ACS ES&T Water

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Article

Impacts of Deicer Salt on Water Quality Performance of Stormwater Bioretention Systems with Varied Vegetation and Hydrology

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Cite This: *ACS EST Water* 2024, 4, 2882–2893

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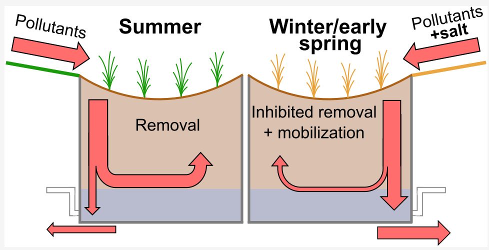


ABSTRACT: Sodium chloride (NaCl) deicers contaminate bioretention and influence effluent water quality, the effects of which are not yet fully understood. We tested this by constructing 48 mesocosms in a greenhouse, each having *Panicum virgatum*, *Eutrochium purpureum*, or no vegetation; having an internal water storage (IWS) zone or not; and being exposed to high or low NaCl doses in the late winters of 2022 and 2023. Synthetic stormwater was applied and effluent was monitored through May 2023 with an end-of-experiment analysis of soil and plant biomass for nitrogen, phosphorus, copper, zinc, and total suspended solids (TSS). Average effluent loads increased in spring, after NaCl application, for total phosphorus (+61%), copper (+61%), zinc (+88%), and TSS (+66%). These four analytes recovered by summer, with average annual percent removals >85%. Vegetation and IWS reduced annual phosphorus (by −33 and −70%, respectively) and copper (by −24 and −40%) loads, while higher NaCl concentrations increased annual phosphorus (+107%), copper (+22%), and TSS (+51%) loads. Nitrogen removal was not linked with NaCl but was dependent upon the presence of IWS or vegetation. Post-NaCl effluent spikes pose seasonal risks to aquatic ecosystems, emphasizing the need for active maintenance, redundant removal mechanisms, and minimized exposure to NaCl.

KEYWORDS: *sodium chloride, runoff, nutrients, heavy metals, saturation, biofiltration, internal water storage, sediment*

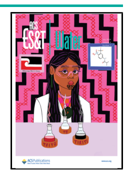
INTRODUCTION

Urbanization seals pervious surfaces and removes vegetation, drastically increasing stormwater runoff.[1] Engineered flowpaths like storm drains rapidly funnel this runoff into urban streams, collecting and transporting pollutants along the way and degrading stream ecosystems.[1] Stormwater control measures (SCMs) prevent degradation by attenuating peak flows and improving water quality.[1] One common SCM, bioretention, along with similar measures like rain gardens and biofiltration, uses a vegetated depression with an engineered soil profile to treat runoff,[2] removing contaminants through filtration, sedimentation, vegetative assimilation, adsorption, ion exchange, precipitation, and microbial activity.[3,4] An internal water storage (IWS) zone may be added, which submerges the bottom of the soil profile, creating reducing conditions, which enhance nitrogen removal via denitrification.[5] Although performance can vary, bioretention has been shown to improve water quality by removing nutrients, heavy metals, and sediment.[6−8]

Over 20 million tons of road salt are applied annually across the United States, most of which is sodium chloride (NaCl), preferred for its low cost and ready availability.[9] NaCl washes from impervious surfaces into stormwater infrastructure like bioretention basins, which pass it into streams or groundwater and soil.[10,11] Chloride concentrations exceeding the EPA acute toxicity limit (860 mg/L) have been recorded in runoff and streams after deicer application.[12−15]

NaCl interferes with bioretention contaminant removal pathways. For example, sodium and chloride compete with contaminants for ion exchange sites,[14] mobilizing phosphorus (P).[12,16] Chloride is a weak ligand, complexing with heavy metals and increasing their mobility.[14,17] Zinc (Zn) loss has been caused by both ion exchange and chloride complexation.[18−20] High exchangeable sodium, or sodicity, disperses colloids and clogs pores,[21,22] increasing total suspended solid (TSS) effluent[22,23] and destabilizing organic nitrogen (N) and P.[16] Copper's (Cu) strong affinity for organic complexes reduces its vulnerability to chloride complexation and ion exchange but makes it susceptible to organic dispersion.[16,21,24] NaCl is toxic to vegetation and microbes, and senescence or lost biological treatment (assimilation and denitrification) can increase nutrient and heavy metal effluents.[16,18,25] Together, these effects create feedback and complex cumulative impacts. For example, the breakdown of soil aggregates by dispersion, especially as chloride kills the roots supporting soil structure, could expose new substrates for P mobilization by mineralization.

Received: January 23, 2024
Revised: June 5, 2024
Accepted: June 7, 2024
Published: June 18, 2024



https://doi.org/10.1021/acsestwater.4c00062
ACS EST Water 2024, 4, 2882–2893

Kratky et al.[26] highlighted knowledge gaps in how deicing salts influence contaminant removal and interactions with design components, such as vegetation and IWS. Kaushal et al.[27] identified several questions among scientists and practitioners about the seasonal trends of salt impacts on SCMs and the storage and release of salt from SCM media, especially under varying conditions (e.g., redox potential). McManus and Davis[16] identified a gap in the literature around how NaCl affects nutrient removal. Moreover, not all studies agree on the response of contaminants to NaCl. For example, Søberg et al.[28] described inconsistencies in the literature on P, in which they linked NaCl with elevated effluent total phosphorus (TP) and not dissolved phosphorus (DP), Szota et al.[18] found that TP decreased and DP increased in response to NaCl, and Valtanen et al.[29] observed no trend. More recently, McManus and Davis[16] and Goor et al.[12] observed delayed spikes in TP, primarily as DP.

We investigated and quantified the effects of NaCl on the event, seasonal, and annual pollutant removal capabilities of bioretention in the presence and absence of vegetation and IWS. We constructed 48 soil columns in a greenhouse and dosed them with either a low or a high NaCl concentration in winter 2022 and 2023, monitoring effluent contaminant concentrations from January 2022 to early summer 2023. The primary contaminants studied were N, P, TSS, Cu, and Zn. We hypothesized that increased NaCl loading would decrease contaminant removal efficiency; that the presence of IWS would increase nitrate (NO_3^-) removal but could adversely affect P, heavy metals, and organic nitrogen removal; and that vegetation would increase contaminant removal but might in turn be adversely affected by NaCl.

METHODS AND MATERIALS

Mesocosm Construction. Forty-eight mesocosms (Figure 1) were built from PVC pipe with inner walls sanded to mitigate preferential flows. The mesocosms were distributed randomly throughout two rows in a greenhouse conditioned to 20−25.6 °C year-round. Mesocosms included a filter media layer to support plant growth and water treatment and a sand layer to stabilize the filter media. The filter media was a topsoil blend from a local nursery with characteristics typical of bioretention media (Figure 1). Woodchips (debarked oak and maple) were added to the sand layer to provide a carbon source for microbes.[30]

Half the mesocosms included an IWS zone via an upturned drain to promote heterotrophic denitrification.[31] Two plant species, *Panicum virgatum* "Cape Breeze" and *Eutrochium purpureum* "Euphoria Ruby" PPAF, commonly known as switchgrass and sweet-scented joe-pye weed, each occupied a third of the mesocosms with the remaining third left unvegetated. *Panicum* and *Eutrochium* are frequently used in the mid-Atlantic region, favored for tolerating salt and various sun exposures and moisture regimes,[32] and generally perform well in bioretention.[32−34] Half the mesocosms received a low NaCl concentration and the other half received a high NaCl concentration. The treatments were allocated among the 48 mesocosms to create 12 groups of 4 replicates, each group with a unique combination of the treatments: an IWS zone or unrestricted outlet; *P. virgatum*, *E. purpureum*, or no vegetation; and the low or high NaCl dose. Using typical effective pore volume values for coarse sand and gravel, the IWS pore space was estimated to be slightly larger than the influent volume, yielding a hydraulic residence time (HRT) of

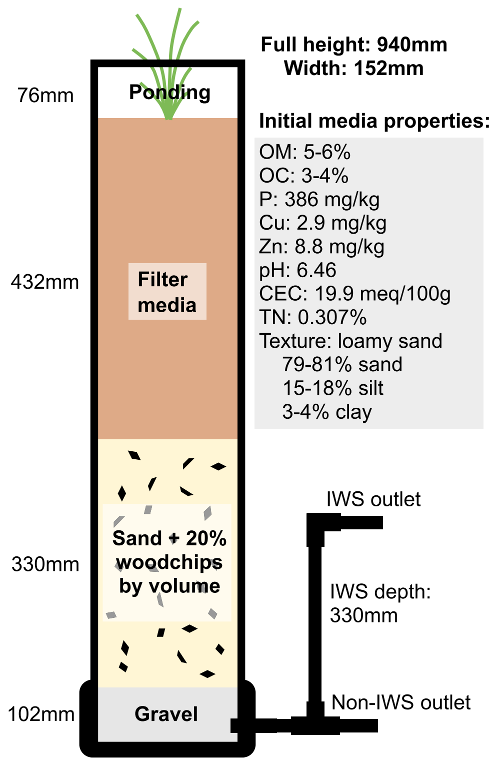


Figure 1. Mesocosm design and initial soil properties. OC: organic carbon.

4−5 days. Effluent volumes often dropped >30% in vegetated columns in the summer (presumably due to evapotranspiration), so actual HRT increased seasonally. Longer HRTs have been linked with higher N removal. 4−5 days is well beyond the minimum thresholds.[36,37]

Synthetic Stormwater Composition and Dosing. The mesocosms received tap water for 2 weeks before switching to non-NaCl synthetic stormwater in Fall 2021. The synthetic stormwater concentration targets and sources in Table 1 were selected from bioretention mesocosm literature.[34,35] The base was rainwater, collected from rain barrels on a suburban house and the greenhouse, both with low contaminant concentrations. The stored rainwater was insufficient for watering one time, and tap water was used. Variability in synthetic stormwater concentrations is attributable to rainwater and

Table 1. Synthetic Stormwater Concentrations, mg/L

constituent	source	target concentration	average concentration (±SD)
PO_4^{3-}−P	K_3PO_4	0.5	0.52 (0.15)
TP			0.62 (0.07)
NO_3^-−N	KNO_3	1.5	1.70 (0.45)
ammonium-N	NH_4Cl	0.5	
TN			2.95 (0.62)
Cu	$CuSO_4$	0.15	0.12 (0.03)
Zn	$ZnCl_2$	0.6	0.61 (0.11)
TSS	leftover filter media	100	108.6 (63.7)
chloride, low	NaCl	500[a]; 300[b]	523 (19)[a]; 331 (1)[b]
chloride, high	NaCl	2000[a]; 1200[b]	2058 (50)[a]; 1291 (29)[b]

[a]First winter (2021−22). [b]Second winter (2022−23).

https://doi.org/10.1021/acsestwater.4c00062
ACS EST Water 2024, 4, 2882−2893

contaminants introduced by TSS. The leftover filter media used for TSS were lightly ground to break up aggregates and placed through a No. 10 sieve. Stormwater quantity was determined by the typical central Pennsylvania annual rainfall (116.84 cm) divided evenly into twice-weekly storms (1.12 cm). By assuming a 1:7 bioretention area/watershed area ratio, the inflow became 7.86 cm, or 1.43 L poured into each mesocosm. Substantial erosion occurred by the end of the experiment, despite the initial addition of a surface gravel layer. While compaction and clogging by filtered sediment may have occurred, drainage was often rapid (<1 h).

After an initial effluent sampling in November 2021 to establish a baseline, the mesocosms were moved outside for winter (wrapped in insulation and tucked against a building to avoid freezing) so the plants could enter dormancy. No stormwater dosing occurred during this period, but the mesocosms received direct precipitation. The mesocosms were brought back inside in February 2022 and stormwater dosing resumed, this time with added NaCl for six doses, the first four consecutive and the last two alternating with non-NaCl. Chloride concentrations (Table 1) were selected after reviewing laboratory and field studies.[12−14,16,28,38] While NaCl application inside the greenhouse was necessary to prevent disruption and complete freezing of the mesocosms/IWS zones, high temperature has been shown to amplify the effects of NaCl on TP, Cu, and Zn.[28,39,40] Inside, plants came out of dormancy and became vulnerable to ongoing NaCl application, a contributing factor to poor survival.

In the spring, all high-NaCl *E. purpureum* died, indicating that NaCl was responsible. These were replaced shortly before the May effluent sampling. The filter media disturbance caused a total nitrogen (TN) spike in free-flowing replicates[34] from an average of 7.67 mg/L (SD = 85) in the previous sampling to 24.22 mg/L (SD = 6.23) in May, 84% as nitrate. TN loads were mediated by volume reduction, with averages increasing from 7.32 mg (SD = 0.72) to 12.19 mg (SD = 2.84). IWS replicates experienced no TN change and no other analytes were affected. All mesocosms were weeded regularly, but unvegetated mesocosms grew a layer of moss that was not removed to avoid filter media disturbance.

Non-NaCl dosing continued until late October 2022, when the mesocosms were moved back outside. A second round of NaCl stormwater dosing began in February 2023, proceeding as before but with lower chloride targets, an attempt to improve the survival of *E. purpureum*. In the second spring, plant survival was poor across all treatments despite the lower NaCl targets, likely the effects of NaCl exposure compounded by harsher weather, false springs, and mesocosm conditions like erosion and compaction. Because the experiment was approaching completion, no plants were replaced. Non-NaCl stormwater dosing continued until early June.

Effluent volume from one *P. virgatum* IWS low-NaCl mesocosm decreased over 2022, entirely stopping by October. Water pooled and evaporated at the surface, which was constantly submerged (except for a brief period in early 2023, after freeze−thaw improved drainage). The mesocosm's failure may have been caused by compaction and media clogging, but several other *P. virgatum* mesocosms were also observed to drain slowly, while other vegetation treatments were unaffected. The reason is unknown.

Sampling and Data Analysis. Effluent samples were collected every 4 weeks, or 2 weeks during and immediately after NaCl application, with 18 total samples. Effluent was collected in containers for 2−3 h before being sampled. Effluent volumes were recorded, and samples were refrigerated immediately and processed within 1 week (or frozen when necessary). Filter media grab samples were collected from the filter media stockpile at the beginning of the experiment. At the end, each mesocosm was sampled 5 cm below its surface. Root and surface plant biomass samples were collected from spare plugs at the beginning and survivors at the end, and growth and health were monitored throughout.

TSS analysis was performed according to USGS I-3765-85 within 24 h. Subsamples were filtered to 0.45 μm for ion chromatography with a Thermo-Fisher Dionex ICS-1100 for NO_3^-−N, nitrite (NO_2^-)−N, sulfate, chloride, and phosphate (PO_4^{3-})−P. Unfiltered subsamples were acidified to pH < 2 with sulfuric acid within 24 h, digested (EPA 200.7), and analyzed via inductively coupled plasma-optical emission spectroscopy (ICP-OES) for total Zn, Cu, TP, calcium, magnesium, potassium, and sodium, though base cation analysis began in August 2022. The subsamples were also analyzed with a Shimadzu TOC-L/TNM-L for total organic carbon (TOC, measured as nonpurgeable organic carbon) and TN.

Filter media samples were analyzed for organic matter by loss on ignition,[41] for texture with a hydrometer,[42] and by Penn State's Agricultural Analytical Services Lab for pH, nitrogen by combustion, and P, Cu, Zn, calcium, magnesium, and potassium by Mehlich III and ICP-OES. Plant biomass samples were dried for 3 days at 60 °C, ground, and analyzed via combustion for N and digestion (EPA 3050B) and ICP-OES for P, Cu, Zn, calcium, magnesium, potassium, and sodium.

Sample concentrations were multiplied by effluent volumes to produce loads. Removal efficiencies—percent removal—were calculated by $100\left(\frac{\text{influent} - \text{effluent}}{\text{influent}}\right)$. Efficiency represents effectiveness, though it has weaknesses, such as failure to account for background media concentrations/removal limits.[43] Annual load and efficiency estimates were calculated for 2022 with linear interpolation of concentrations and effluent volumes between samplings. While concentrations and loads generally showed the same trends for all analytes, load data is presented below because it captures differences in effluent quantity (vegetation lowered outflow in warm months).

Statistical analysis was completed in R version 4.1.2. This did not include the fall 2021 sampling because it was not representative of NaCl exposure. Treatments were converted to binary variables, indicating their presence. Multiple linear regression was performed, with model assumptions confirmed before analysis using analysis of variance (ANOVA) and Student's *t*-test. Detection limits were substituted for non-detects, affecting TP (~22% of measurements <0.01 mg/L) and Cu (~11% <0.005 mg/L), to avoid overestimating the abilities of bioretention. Though nondetects were fairly low, we anticipate substitution to have caused an overestimation of averages and annual loads, especially affecting treatments more likely to produce nondetects like IWS. Analysis will consequently underestimate the benefits of those treatments and overestimate the unfavorable effects of others. This overestimation is somewhat negated by the smaller data range. Variability in the data was generally attributable to seasonal or weather-related trends, initial media conditions, column characteristics slowly changing over time, small variation in influent concentrations, and any random or

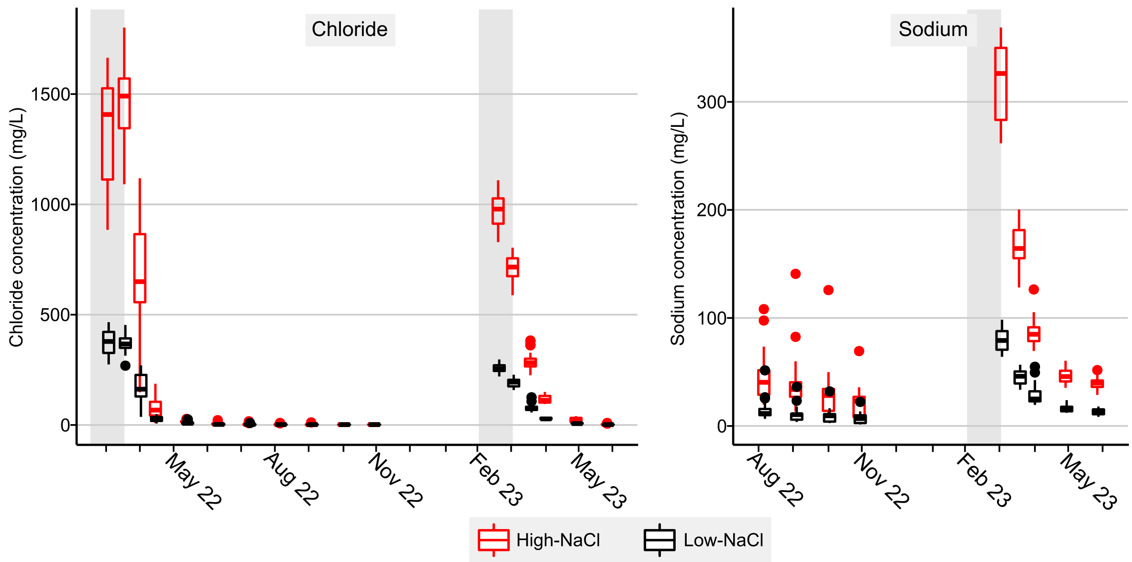


Figure 2. High- and low-NaCl treatment chloride and sodium effluent concentrations. Gray shading indicates NaCl dosing periods. Sodium data collection began in August 2022, and sodium data from February 2023 was not included due to instrument error.

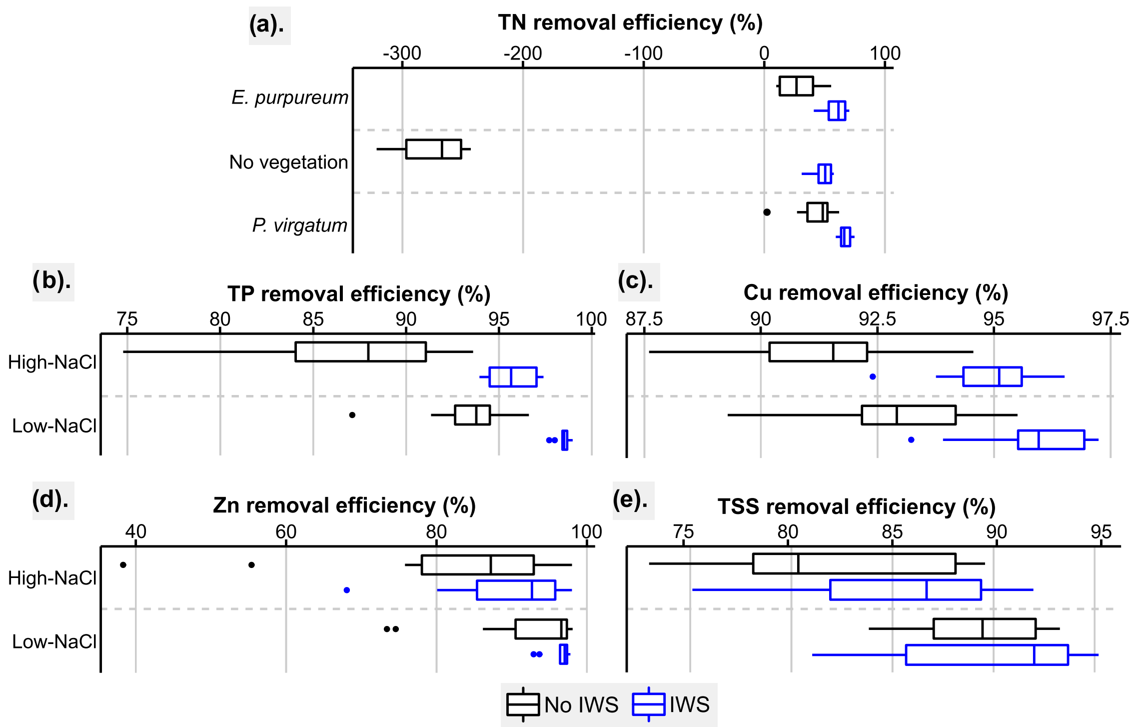


Figure 3. 2022 annual load removal efficiencies for TN by IWS and vegetation treatment, and TP, Cu, Zn, and TSS by IWS and NaCl treatment.

systematic error introduced in the experimental setup or sample analysis. Annual removal efficiency was controlled for seasonal trends, yielding higher R^2 values.

RESULTS AND DISCUSSION

Water Quality Data. *Sodium and Chloride.* During NaCl dosing, chloride effluent concentrations (Figure 2) ranged from 44–99% of inflow concentrations, averaging about 72% (SD = 12%). After dosing ended, effluent approached background concentrations (1–2 mg/L, the non-NaCl influent concentrations) within 2–4 months depending on NaCl treatment, high-NaCl mesocosms remaining slightly elevated (2–4 mg/L) into fall. Chloride concentrations in November 2021 averaged 17.5 mg/L (SD = 8.5), and the filter media or sand may have been exposed to chloride before the experiment, possibly at the nursery. Short-term retention on exchange sites and in micropores was expected and has been recorded in green infrastructure and soil.[10,11,27] IWS influenced persistence, first by dilution, reducing average chloride concentrations in the initial samples of 2022 and 2023 by 17% relative to non-IWS columns. When application ended, IWS stored chloride, increasing average effluent concentrations by 47%. While the actual concentration difference was increasingly marginal and substantial flushing occurred at nearly the same rate as non-IWS, many remained elevated by

Table 2. Mean Effluent Performance Values and Effluent Load ANOVA Results for Major Analytes by Treatment[a]

treatment	TN		NO_3^-−N		TP		Cu		Zn		TSS	
mean event	load	(±SD)	load	(±SD)	load	(±SD)	load	(±SD)	load	(±SD)	load	(±SD)
mean event	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)
mean annual	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)	efficiency	(±SD)
unvegetated	7.81	7.55	5.33	6.28	0.110	0.130	0.0100	0.0100	0.0500	0.190	24.4	25.8
	−84.8	179	−119	258	87.8	14.6	91.8	4.68	93.9	21.8	84.3	16.6
	−113	162	−142	230	91.7	6.87	92.6	2.58	91.7	9.93	86.5	5.70
E. purpureum	4.06	5.44	1.99	3.84	0.0600	0.0700	0.0100	0.0100	0.0600	0.240	19.3	15.2
	3.81	129	18.5	158	93.3	7.59	93.2	4.84	93.4	27.0	87.6	9.70
	43.8	20.6	64.0	32.9	94.6	3.61	94.4	1.62	90.2	9.53	89.3	3.60
P. virgatum	1.96	1.87	0.630	1.19	0.0500	0.0800	0.0100	0.0100	0.0700	0.320	46.7	59.5
	53.6	44.3	74.3	48.7	94.1	9.30	94.0	4.72	92.0	36.6	70.0	38.3
	53.6	18.6	70.7	25.6	94.2	4.10	94.3	2.03	86.9	15.2	83.2	5.40
no IWS	7.41	7.42	5.07	5.78	0.110	0.120	0.0100	0.0100	0.0800	0.320	29.3	29.9
	−75.4	175	−108	237	87.3	13.6	91.4	5.07	91.3	36.4	81.2	19.2
	−67.9	148	−95.3	196	90.1	5.26	92.2	1.96	86.6	14.5	85.5	5.70
IWS	1.84	1.21	0.280	0.740	0.0300	0.0500	0.0100	0.0100	0.0400	0.160	30.7	48.1
	56.6	27.7	88.4	30.3	96.2	5.38	94.6	3.99	95.0	18.4	80.3	30.9
	57.4	11.9	91.3	10.8	97.0	1.68	95.4	1.24	92.9	7.10	87.3	5.20
low salt	4.72	6.37	2.79	4.97	0.0500	0.0500	0.0100	0.0100	0.0300	0.150	24.2	33.1
	−11.6	151	−14.7	204	94.3	5.97	93.8	3.80	95.6	16.9	84.4	21.3
	−3.27	129	−5.52	176	95.8	3.08	94.4	2.00	94.0	6.72	89.2	3.90
high salt	4.57	5.65	2.55	4.55	0.100	0.130	0.0100	0.0100	0.0800	0.330	35.7	45.1
	−8.08	134	−4.73	187	89.2	14.3	92.2	5.56	90.6	37.0	77.1	29.0
	−9.72	117	−2.48	162	91.2	5.90	93.2	2.36	85.5	14.1	83.7	5.50
Event	*p*-Value	Effect	*p*-Value	Effect	*p*-Value	Effect	*p*-Value	Effect	*p*-Value	Effect	*p*-Value	Effect
annual	*p*-value	effect	*p*-value	effect	*p*-value	effect	*p*-value	effect	*p*-value	effect	*p*-value	effect
E. purpureum	<0.0001	−	<0.0001	−	<0.01	−	<0.001	−	ns		ns	
	<0.0001	−	<0.0001	−	ns		<0.05	−	ns		<0.1	−
P. virgatum	<0.0001	−	<0.0001	−	<0.0001	−	<0.0001	−	ns		<0.0001	+
	<0.001	−	<0.001	−	<0.01	−	<0.001	−	ns		<0.01	+
IWS	<0.0001	−	<0.0001	−	<0.0001	−	<0.0001	−	<0.1	−	ns	
	<0.0001	−	<0.0001	−	<0.0001	−	<0.0001	−	<0.05	−	ns	
high salt	ns		ns		<0.0001	+	<0.0001	+	<0.05	+	<0.0001	+
	ns		ns		<0.0001	+	<0.01	+	<0.05	+	<0.0001	+
event Adj R^2	0.380		0.427		0.273		0.175		0.009		0.102	
annual Adj R^2	0.636		0.639		0.677		0.680		0.164		0.396	

[a]Loads given in mg, efficiencies in %. Event is effluent across all samplings. ns not significant; + increased event/annual load; − decreased event/annual load.

1−2 mg/L over non-IWS mesocosms into October, especially those that received the high-NaCl treatment.

Sodium 2023 influent concentrations were expected to contain about 195 mg/L sodium (for the 300 mg/L chloride dose) and 780 mg/L sodium (for the 1200 mg/L chloride dose). Effluent concentrations (Figure 2) during NaCl dosing ranged from 32−51% of inflow, averaging 41% (SD = 5%), rapidly declining thereafter, with IWS columns showing slightly elevated persistence similar to that of chloride. Fall 2022 concentrations were unstable and greater than non-NaCl inflow concentrations (<2 mg/L), suggesting that sodium did not fully flush before the next winter. Sodium persistence greater than chloride has been recorded in green infrastructure.[10,11,27] Chloride is negative and thus limited by the predominantly negative exchange sites, whereas sodium ions are positive and readily interact with soil, though high concentrations overwhelm capacity.[23,33] Ion exchange was demonstrated by calcium, magnesium, and potassium, which spiked during NaCl dosing (relative to October concentrations) by 99% (SD = 80%), 110% (SD = 81%), and 112% (SD = 61%), respectively. Relative to these averages, high-NaCl exposure increased the spikes by 113% for calcium, 117% for magnesium, and 63% for potassium.

Nitrogen. Unvegetated non-IWS replicates experienced TN leaching, with removal efficiencies ranging from −243 to −321% annually (Figure 3a), culminating in September 2022 (Figure S1), which averaged −492% removal (SD = 58.4%). September effluent concentrations averaged 27.19 mg/L (SD = 2.29). NO_3^-−N made up 72% of annual effluent TN from these replicates, measurements correlating well with TN across all replicates (R^2(adj) = 0.90, Figure S2). N leaching exceeded observations in other studies,[6−8] the filter media were evidently too coarse to form anoxic microsites considered important for denitrification.[44] Without a N removal mechanism, the filter media organic matter and woodchips are nitrified and leached, peaking in the summer with seasonal mineralization rates. Despite leaching, initial media TN was about the same as at the end of the experiment, 0.31 versus 0.30%, respectively. With a range of 0.24−0.34%, some samples even gained N, perhaps by accumulation of organic matter at the surface. With

https://doi.org/10.1021/acsestwater.4c00062
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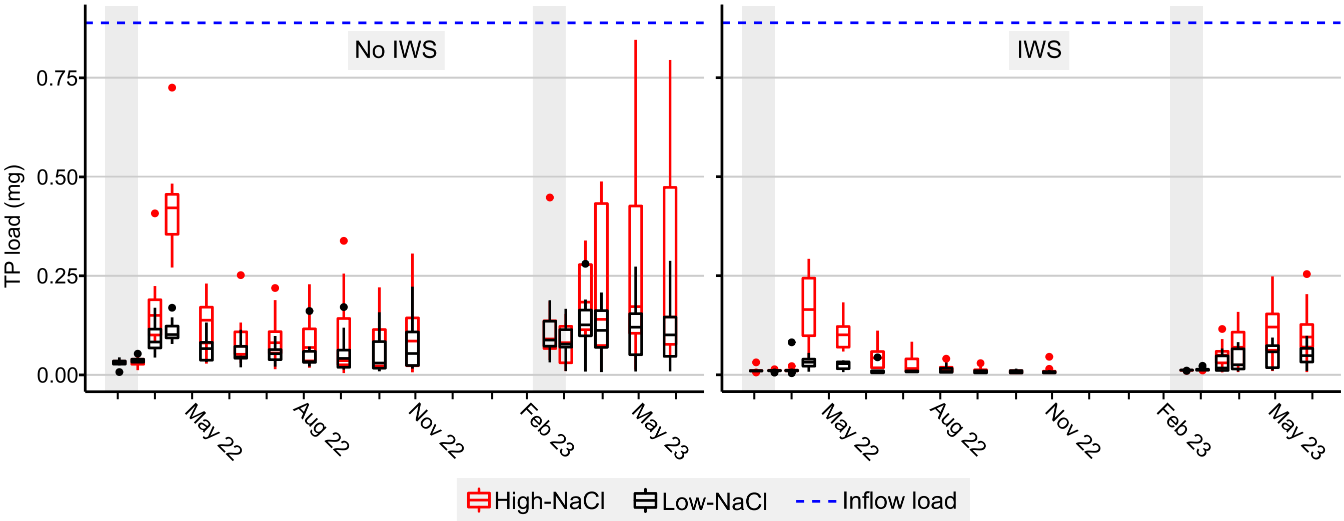

Figure 4. Effluent TP loads by IWS and NaCl treatment. Gray shading shows NaCl dosing periods.

the addition of vegetation, non-IWS annual removal efficiencies increased to 35% (SD = 19%, Figure 3a), with both *P. virgatum* and *E. purpureum* as statistically significant predictors of higher TN removal efficiency ($p < 0.001$, Table 2). In early 2022, TN and $NO_3^-{-}N$ removal efficiencies were similar to unvegetated replicates, and effluent TN loads averaged 6.47 mg (SD = 3.7) without vegetation and 5.69 mg (SD = 3.1) with it during March and April. Removal increased as plants came out of dormancy and grew in May and June, from July onward averaging 78% (SD = 25%, Figure S1), enabling higher removal in vegetated replicates annually. The high-NaCl *E. purpureum* replacement in May prevented net N export that year. In 2023, the replicates which died began to behave similarly to unvegetated mesocosms, and by May, their removal efficiency averaged −441% (SD = 59%), while those which survived removed >80% TN. Despite poor 2023 survival, *P. virgatum* non-IWS mesocosms continued to remove N, averaging 74% (SD = 13%) that year. This may be connected to the slower drainage observed in these replicates, which could have created anoxic conditions.

IWS effectively suppressed effluent TN and $NO_3^-{-}N$ year-round, regardless of vegetation ($p < 0.0001$), removing 57% (SD = 12%) of TN and 96% (SD = 11%) of $NO_3^-{-}N$, annually (Figure 3a). This indicates that IWS and carbon provision successfully facilitated denitrification through anoxia and increased storage capacity.[31] IWS TN removal efficiency was lowest in March, averaging 35% (SD = 22%), and peaked in October, averaging 87% (SD = 11%, Figures S1 and S2), potentially indicating a recovery period for microbes after winter, or continued maturing of the filter media. The average 2022 effluent concentration was 2.05 mg/L (SD = 1.33). $NO_3^-{-}N$ made up 11% of the annual average IWS TN effluent, substantially less than in the unvegetated non-IWS mesocosms, and the $NO_3^-{-}N$ component generally decreased in importance as TN decreased for all treatments. While $NO_2^-{-}N$ suffered from instrument interference with chloride, the data collected indicated it was stable, leaving much of the variance in IWS TN removal efficiency (−203 to 99%) to total Kjedahl nitrogen (TKN). This could have leached from woodchips (influenced by seasonal mineralization rates) in the IWS zone, where anoxia prevented nitrification.[31] In vegetated mesocosms, during periods of high nitrate removal, root exudates and decomposing organic material could have contributed to TN variability.

NaCl treatment was not a statistically significant predictor of TN or $NO_3^-{-}N$, and the change to lower NaCl influent concentrations for winter 2023 had no observable effect. While Denich et al.[33] and Valtanen et al.[29] also observed no link between NaCl and N, NaCl did indirectly affect our mesocosms through the death of plants, the loss of assimilation, and tissue decay, contributing to N leaching in non-IWS mesocosms.[18] It is possible that other indirect effects of NaCl may have been masked by variability, such as that from seasonal trends. For example, Endreny et al.[25] observed NaCl to affect microbe communities. This could have contributed to relatively low IWS replicate early season removal efficiency (40%, SD = 22% in March 2022), in addition to postwinter recovery. McManus and Davis[16] observed N response to NaCl, possibly caused by organic colloid dispersion, but while the relationship between TN and TOC was statistically significant in our mesocosms, it was of little practical effect ($p < 0.0001$, R^2(adj) = 0.01). The November 2021 sampling reveals no further insights, averaging 366% higher TN concentrations than late October 2022, with 65% as $NO_3^-{-}N$, indicating that stabilization and plant/microbe establishment were ongoing.

Phosphorus. High-NaCl treatment increased TP effluent load ($p < 0.0001$), decreasing the average annual removal efficiency by 4.5 percentage points (Table 2, Figure 3b). In March 2022, during NaCl dosing, all mesocosms maintained high TP removal, ranging from 94 to 99%, with a maximum effluent concentration of 0.06 mg/L. In April and May, effluent spiked, with average removal efficiencies dropping to 94% (SD = 5%) for low-NaCl and 81% (SD = 16%) for high-NaCl mesocosms (Figure 4). Average effluent concentrations were 0.07 mg/L (SD = 0.05) and 0.18 mg/L (SD = 0.15) for low-NaCl and high-NaCl mesocosms, respectively. After summer recovery, lasting impacts emerged specifically for non-IWS, unvegetated columns, whose average TP loads from August to October were 280% higher than in March after low-NaCl exposure, and 561% higher after high-NaCl exposure (Figure S3). 2023 trends generally replicated those in 2022, and non-IWS unvegetated removal continued to decline. In 2023, efficiency averages for the rest of the mesocosms were 93%

https://doi.org/10.1021/acsestwater.4c00062
ACS EST Water 2024, 4, 2882−2893

(SD = 5%) for low-NaCl replicates and 88% (SD = 8%) for high-NaCl replicates, showing little effect of the NaCl concentration decrease.

The delay between dosing and response may be explained by a minimum NaCl load or accumulation threshold, as proposed by McManus and Davis[16] and Goor et al.[12] While the response magnitude was controlled (at least in part) by NaCl load, more thresholds at different loads or exposures may explain the lack of change after the reduced NaCl application in 2023. Excess NaCl overwhelming media and flushing before interacting substantially with the filter media[23] may impact the function of thresholds, and accumulation of P or cumulative/priming effects of NaCl (e.g., dispersion exposing new substrates for later mineralization or ion exchange) could have increased mobility in the second year or explained long-term impacts in non-IWS unvegetated replicates.

Similarly, the TP response timing was the same regardless of NaCl treatment, and the high-NaCl treatment did not experience an earlier peak than low-NaCl columns, as might be expected. While perhaps the sampling schedule was too coarse to pick up on this trend, it suggests that response timing is controlled by other factors as well, like a threshold, the NaCl exposure rate and timeline, or overwhelming of the media by large, rapid NaCl application. NaCl has been linked variously with TP, DP, and soluble reactive phosphorus through ion exchange and colloid dispersion.[12,16,25,28] PO_4^{3-}−P was consistently below its detection limit (0.1 mg/L) and the relationship between TP and TSS was poor ($p < 0.01$, R^2(adj) = 0.01). TP was better related to TOC ($p < 0.0001$, R^2(adj) = 0.14), the R^2 increasing further when considering high-NaCl mesocosms, indicating that NaCl mobilized more in dissolved/organic forms. TOC loads (Figure S4) spiked in early 2022 and 2023, alongside TP, averages about 108% higher than in the fall, influenced by NaCl ($p < 0.0001$). Thus, NaCl released P through organic colloid dispersion,[23,24] possibly alongside anion exchange.

IWS decreased TP loads ($p < 0.0001$), increasing annual removal efficiency by 7 percentage points (Table 2, Figure 3b) and mitigating the effects of NaCl by delaying and reducing the magnitude of P loss and accelerating recovery. For example, during the spring 2022 TP effluent spike, IWS replicate removal efficiency averaged 11 percentage points higher than non-IWS, and during the summer, IWS unvegetated replicate removal was >90%, with effluent concentrations averaging 0.02 mg/L (SD = 0.03) (Figure 4). This was unanticipated; reducing conditions are often thought to worsen P sorption by increasing iron and manganese solubility and producing sulfide, which competes with P for iron.[6,46,47] Various bioretention studies support higher, neutral, or lower P removal with IWS.[28,31,45,48−51] Potential explanations for higher P removal include changes in pH and trade-offs between sorption strength/iron solubility and sorption capacity/interaction with P,[46,47,52] increased retention time, redox potential not low enough to reduce iron or sulfate, and greater system stability with respect to redox potential, pH, and moisture.[47,53] While P stored in the IWS zone may be sorbed relatively weakly, it evidently resisted mobilization by NaCl.

Vegetation was linked with greater P removal efficiency ($p < 0.01$), increasing the event average by 5−6 percentage points. Annually, *E. purpureum* was not a significant predictor of TP, and the *P. virgatum* removal efficiency was only 2 percentage points higher than the unvegetated mesocosms (Table 2). Dormant vegetation could not suppress early-season TP spikes but was critical in mitigating the long-term declining removal efficiency in unvegetated non-IWS replicates (Figure S3). While the annual effect was less substantial than IWS, assimilation is often considered a less important pathway than sorption, at least in the short term.[4,18,44,48] Contribution by senescence in 2023 could not be determined; P from dying plants was either quickly sorbed by the media or more time was needed for release. The effects of plant death may have become clearer with more time.[25]

Copper. Annually, high NaCl dose was a statistically significant predictor of higher Cu effluent load but only decreased the average annual removal efficiency by about 1 percentage point compared to the low-NaCl treatment ($p < 0.001$, Table 2, Figure 3c). Cu responded to NaCl with an immediate spike lasting until June−August (Figure S5). Between March and July 2022, high-NaCl mesocosms averaged 91% Cu removal (SD = 5%) and low-NaCl 93% (SD = 4%), measurements varying between 76−99% (effluent concentrations ranging from <0.005−0.053 mg/L). Average removal increased to 96% (SD = 3%) across all mesocosms in August−October, always >83% (effluent concentrations <0.046 mg/L). The 2023 NaCl concentration reduction did not change the average high- or low-NaCl efficiencies compared to 2022, and the general similarity between Cu response to different NaCl doses suggests Cu response like TP is controlled by thresholds, priming, or other factors like dose timing. The relationship between Cu and TOC was better than TSS ($p < 0.0001$, R^2(adj) = 0.14 and $p < 0.0001$, R^2(adj) = 0.01, respectively), especially when considering high-NaCl replicates, indicating that effluent Cu was not strongly associated with particulate material but was better linked to organic material. Thus, some Cu mobilization occurred by organic colloid dispersion, alongside mobilization of dissolved Cu by cation exchange and chloride complexation, which previous studies have identified as response mechanisms after NaCl exposure.[19,21,22,24,39]

The presence of vegetation was linked with greater Cu removal efficiencies, an increase of about 2 percentage points annually over unvegetated replicates ($p < 0.05$, Table 2). This difference is small, and vegetation is known to play a lesser role in Cu retention relative to sorption.[32,54,55] IWS increased annual removal by 3 percentage points ($p < 0.0001$), and the lowest observed removal was 69% (versus 63% without IWS). While this effect is fairly small, it mitigated NaCl, and annual high-NaCl IWS removal was 3 percentage points greater than low-NaCl non-IWS (Figure 3c). Like P, Cu is often considered vulnerable to reducing conditions,[6,31,39] attributed to changes in the solubility of metal oxides and Cu complexes and to interactions with sulfide.[47] Some bioretention studies have found a neutral or positive effect,[5,39,49] attributable to increased retention time, IWS organic amendments,[5,31] increased sorption capacity,[52] and system stability.[47,53]

Zinc. Effluent Zn loads (Figure 5) were low in November 2021 and early March 2022, averaging 99% removal (SD = 0.8%), all mesocosms >93% (effluent concentrations <0.029 mg/L). Zn loads slowly increased after NaCl exposure, spiking by 1−2 orders of magnitude in May, with removal efficiency averages falling to 66% (SD = 61%) for low-NaCl and −8% (SD = 115%) for high-NaCl replicates. The lowest removal recorded was −376%, representing an effluent concentration of 6.62 mg/L. After a rapid removal increase between May and June, summer recovery yielded 99% average removal (SD = 0.7%) between September−October. While spring 2023

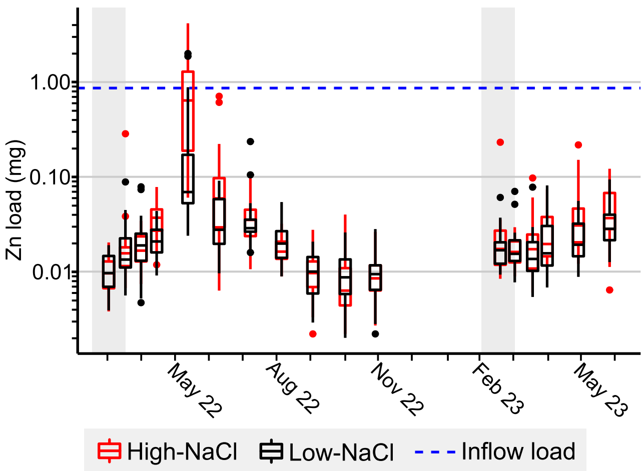

Figure 5. Effluent Zn loads by NaCl treatment. Gray shading shows NaCl dosing periods. Note the logarithmic *y*-axis.

removal decreased, following a similar trend to the previous year (Figure 5), no large spike occurred, and May removal efficiencies averaged 95% (SD = 3%), all mesocosms >85%. It is possible that a spike would have occurred later, that it did occur and sampling was too infrequent to capture it, or that the reduction in applied NaCl concentrations increased removal. TOC and TSS were poorly related to Zn ($p < 0.05$, R^2(adj) = 0.01, and $p < 0.01$, R^2(adj) = 0.01, respectively), indicating that particulate and organic forms of Zn were not substantial components of effluent. This suggests that mobilization of dissolved Zn by processes like ion exchange, chloride complexation, and soil changes (e.g., soil solution ionic strength, pH, cation exchange capacity (CEC)) were of greater importance. While Zn is often considered more exchangeable than Cu,[19,56] and studies have found Zn mobility in response to NaCl,[16−18,33,39,57] the magnitude of leaching observed was surprising.

The average annual removal efficiency was 9 percentage points lower for high-NaCl replicates, but the relationship between higher NaCl dose and Zn was poor relative to other analytes ($p < 0.05$, R^2(adj) = 0.16, Table 2), so, like TP and Cu, other factors (e.g., NaCl dosing, accumulation, and flushing schedule) may have influenced the response timing and magnitude. Vegetation was not linked with Zn (Table 2, Figure S6), an absence which other studies have observed as well.[32,55,58] While IWS was statistically significant in predicting annual Zn loads ($p < 0.05$) and did increase annual removal by 6 percentage points (Table 2, Figure 3d), it remained a poor predictor statistically. Clary et al.[6] characterized Zn as "redox-insensitive," with precipitation possibly enhanced under reducing conditions, but studies on Zn retention have had varying results.[5,18,39,45,49,59] If IWS did increase Zn removal by enhanced precipitation, increased retention time, or some other means, it did not meaningfully affect removal or mitigate the NaCl-induced spring leaching.

TSS. In November 2021, TSS removal efficiency averaged 93% (SD = 4%). In early 2022, TSS effluent loads increased in response to NaCl, with average removal efficiencies dropping to 74% (SD = 21%, minimum = −21%) in high-NaCl replicates and 85% (SD = 10%, minimum = 23%) in low-NaCl replicates (Figure S7). The onset of the effect was rapid and lasted until May. From June onward, mesocosms recovered to an average of 91% removal (SD = 8%), average effluent concentrations at 24.7 mg/L (SD = 21.4). Notably, *P. virgatum* IWS replicates experienced variability in late 2022 and operated 10 percentage points below the overall average. In 2023, non-*P. virgatum* mesocosms responded to NaCl again, but removal efficiency averages were 7 and 2 percentage points higher than the previous year for high- and low-NaCl replicates, respectively. Higher removal was potentially caused by reduced NaCl concentrations, but not all mesocosms experienced this effect. *P. virgatum* replicates experienced variability in TSS effluent, dropping as low as −137% removal (314 mg/L), while averaging 44% (SD = 53%). The unusually high[6−8] 2023 *P. virgatum* loads were accompanied by a TOC spike (Figure S4), and both could be attributed to washout of organic material, potentially enhanced by sodium-induced dispersion (potentially primed by the first year) and IWS moisture availability, produced by microbes or decomposing *P. virgatum*. The surviving *P. virgatum* replicates did average a 30-percentage-point greater removal than the rest of their cohort.

Given the similar particle characteristics of influent TSS to the filter media, it is likely that these particles were captured by the media surface and that effluent TSS was existing sand or filter media washing out from the bottom of each column. Filter media washout has been observed in other studies, varying with media stability over time in response to factors like construction or wetting and drying.[60,61] Variation in effluent TSS could therefore represent media stability over the course of the experiment, showing destabilization by NaCl-induced dispersion and aggregate deterioration before recovery.

Annually, high-NaCl replicates had 5-percentage-point higher removal averages ($p < 0.0001$, Table 2, Figure 3e). NaCl, through colloid dispersion, has been linked with soil clogging and increased particulate outflow.[16,33,39] Some studies have found mixed or stabilizing effects when soil solution sodium is high, colloids dispersing when electrolyte concentrations lower after flushing,[18,23,24] which might explain the variability in onset of NaCl effects, alongside contributions of freeze−thaw and winter recovery.[62] While IWS and *E. purpureum* were not good predictors of TSS effluent, *P. virgatum* had a 5-point lower average annual TSS removal ($p < 0.01$, Table 2). High *P. virgatum* effluent loads were surprising, and previous studies have variously found IWS and vegetation to mildly decrease or have no effect on TSS effluent.[5,28,49,51,53,58]

Media and Vegetation. Despite the higher-than-ideal initial filter media P content (386 mg P/kg media, Figure 6), TP removal efficiencies were often >90% and there was no net export. Final average filter media P content was 18% lower than the start, indicating that P was flushed deeper into the filter media or removed by vegetation. Downward transport of contaminants in response to NaCl has been observed in other studies[14,23,24] and the presence of vegetation was statistically significant, decreasing average P content by 14% ($p < 0.01$, R^2(adj) = 0.18). The declining unvegetated non-IWS TP removal efficiencies might indicate saturation given the high initial P content, but this would be surprising given the normally lengthy time for P saturation to occur in bioretention[4,63] and the fact that P content was declining. IWS had no effect on the filter media and there were no identifiable trends in media N. Cu content increased by 122% and Zn by 169% by the end of the experiment (Figure 6), with the increase positively associated with vegetation presence (Cu: $p < 0.05$, R^2(adj) = 0.12, Zn: $p < 0.001$, R^2(adj) = 0.13).

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ACS EST Water 2024, 4, 2882−2893

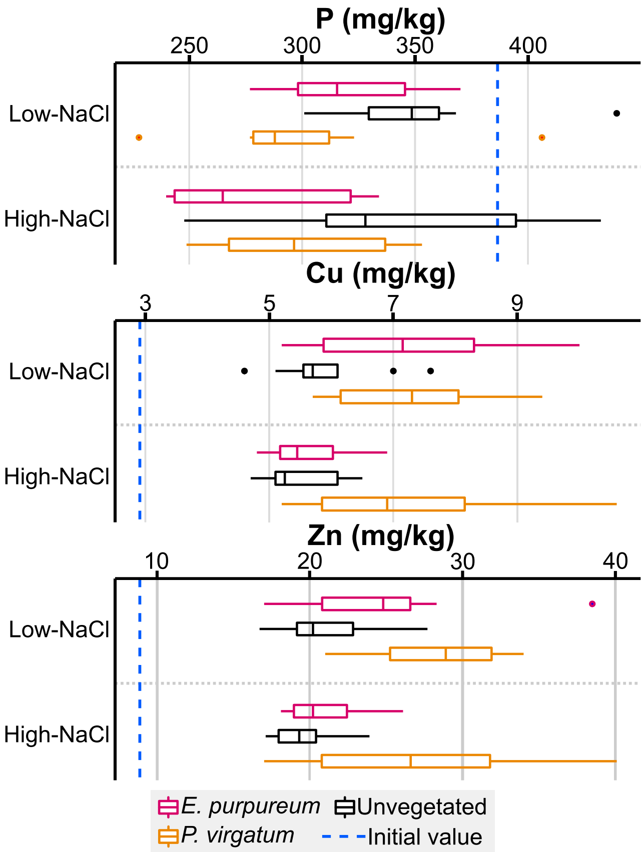

Figure 6. Soil TP, Cu, and Zn content at the end of each experiment.

NaCl treatment had no effect, but the Zn effluent export would indicate that some downward transport occurred.

Filter media potassium, magnesium, and calcium contents were 41, 28, and 7% lower at the end. The decrease was not linked to NaCl treatment, and base saturation proportions were unchanged. Average end pH increased very slightly (0.2), linked to higher NaCl dose (alkalinization has been partially attributed to NaCl)[27] and negatively associated with the presence of *E. purpureum* and IWS ($p < 0.001$, R^2(adj) = 0.43). Cation exchange capacity (CEC) had slightly decreased at the end of the experiment (19.9−17.9 mequiv/100 g), made lower by high NaCl, possibly an effect of sodium exposure,[19,39] and higher by *E. purpureum* ($p < 0.01$, R^2(adj) = 0.28). Redoximorphic features (large depletions with small concentrations around roots) were visible in the lower 5−10 cm of sand in IWS mesocosms, as well as in the bottom 2−5 cm of some *P. virgatum* non-IWS mesocosms (an area where roots had grown densely), indicating that the redox potential was low enough for manganese and iron reduction.

Plants came out of dormancy soon after NaCl exposure. Higher NaCl inhibited growth in early 2022, and necrosis and chlorosis were observed. By the end of 2022, surface height and weight evened out across both NaCl treatments, low-NaCl *P. virgatum* averaging 5 cm taller (SD = 3.9) and 4 g heavier (SD = 6.6). NaCl alters soil structure, nutrient availability, and osmotic potential,[52] and negative effects on vegetation have been observed in other experiments.[16,18,33] Research has shown IWS to improve growth, especially under dry conditions,[64] but growth was not linked with IWS in our mesocosms, perhaps because water was never scarce. The low 2023 effluent NO_3^-−N discussed for non-IWS *P. virgatum* replicates even after plants had died, along with redoximorphic features observed in those mesocosms, provides evidence of denitrifier activity and reducing conditions. This is surprising when compared to the absence of denitrification in non-IWS unvegetated or *E. purpureum* columns, suggesting a unique microbiome to which other unusual behaviors of *P. virgatum* replicates might be attributed. For example, clogging and high effluent TOC/TSS could have been caused by bacteria, their byproducts, and NaCl-induced dispersion. IWS seemed to enhance these effects, the moisture possibly increasing microbial activity.

The death of most plants in spring 2023 made the analysis of biomass inconclusive. Combined root and surface removal averaged 0.53 g N, 0.15 g P, 1.46 mg Cu, and 3.59 mg Zn. Plant death would release this material. NaCl and IWS were not linked with biomass contaminant accumulation. Anecdotally, roots were dense and grew to the bottom of all non-IWS columns, but IWS zones created a barrier, and fewer roots grew into them.

CONCLUSIONS

1) Higher NaCl loads reduced early 2022 TP, Cu, Zn, and TSS average removal efficiencies by 6, 4, 14, and 12 percentage points, respectively, before they recovered in summer. Effluent loads spiked during the late winter and early summer, varying by pollutant, with onset delayed by weeks or months from NaCl application. While annual removal efficiencies were positive, the spring effluent contaminant spikes are concerning, coinciding with increased biological activity in stream ecosystems,[27] exceeding EPA acute toxicity criteria for Cu and Zn.[15] While studies show salt concentration to influence contaminant mobilization,[65] other influences include bioretention design/maintenance and NaCl application rate/schedule.
2) With live vegetation, TN annual removal efficiency was 49%, but plant health was susceptible to NaCl. Timely replacement after the death of some *E. purpureum* in 2022 prevented annual TN export, and regular maintenance and monitoring are important for bioretention exposed to NaCl. Effects were less pronounced for other analytes, but vegetation mitigated TP and Cu response to NaCl, increasing average TP removal efficiency by 11 percentage points in non-IWS replicates.
3) While IWS influenced NaCl persistence, increasing chloride effluent concentrations by 47% after NaCl dosing, it also mitigated the effects of NaCl, increasing annual removal efficiencies by 3 percentage points for TP and 7 for Cu. IWS provided redundancy for removal processes, especially for nitrate, when vegetation was absent or inactive or NaCl interfered with soil removal mechanisms.
4) While reducing NaCl exposure is the best way to ensure effective bioretention performance, selecting salt-tolerant plants, diligent replacement of dead plants, and addition of media amendments or IWS that create redundant removal mechanisms can mitigate the effects of NaCl.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.4c00062.

https://doi.org/10.1021/acsestwater.4c00062
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Effluent loads by treatment for TN, NO_3^-−N, TP, TOC, Cu, Zn, and TSS (Figures S1−S7) (PDF)

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Author Contributions

This manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Alexander H Brown** conceptualization, data curation, formal analysis, investigation, methodology, visualization, writing-original draft, writing-review & editing; **Margaret C Hoffman** conceptualization, funding acquisition, methodology, writing-review & editing; **Lauren Elyse McPhillips** conceptualization, funding acquisition, investigation, methodology, project administration, resources, supervision, writing-review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was funded by the Chesapeake Bay Trust Pooled Monitoring Initiative's Restoration Research Program. Funding was provided in part by the U.S. EPA under assistance agreement CB96358101 and CB96358201 to the Chesapeake Bay Trust. Support was also provided by the USDA National Institute of Food and Agriculture and Hatch Appropriations under Project #PEN04873 and Accession #7005725. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors, and the contents of this document do not necessarily reflect the views and policies of the EPA, nor does the EPA endorse trade names or recommend the use of commercial products mentioned in this document. Thanks to Randall Bock, Scott DiLoreto, and the McPhillips research group for providing advice and assistance. Thanks also to Metzler Forest Products and North Creek Nurseries for donating woodchips and plants. Thank you to the three anonymous reviewers who provided constructive feedback that improved the paper.

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https://doi.org/10.1021/acsestwater.4c00062
ACS EST Water 2024, 4, 2882−2893