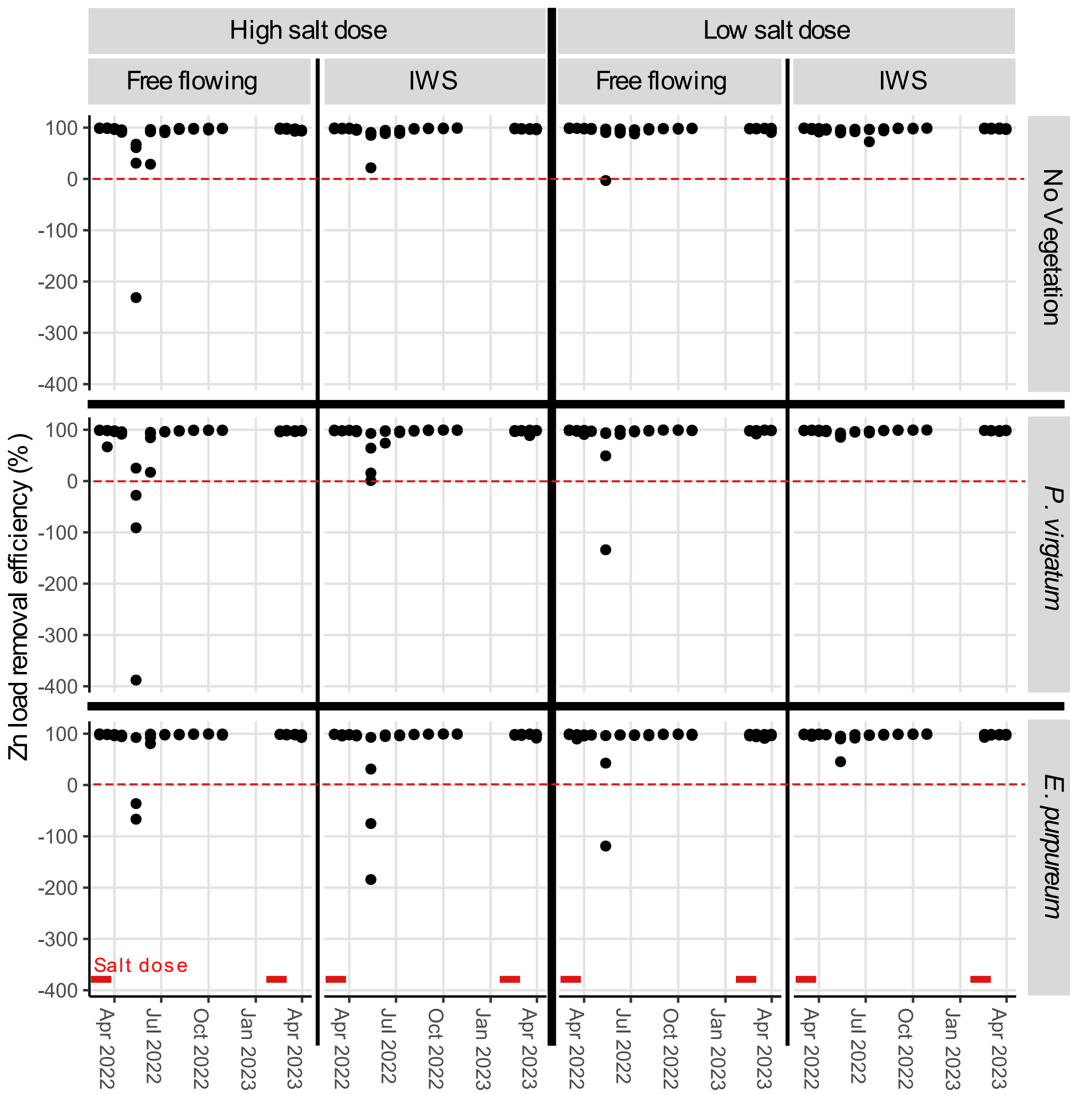

Figure 29: Total zinc load removal efficiency over the course of the experiment. Dashed red line shows 0% removal efficiency. Red bars indicate salt application.

In 2023, recent data appeared to indicate that the columns were repeating their trends from the previous year. There was a marked increase in zinc concentration over the first four samplings. After a full year of zinc dosing and buildup in the soil, it is possible that flushing could be worse in 2023. Many columns have appeared to show higher zinc levels than during equivalent sampling times in the previous year.

The dip in performance immediately after salt application strongly implies that the effects of NaCl, such as dispersion of mineral colloids, competition for ion exchange sites, chloride complexation, altered soil properties (like CEC), and acidification negatively affected zinc

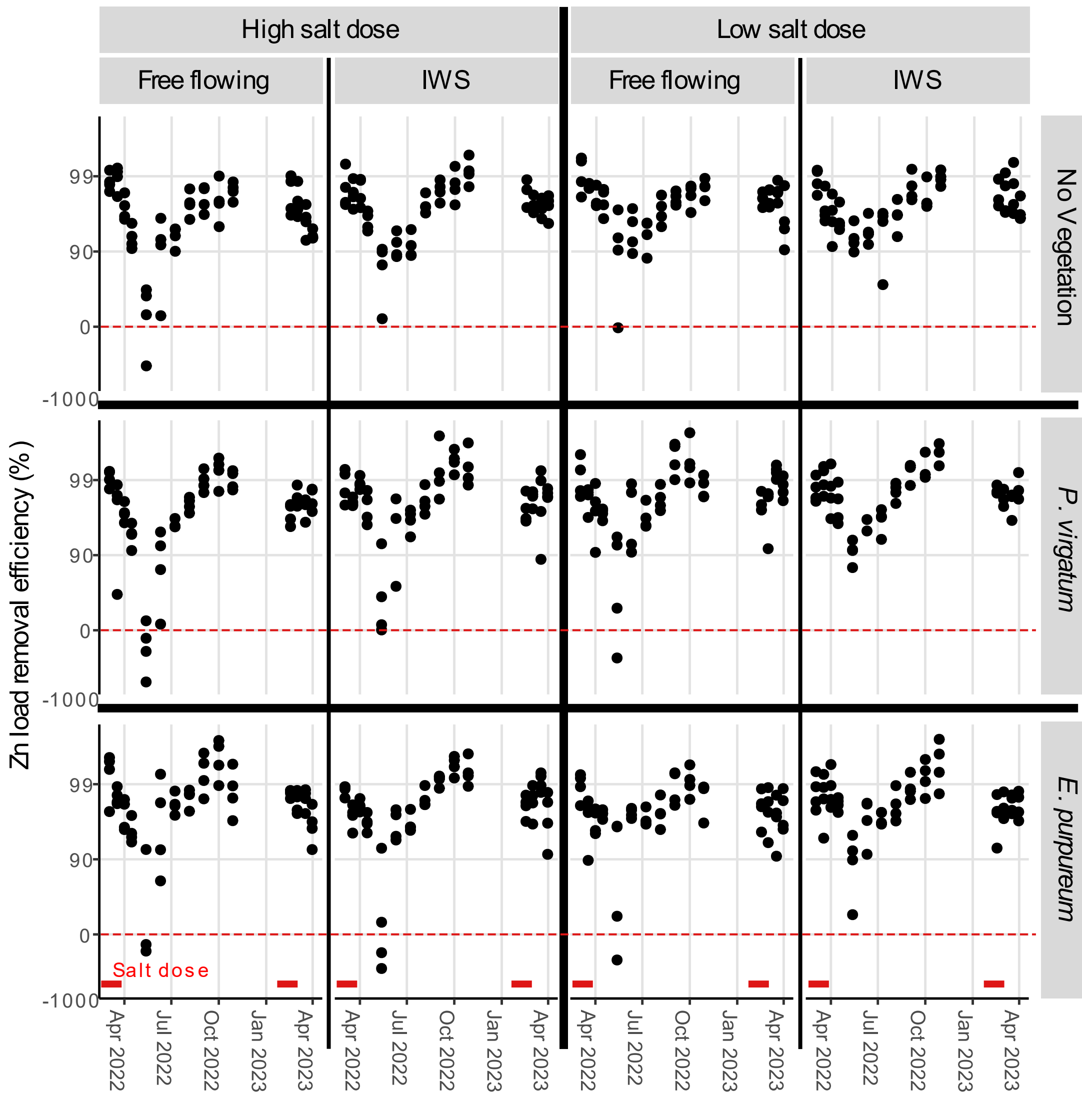

Figure 30: Total zinc load removal efficiency. Data was recalculated to be positive, placed on a log scale, then reflected and translated to its original position, creating a log scale which gets increasingly negative. Dashed red line shows 0% removal efficiency. Red bars indicate salt application.

retention in the columns. However, there were no discernible trends among high versus low salt concentration mesocosms. Both treatment groups appeared to respond to salt in the same way, with similar changes in performance and a seemingly random distribution of the columns showing flushing. It is possible that the salt concentration required to mobilize available zinc was lower than the 500-mg/L Cl treatment and that salt over this amount did not have a significant affect. The same is true for IWS versus free-flowing and unvegetated versus *E. purpureum* and *P. virgatum* treatments. There was no major pattern indicating better or worse performance for any of these mesocosms.

Statistical analysis generally supports this conclusion. Of the various treatments, as seen in Table **3**, only salt concentration near significant, passing at $\alpha = 0.05$ (though IWS did pass at $\alpha = 0.1$, this was an undesirable result). The model had an adjusted R^2 of less than 0.01, indicating that almost none of the variation was attributable to salt concentration and that the statistically significant effect was not of any practical significance. Table 8 shows that averages and medians of zinc load removal efficiency that support this conclusion. There were no notable trends in vegetation treatment. While the IWS averaged better than the free-flowing mesocosms, the medians were nearly the same, likely because outliers and flushing had an outsized effect. Note that all treatments showed some sort of flushing. The same can be said for salt. While the low-concentration treatment averaged higher zinc load removal than the high-salt mesocosms, their medians are the same.

Annual load removal trends (statistics in Table 8, annual removal graphed in Figure 31) showed more differences between treatments. There was generally little difference between vegetation treatments. The *P. virgatum* mesocosm average was a few percentage points lower than the *E. purpureum* and unvegetated mesocosms, but the medians were roughly the same and the dip was likely the result of a few outliers leaching zinc in May. Both the average and median of the free-flowing mesocosms were lower than those of the IWS mesocosms, and there is a noticeable difference in Figure 31, so IWS may have slightly mitigated some effects of salt. The low-salt concentration average and median were also higher than those of the high-concentration mesocosms, indicating that higher salt concentrations may slightly increase zinc leaching. Statistical analysis confirms these results, as shown in Table 3. Only salt concentration was statistically significant at α = 0.05, and the resulting model had an adjusted R^2 of 0.11. Hydrology was significant at α = 0.1, and though this was undesirable, adding it to the model yielded an adjusted R^2 of 0.17. Clearly the effects of the predictors were minor and much of the data's variation was attributable to outside factors. The poor annual performance of some mesocosms is alarming, especially if flushing in other mesocosms was indeed underestimated.

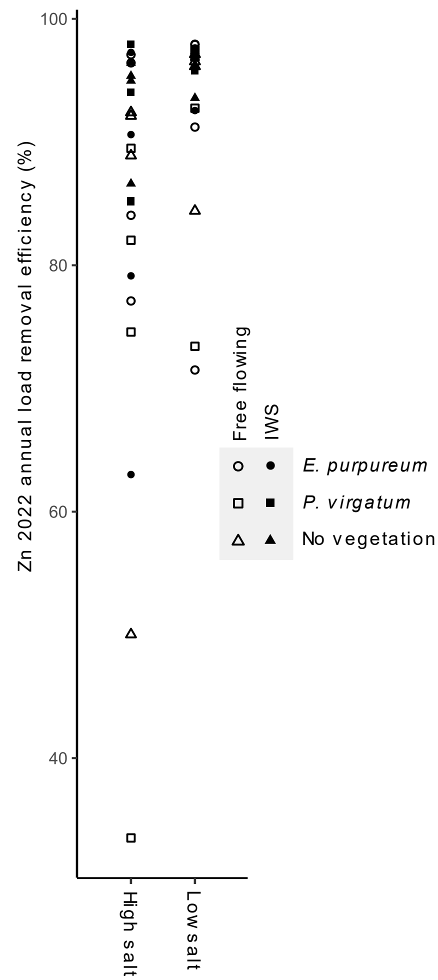

Figure 31: Annual 2022 total zinc load removal efficiency.

Table 8. Total zinc load and annual load removal efficiencies by treatment.

Treatment	Average removal (%)	Median removal (%)	Annual average removal (%)	Annual median removal (%)
Vegetation	92.1	98.3	88.1	93.4
No vegetation	93.8	97.6	90.9	95.2
E. purpureum	92.9	98.2	89.2	94.5
P. virgatum	91.3	98.3	86.9	93.4
IWS	94.9	98.2	92.6	96.0
Free flowing	90.5	98.0	85.5	91.7
Low salt	95.4	98.1	93.6	96.9
High salt	90.0	98.1	84.3	89.2

With an average and median event load removal efficiency of 92.7% and 98.1%, respectively, and an average and median annual load removal efficiency of 88.8% and 94.0%, respectively, zinc removal was extremely high throughout the year. The effluent concentration range was 0.005 to 6.621 mg/L, with an average and median of 0.09 and 0.02 mg/L and average and median concentration removal efficiencies of 84.2% and 96.7%. Similar results have been recorded in many other studies (including (BIRCH et al., 2005; Blecken et al., 2010; Davis et al., 2001). The high results in this study occurred in spite of the salt application, a promising indication of good zinc performance even in cold climates. Other studies of bioretention involving NaCl deicing salt have found similar results (McManus & Davis, 2020a; Muthanna et al., 2007; Paus et al., 2014; Soberg et al., 2014).

While this study does not establish a clear link between zinc removal and IWS, negative or positive, the literature is mixed. Clary et al. (2020) describe zinc as a “redox-insensitive” metal, which is less soluble and more likely to precipitate under reducing conditions. Dietz & Clausen (2006) found IWS to improve zinc performance, and Blecken et al. (2010) found only a slight improvement. Norrström & Jacks (1998) noted zinc to be vulnerable to reducing conditions. There was also no clear link between vegetation and zinc removal. While the general consensus seems to be that soil sorption is the primary removal pathway, other plant species may vary in performance.

While salt concentration appeared to have little effect on zinc removal efficiency in this experiment, there was a clear decline in removal attributable to the effects of salt. Zinc mobility in response to NaCl application is well documented by studies like Kakuturu & Clark (2015), but the large extent to which some columns leached zinc relative to normal zinc and copper performance is surprising, and it stands out from the existing literature. Studies of bioretention and soil in response to NaCl such as Endreny et al (2012), Denich et al. (2013), Søberg et al. (2014), Bäckström et al. (2004), Norrström & Jacks (1998) have found similar relatively minor dips in copper and zinc performance. It should be noted that Paus, et al. (2014) linked higher temperatures to amplified effects of NaCl on heavy metals in bioretention, so the unseasonal greenhouse temperatures could have played a role in zinc mobilization.

The effects of salt on copper versus zinc have had mixed results in other studies. McManus & Davis (2020) tested bioretention in response to NaCl, finding slight effects on the mobility of both copper and zinc, but they also found zinc effluent concentrations to be higher than those of copper. Copper is usually lower in concentration than zinc, and removal efficiencies in their study were even. Lange et al. (2020)(Lange et al., 2020), another bioretention study, found fairly even effects of salt on copper and zinc, though copper performance was slightly worse. There was no export of either metal. Amrhein et al. (1992) found copper to be vulnerable to salt, the result of organic colloid dispersion; and Acosta et al. (2011) found copper to be more vulnerable than zinc. However, Paus et al. (2014), Szota et al. (2015), and Søberg, et al. (2014) found zinc to be substantially more sensitive than copper. Doner (1978) found zinc specifically to be more vulnerable than copper due to chloride complexation (Doner, 1978). The greater vulnerability of zinc has been attributed to copper’s preference for strong organic complexes and zinc’s general strength of sorption relative to copper, protecting it from effects of salt like chloride complexation, ion exchange, and so on. Zinc is more significantly sorbed to metal oxides and exchange sites and is generally considered to be more exchangeable than copper, increasing its vulnerability to NaCl. It is likely that, while copper is mobilized by physical transport processes like dispersion, zinc is affected more by chemical desorption. It is therefore not that surprising that zinc breakthrough would occur without copper export; which is worse probably depends strongly on soil properties.

Mesocosm study: Total organic carbon

TOC, visible in Figure 32, follows distinct trends similar to those of phosphorus and copper. The figure's leftmost column, the free-flowing high salt mesocosms, all show a spike in TOC concentrations which peak in early April and declines over the rest of 2022. This peak is attributable to organic colloid dispersion induced by deicing salt. In the IWS high salt mesocosms, however, this peak is suppressed and slightly delayed. IWS appears to stabilize the soil. The free-flowing low salt mesocosms appear similarly suppressed and delayed, and the IWS high salt mesocosms perform the best, suggesting that salt concentration also plays a role in dispersion. The peaks and periods of dispersion generally line up with peaks in TSS, phosphorus,

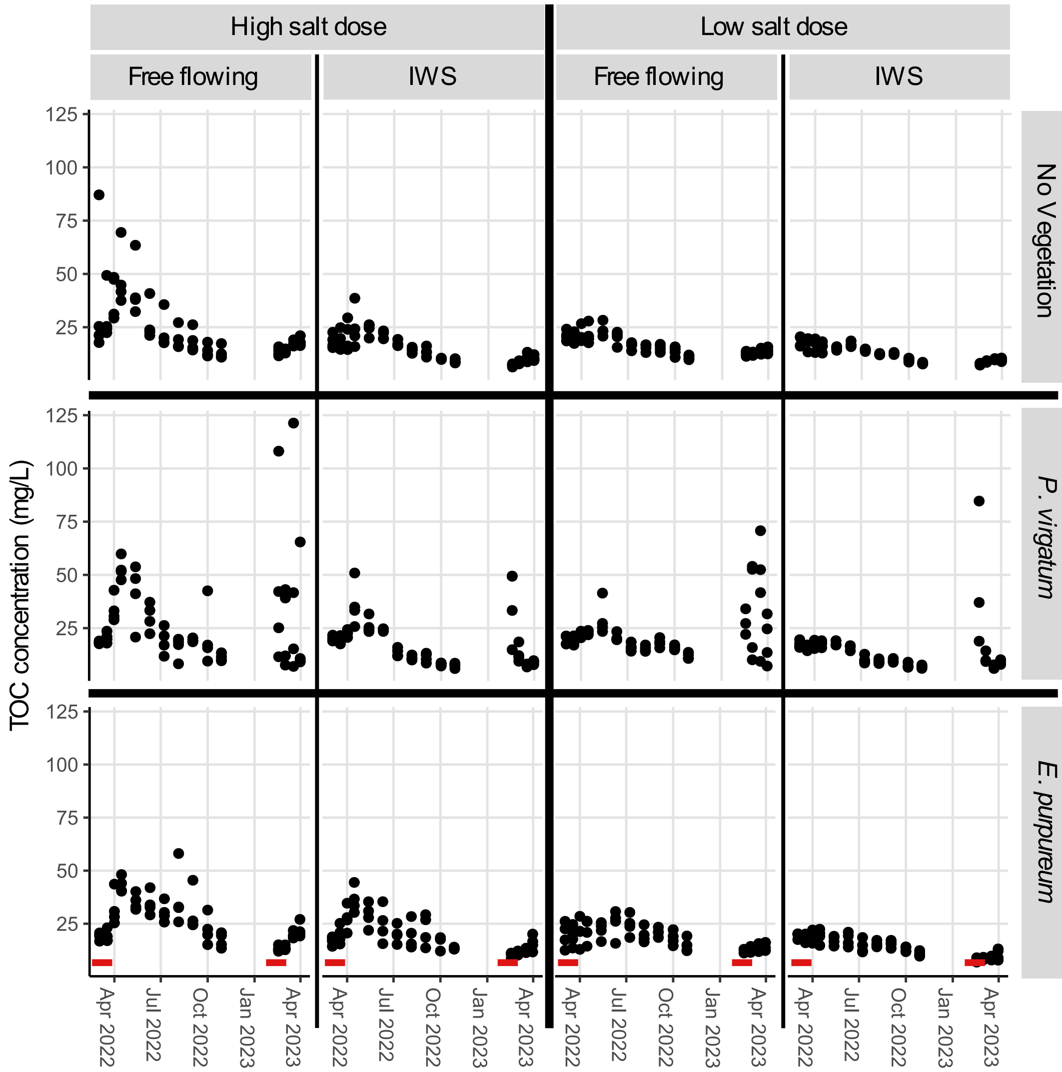

Figure 32: Total organic carbon (TOC) concentration over the course of the experiment. Red bars indicate salt application.

and copper, supporting the theory that organic colloid dispersion was at least partially responsible for drops in their performance. There is little difference in performance between vegetation treatments in 2022.

Interestingly, in 2023, while both unvegetated mesocosms and *E. purpureum* columns appear to begin following the same trends as in 2022, with higher concentration and absence of IWS worsening performance (though performance is generally better than the previous year due to lower salt doses), the *P. virgatum* columns perform especially poorly. This same trend was observed with TSS, though it is surprising that IWS seems to stabilize the loss of TOC to some while worsening TSS. Regardless, this supports the idea that *P. virgatum* is somehow destabilizing the soil in its columns or increasing colloidal transport.

Organic colloid dispersion in response to NaCl has been observed in many studies, such as Norrström & Jacks (1998), Amrhein et al. (1992), Nelson et al. (2009), McManus & Davis (2020). It has been linked to salt concentration, with lower concentrations generally increasing dispersion in Amrhein et al. (1993), Kakuturu & Clark (2015), and Norrström (2005). High sodium concentrations increase the soil electrolyte concentration, decreasing the width of the diffuse double layer, favoring forces of coagulation and aggregation in the soil. However, because salt dosing was only for a few weeks in this experiment, sodium dropped after salt dosing had ended, decreasing the electrolyte concentration and eventually creating conditions favorable for dispersion in both high and low salt mesocosms. This seems to reveal that in the long term, high salt concentration worsens the effects of organic dispersion.

Mesocosm study: Outflow volume

Note that outflow was collected for 2-3 hours after watering, and while most flow occurred during this time, occasional drips and minor flows were observed up to several days after watering. This data should be considered a conservative estimate of total outflow. All mesocosms (visible in Figure 33) start at about the same point in early 2022, already substantially reducing outflow (relative to the inflow volume of 1,433 mL). Vegetated mesocosms rapidly dropped in the spring and increased a bit in the fall, while the unvegetated columns remained mostly the same year-round.

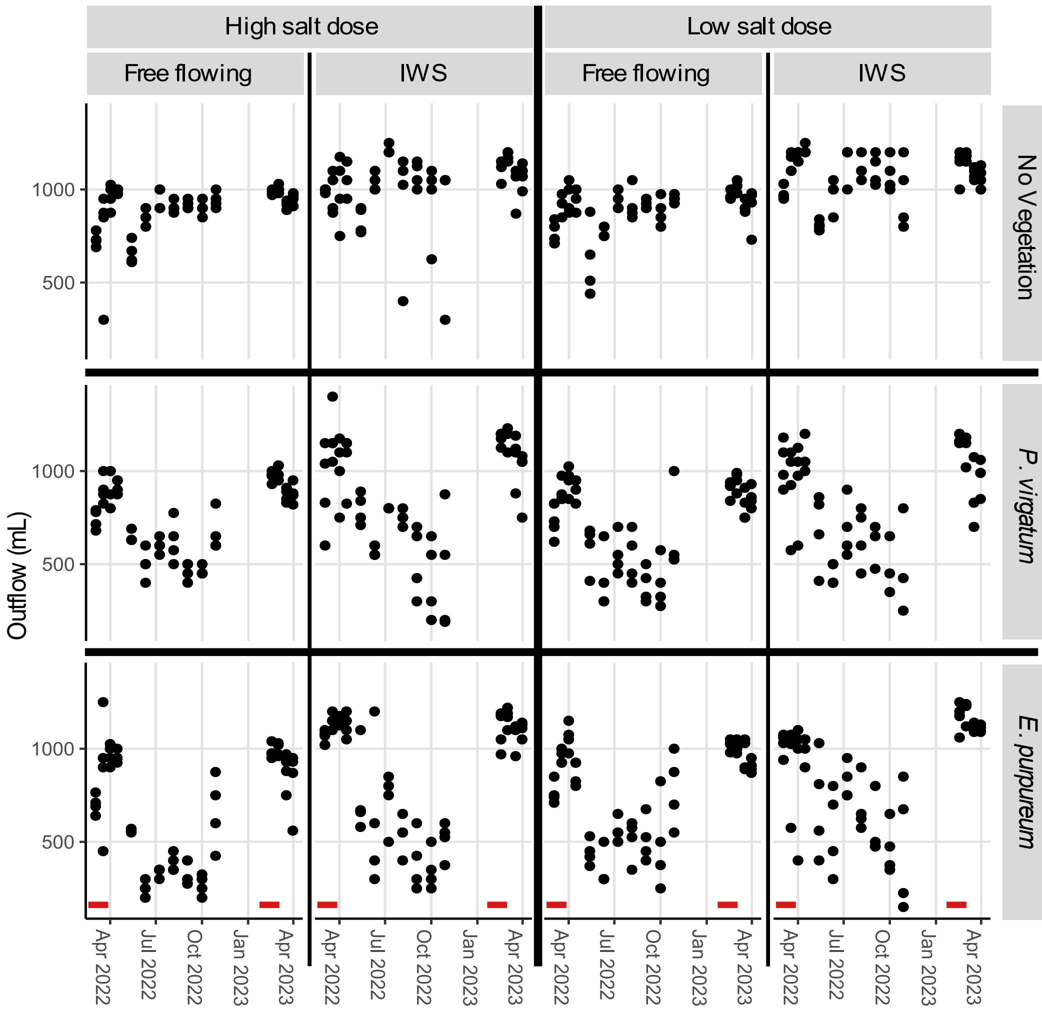

Figure 33: Mesocosm outflow over the course of the experiment. Red bars indicate salt application.

The drop is attributable to evapotranspiration in the summer, emphasizing the importance of vegetation rather than soil alone for reducing total stormflow. Surprisingly, the results of IWS are unclear, and even seem to slightly increase outflow relative to their free-flowing vegetated/unvegetated counterparts. It was anticipated that increased water storage would increase evapotranspiration, as observed by Li et al. (2014), Hess et al. (2017), Sharkey & Hunt (2012). This likely cannot be attributed to the 2-3-hour sampling period because the increased retention time provided by IWS was expected to slow down the drainage rate, not increase it. While the outflow volume reductions provided by vegetation may still have played a role in reducing effluent loads, trends in analyte loads cannot be attributed to increases or decreases in outflow volume because they generally correspond almost exactly with trends in effluent concentrations.

The reduction in total effluent volume from bioretention basins or columns has been observed by many studies (Bratieres et al., 2008; Davis, 2008; Geheniau et al., 2015; Muthanna et al., 2007; Roseen et al., 2009; Sharkey & Hunt, 2012). It is been generally attributed to evapotranspiration and storage provided by the basin and soil, responding to seasonal trends in temperature and plant growth.

Mesocosm study: Plant analysis

Analysis of plant height reveals some significant differences in direct response to salt. In April 2022, Joe Pye weed plants largely did not emerge in the high salt treatment. For switchgrass mesocosms, plants were taller in low salt treatments, as well as in mesocosms with internal water storage (Figure 34).

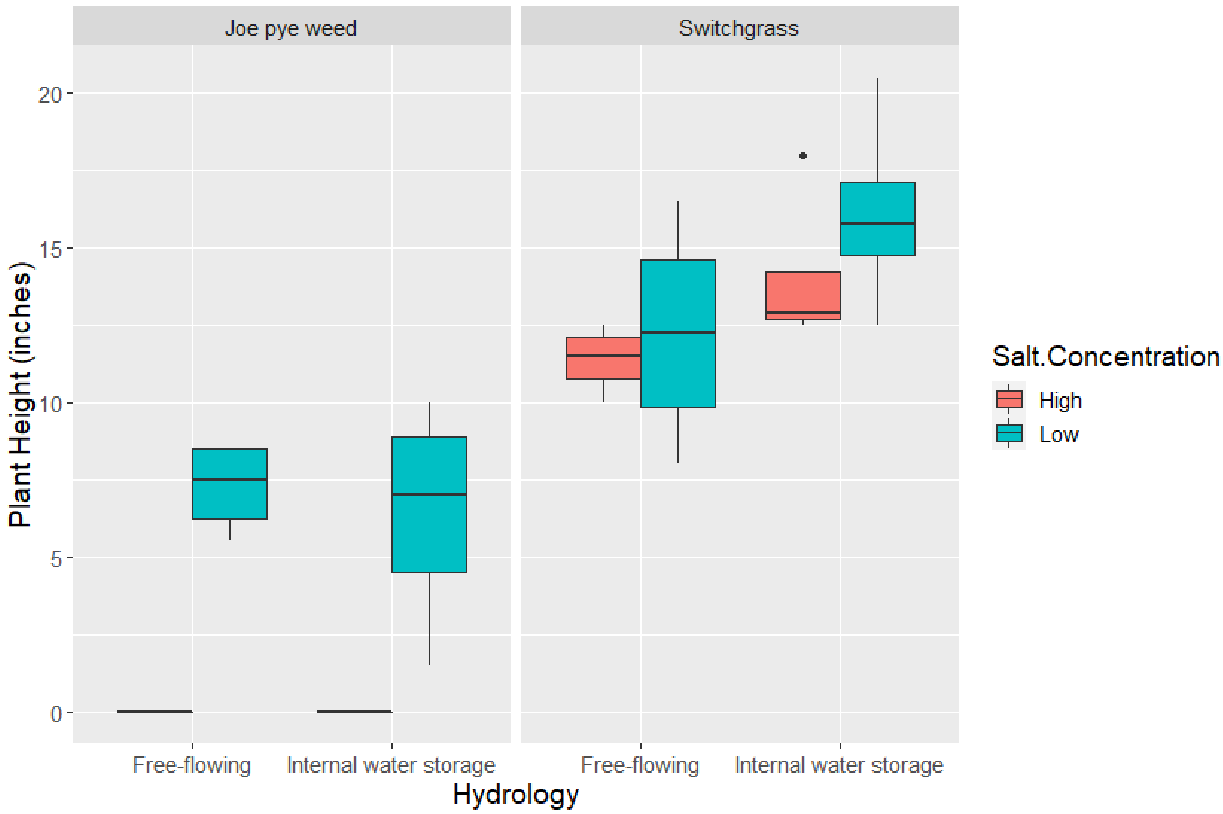

Figure 34. Plant height as measured for mesocosms in April 2022 (shortly after salty stormwater inputs had ceased)

At the end of the season in November 2022, differences were less pronounced (Figure 35). It is important to remind that Joe Pye weed plants in the high salt treatment were replaced in late spring 2022. There was no difference based on salt concentration at the end of the season, demonstrating the ability of plants to recover after more time had passed since salt application. However, there was a slight (p=0.01) effect of internal water storage on plant height. Surprisingly, it was a slight negative effect. While IWS can potentially support sustained moisture for plants in some systems, in these systems the interaction with salt may have led to this slight negative effect on plant height.

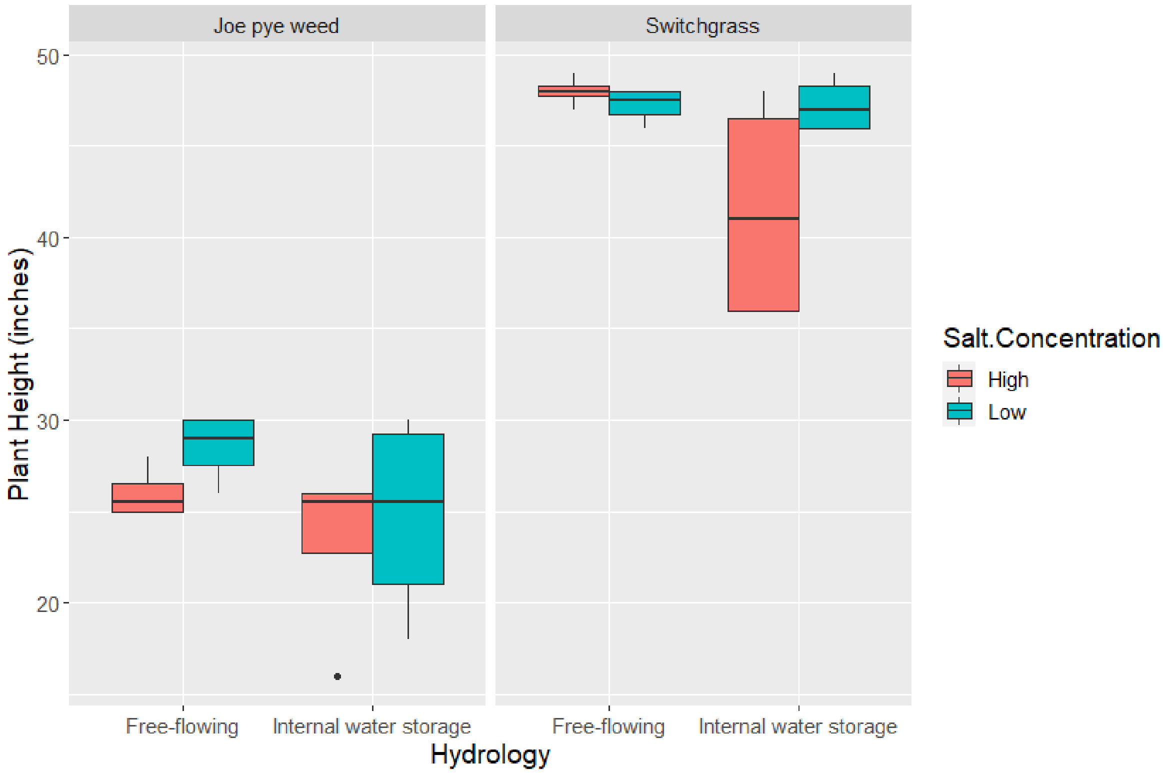

Figure **35**. Plant height as measured for mesocosms in November 2022, shortly before plants were cut back for the season

Mesocosm study: Soil analysis

For soils, there were not many clear trends. One clear trend is that all mesocosm soils showed increases in copper and zinc concentrations at the end of the experiment compared to the initial soil media. The initial soil media contained 2.9 ppm Cu and 8.8 ppm Zn. Figure 36 and 37 indicate that mesocosm soils had significant accumulation as compared to these initial concentrations. Comparing Cu and Zn between mesocosm treatments, the only factor that was statistically significant was presence of switchgrass ($p=0.04$), indicating slightly enhanced metals accumulation.

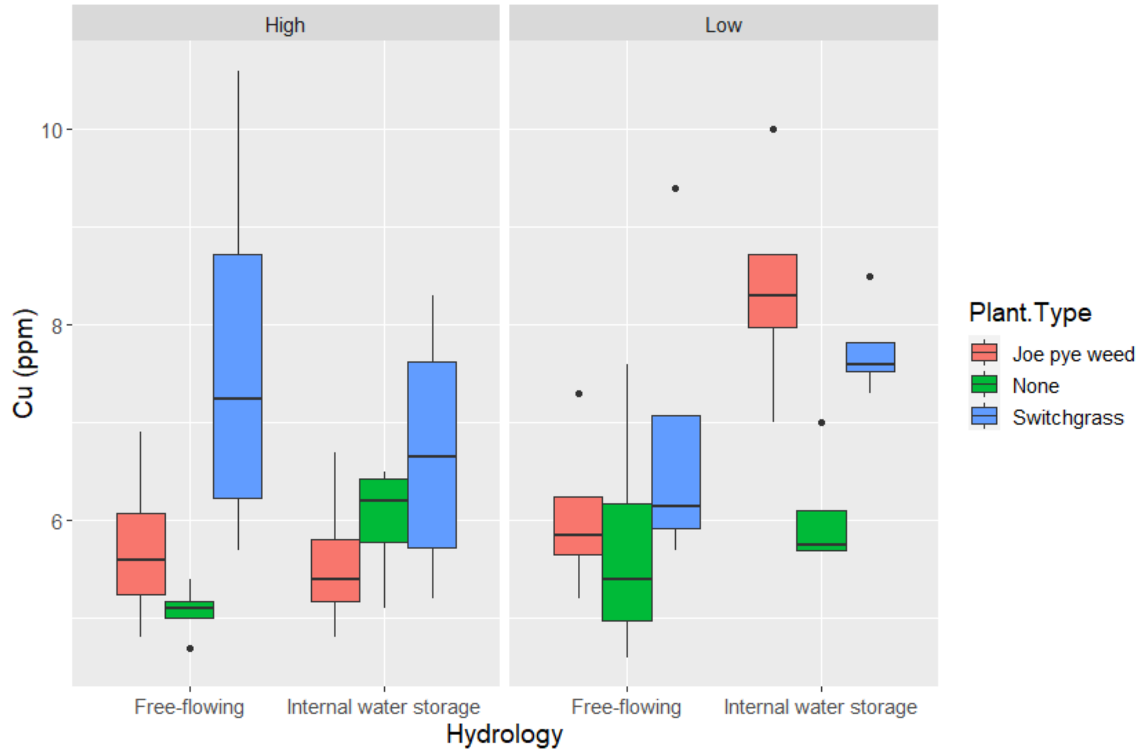

Figure **36**. Copper concentration in mesocosm soils at the end of the experiment (May 2023). For reference, initial concentration at start of experiment was Cu= 2.9 ppm.

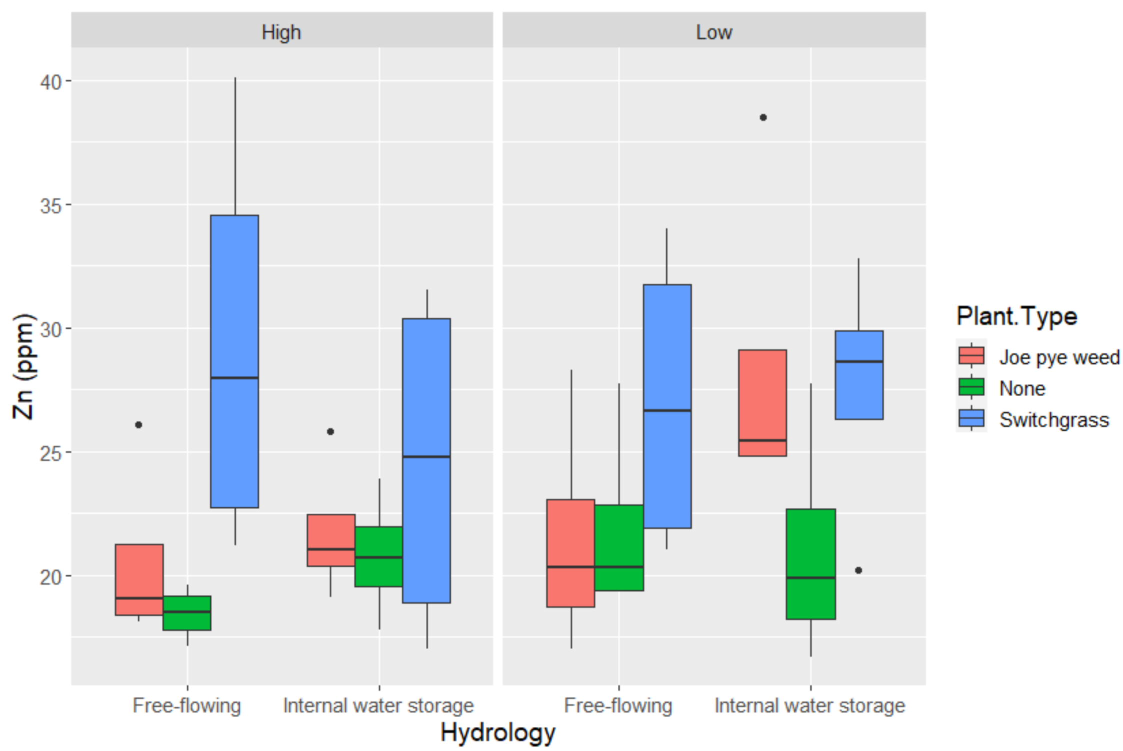

Figure **37**. Zinc concentration in mesocosm soils at the end of the experiment (May 2023). For reference, initial concentration at start of experiment was Zn= 8.8 ppm.

Limitations and Challenges

While we were able to generate some useful insights from the field study, there were quite a few unanticipated challenges, and many lessons were also learned. While we did our best to initially select sites that appeared to demonstrate differences in salt loading and associated soil salinity patterns, the events we were able to capture did not have salt trends that aligned with these trends. Part of the reason was less-than-ideal weather during the sampling period. We initiated our water sampling just after the larger de-icer events of winter 2021-2022, and then winter 2022-2023 ended up being one of the most mild in recent memory. This led to chloride trends in water samples that did not necessarily align with long-term trends in the basin (previous grab samples before this study had concentrations on the order of 500-1000 mg/L), and chloride concentrations from the basin samples were generally much lower than those observed in the mesocosm study. With regards to site choice, if we were to conduct this study again, we would select sites that did not have pre-treatment systems up-flow, as this also reduced some of the salt inputs to the sites. The sheds that were used to house the automated samplers along with other necessary sampling equipment were constantly vandalized. There were various unexpected issues encountered at the field sites, such as not triggering of the automated water sampler during a storm event, draining out of batteries sooner than expected, sudden failure of solar powered modules for salinity and moisture measurements, and lysimeters pulled out from the ground. We did our best to manage these issues and identify solutions to continue sampling again as soon as possible. There was also a break in the underground drinking water pipeline adjacent to the basin with high salt loading which led to the maintenance activities in the vicinity, possibly causing more metals and sediments entering directly into the basin, which would not be accounted in the inlet concentration.

While it is helpful to have data from actual basins, we see great value in also having an accompanying greenhouse mesocosm study. We were able to explore many of the same factors, but while varying them more systematically, to better identify which characteristic may be responsible for a particular change. Additionally, we could actively introduce interventions that were not present in the field sites, in order to understand possible management strategies to induce better outcomes. If repeating such a study in the future, we would likely adjust the way by which we conducted the salty stormwater dosings; while we added salty water in back-to-back events, we believe that interspersing some events with lower or no salt may better mimic real conditions.

Conclusions

Field study

A field investigation was conducted in two stormwater bioinfiltration basins in Brandon Park, Lancaster, PA from February 2021 to May 2023. Soil salinity levels peaked shortly after salt application, indicating the immediate impact of salt loading on soil salinity in receiving stormwater basins. It is noteworthy that the salinity levels did not return to their original values during the study period, suggesting a prolonged influence of salt application (i.e. storage in basin soils). Further long-term monitoring is warranted to explore the dynamics of salinity levels in the basins over an extended timeframe. At the basin with higher soil salinity (BH basin), the chloride concentrations in the inflow and outflow indicated overall chloride flushing in the basin. Interestingly, at the basin with lower overall soil salinity and assumed salt inputs (BL basin), the average chloride concentrations for sampled storm events were higher compared to the high salt basin during our sampling period; however, this anomalous relationship is likely due to sampling that occurred during a relatively mild winter period with overall low chloride loading. The lower inflow volume in the basin may have allowed for a longer retention of chloride by the soil, which resulted in a delayed release of chloride when the basin received subsequent inflow. These results emphasize the importance of understanding the temporal dynamics of chloride in bioretention basins and their implications for water quality. In future work, it would be ideal to capture de-icing events across multiple seasons to better understand variability.

Overall water quality performance of the two basins was pretty good for some pollutants, while mediocre for others. In general, removal efficiencies were better at the BH basin (Brandon Park High) as compared to the BL (Brandon Park low) basin. Total suspended solids (TSS) performance was strongest overall, with most events exceeding 90% retention. Total phosphorus (TP) removal was next best, at a median of 87% for BH basin, and 35% for BL basin. For metals, median removal efficiencies were 20-45% at BH basin, while they varied from just over zero to net negative for the BL basin. Total nitrogen (TN) removal was 30% at BH basin and negative (indicating net export) at BL basin. For base cations, such as sodium, calcium, and magnesium, there was consistent export, particularly closer to the winter season.

Dynamics of metals and nutrients by the bioretention basins were affected by the soil salinity to some extent, though rainfall magnitude also had a clear influence on metals and nutrients. Both copper (Cu) and zinc (Zn) removal efficiency were impacted by de-icer salt application. There were clear patterns of decline in total nitrogen (TN) removal efficiency due to salt application and instances of nitrogen export. Although total phosphorus (TP) removal efficiency was affected by salt dynamics with instances of TP leaching, the overall performance demonstrated effective TP removal capability of the basins. It also was clear that other factors in addition to de-icing salts were influencing pollutant retention; several pollutants had greater removal efficiencies in smaller storm events.

This study provides insights into the interactions between effluent concentrations, removal efficiencies, and various environmental parameters in bioinfiltration basins. Results indicate the influence of rainfall magnitude and salinity on the behavior and removal of metals and nutrients in the basins. They also indicate the high heterogeneity that can exist in stormwater treatment systems, and the challenges in interpreting many interacting variables. Though several water quality constituents have overall high retention/removal, there were also several instances of export. Though several interesting insights were generated from this field study component, it was also hampered by several challenges related to vandalism and extremely mild winter weather. Further research is necessary to better understand these relationships and their implications for optimizing the performance of bioinfiltration and bioretention systems.

Mesocosm study

A greenhouse experiment studied pollutant removal in 48 mini bioretention systems, referred to as mesocosms. This study allowed a more controlled evaluation of de-icer salt impacts on bioretention performance, in addition to consideration of vegetation and hydraulic-related factors. Overall, both event and annual average removal were good for all pollutants assessed in the study. On average, more than 80% and often more than 90% of the TSS and total phosphorus were removed. On average, more than 85% of the copper and zinc were removed, and their removal efficiencies often surpassed 90-95%. While nitrate and total nitrogen averages suffered as a result of the unvegetated free-flowing mesocosms, average removal in the mesocosms with internal water storage (IWS) was greater than 55%; and with vegetation as well as under ideal conditions, removal efficiencies greater than 70% could be achieved. While other studies have found removal efficiencies to vary quite widely, this data shows the potential of bioretention to effectively remove common contaminants from stormwater.

With that being said, NaCl deicing salt application did have significant negative effects on mesocosm performance. Total suspended solids, total phosphorus, and copper all showed rapid declines in performance, to varying degrees, after salt application. The declines were worsened by higher salt concentration but improved over time, and performance eventually returned to normal. Zinc showed an extreme decline, even resulting in significant export, but its performance too eventually returned to normal, although the extent of leaching may be underestimated due to low temporal resolution of data collection. The effects of NaCl deicing salt, which include colloid dispersion, chloride complexation, ion exchange, short-term acidification, and other indirect effects or interactions with sorption processes and vegetation, do negatively affect bioretention performance, though there was no clear effect of salt on nitrogen. There was also some indication, at least for some analytes (TSS, phosphorus, and potentially copper), that soil buildup over time or previous salt application may increase vulnerability to the effects of NaCl, although there were not sufficient results to confirm this theory and further research is needed. The presence of IWS was extremely important for nitrogen, mitigating nitrogen leaching even in the absence of vegetation and potentially mitigating some effects of salt. Internal water storage was shown to have beneficial effects on phosphorus and copper sorption, reducing the effects of deicing salt application. There was little effect of IWS on zinc and TSS; in 2023, however, IWS appeared to begin negatively affecting TSS removal in some mesocosms. Internal water storage generally seems to have a positive impact (and for nitrogen extremely positive) or no impact on contaminant removal, depending on the analyte, net-benefiting bioretention by increasing retention times, facilitating denitrification, and potentially increasing sorption of some contaminants.

Vegetation had effects that varied with the pollutant and to some extent the plant species. For nitrogen, both evaluated species were shown to be critical for good removal, mitigating the nutrient leaching shown by unvegetated mesocosms. For phosphorus, the effects were fairly small, and the presence of both plant species (though *P. virgatum* (switchgrass) performed slightly better than *E. purpureum* (Joe Pye weed)) did seem to improve the variability and removal of phosphorus a bit. There were no discernible effects of either species on copper or zinc, suggesting that sorption is the primary removal mechanism (and is likely dominant for phosphorus too). Vegetation mostly had little effect on TSS removal, although *P. virgatum* actually worsened performance. Generally, vegetation improves the performance of bioretention and mitigates some effects of salt, positively influencing bioretention by assimilating contaminants and supporting the soil microbiome. It may be of even greater importance in the long term, though trends vary by species and more research is needed.

Summary

1. Sodium chloride (NaCl) deicing salt application negatively affects the seasonal performance of bioretention for nutrients, sediment, and heavy metals. NaCl deicing salt use should be reduced where possible by maximizing distribution efficiency or finding alternatives. Sodium chloride may also affect maintenance costs by causing filter media failure and killing vegetation.
2. Though it can take months, bioretention recovers after salt flushes from the soil and can still effectively reduce annual loads of nutrients, heavy metals, and sediment after receiving significant amounts of salt.
3. The effects of NaCl deicing salt may be mitigated and the general performance of bioretention improved by ensuring that basins are well designed and maintained, such as by including an internal water storage (IWS) zone where possible, selecting appropriate plant species based on their preferred environments and durability, and replacing plants damaged by salt application or other stressors.
4. The effects of salt on bioretention likely vary with soil properties, and more research may be needed as the recommended designs for bioretention continue to evolve. Different plant species also have unique effects on bioretention and interactions with the soil and salts. Field work is also needed to verify these results in actual bioretention basins over longer periods of time.

Results indicate that stormwater bioretention and bioinfiltration is an effective management practice for removing nutrients, sediment, and metals. For nitrogen, bioretention may be subject to leaching; results indicate that presence of an internal water storage zone can ensure best nitrogen retention. Nitrogen performance is also strongly linked to plant health, and thus can be reduced when salt toxicity affects plant health. Bioretention generally does an excellent job of removing phosphorus, sediment, and metals; however, reduced removal efficiencies were observed under increased salt, with some zinc leaching occurring. Better phosphorus removal was observed with IWS implementation. While performance of bioretention can be enhanced by use of salt tolerant plants and presence of an IWS zone, it is clear that reductions in salt application are also critical.

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Appendix

Table A1. Soil chemistry for stormwater basin field study, based on a Mehlich 3 digestion

Basin	*Time of Sampling*	*Zinc (mg/kg)*	*Copper (mg/kg)*	*Calcium (mg/kg)*	*Phosphorus (mg/kg)*
BH	Nov 2022	15.1	3.6	2721	109
BL	Nov 2022	4.8	1.4	1307	39
BH	May 2023	20.7	4.9	3419	130
BL	May 2023	4.4	1.4	1298	39

Table A2. Vegetation chemistry for stormwater basin field study

Basin	*Location Within Basin*	*Copper (mg/kg)*	*Zinc (mg/kg)*	*Sodium (mg/kg)*	*Nitrogen (%)*
BH	Near inlet	14	40	30	1.9
	Mid basin	8	19	16	2.3
	End of basin	10	21	34	2.5
BL	Near inlet	14	34	17	1.7
	Mid basin	9	37	20	2.1
	End of basin	9	35	10	1.6