

Study on bioretention for stormwater management in cold climate, part II: water quality

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ABSTRACT

Typical continental, cold climate conditions were applied to four large, laboratory columns to simulate temperatures ranging from -20 to $+20$ °C over summer, winter, and spring runoff. The goal of this research was to assess the seasonal effectiveness of bioretention application in cold climate regions that are currently experiencing the impacts of climate change. 1.6 years' worth of equivalent Edmonton precipitation volume was applied over a 10-month period to evaluate the water quality improvement through two soil types (i.e., loam and sandy loam) with and without amendments intended to enhance nutrient removal. During summer, excellent removal of total suspended solids (TSS), phosphate, and ammonium (i.e., $\geq 90\%$ average concentration reduction) was observed in both the loam and sandy loam columns without the nutrient removal amendments. The columns containing the amendments also reduced TSS, ammonium, and phosphate, but not as effective as the non-amended columns for TSS and ammonium. During winter and spring runoff, if infiltration occurs, physical removal of TSS, phosphate, and ammonium was still achieved, only days after the complete freezing (and subsequent thawing) of bioretention media at -20 °C. After an initial maturation and leaching period, nitrate was well removed ($\geq 65.2\%$ average concentration reduction) via denitrification in the columns with the nutrient removal amendments and submerged zone.

Key words: bioretention, climate change, cold climate, low impact development, stormwater, water quality

HIGHLIGHTS

- Four large bioretention columns with two soil media (loam and sandy loam) underwent simulated summer, winter, spring runoff, and another summer of stormwater applications.
- All columns effectively reduced TSS, ammonium, and phosphate concentrations in the effluent during the summer.
- If infiltration occurs during winter and spring runoff, physical removal of TSS, phosphate, and ammonium can still be achieved.

INTRODUCTION

Extensive research has been conducted on the performance of bioretention utilizing different media, configurations, and amendments, typically in temperatures above 10 °C. A few studies have also been conducted in cold climates such as Norway, Sweden, Finland, New Hampshire, Washington, Calgary, Alberta, and cities in Quebec and Ontario, Canada (Muthanna *et al.* 2007b; Al-Houri *et al.* 2009; Roseen *et al.* 2009; Blecken *et al.* 2010; Khan *et al.* 2012a, 2012b; Denich *et al.* 2013; Géhéniau *et al.* 2015; Moghadas *et al.* 2016; Valtanen *et al.* 2017; Ding *et al.* 2019). While some cold climate studies conducted experiments on soil above 0 °C (Blecken *et al.* 2010; Khan *et al.* 2012a, 2012b; Søberg *et al.* 2020), only limited studies researched the impact from freeze-thaw cycles (Al-Houri *et al.* 2009; Moghadas *et al.* 2016; Valtanen *et al.* 2017; Ding *et al.* 2019). In winter, bioretention systems experience freeze-thaw cycles and receive high sediment loadings and a large volume of spring runoff with higher contaminant concentrations; the freeze-thaw cycles impact water quality treatment due to reduced retention time and reduced biological processes. Many bioretention studies in cold climates utilized coarse filter media to maintain infiltration rate and prevent the higher total suspended solids (TSS) concentrations in snow-melt and spring runoff from clogging the filter media (Muthanna *et al.* 2007b; LeFevre *et al.* 2009; Blecken *et al.* 2010; Denich

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et al. 2013; Géheniau *et al.* 2015; Soberg *et al.* 2017), but experienced deteriorated water quality treatment (Khan *et al.* 2012b; Denich *et al.* 2013; Géheniau *et al.* 2015). However, Soberg *et al.* (2014) observed similar removal of TSS and metals in both fine and coarse bioretention media subjected to cold climate conditions.

This research is the first of its kind to study bioretention performance tailored to a continental region characterized with extreme cold temperatures during long, dry winters with intermittent warming and thawing periods, large snowmelt volumes from spring runoff, short growing seasons, clay soils, and relatively low precipitation volumes. A particularly dry cold climate region is Edmonton, Alberta, Canada, and their historical precipitation volumes were used to simulate the rainfall events in this research. Average low and record low temperatures in Edmonton's winter are -11 and -48.3 °C, respectively, with an average annual snowfall of 123.5 cm and rainfall of 347.8 mm (GoC 2018). Freezing temperatures in Edmonton and other cold climate regions can last for 7 months, however, in recent years, intermittent warming periods with stretches of above freezing temperatures that can melt the snowpack have been observed. With global climate change, instances of these warming periods may be occurring even more frequently in years to come.

Additionally, this research is the first of its kind to study large column bioretention performance in a laboratory setting where the extreme weather and precipitation conditions could be carefully controlled such that all influent and effluent could be analyzed and temperatures as low as -20 °C could be produced in a controlled environment. Typically, large bioretention systems are studied outdoors where sampling procedures rely on the ability of the researchers to accurately predict the weather and their speed in getting to site and collect samples once a rain event begins (Géheniau *et al.* 2015); often, the first flush can easily be missed, and it is also sometimes impractical to collect samples at all during winter conditions. The experimental setup of this research allowed these issues to be overcome. This research was also novel as winter temperatures reached as low as -20 °C in a controlled environment, whereas other research typically utilizes temperatures only as low as -10 °C (Ding *et al.* 2019), winter and spring runoff was applied with elevated contaminant concentrations to simulate field conditions, and it evaluated water quality performance after winter to assess the ability of bioretention water quality improvement to rebound after experiencing a typical harsh, cold climate winter.

Approximately 24.6% of global land is classified as cold climate, characterized with an average temperature ≤ -3 °C for the coldest months, and includes 13 of 100 of the world's largest cities (Peel *et al.* 2007). Therefore, this research can be useful for bioretention designers and researchers in numerous regions around the world that experience long, cold, and dry winters and have low permeability soils. This paper serves to fill a knowledge gap currently existing in cold climate bioretention scientific literature. Additionally, due to climate change, regions that have historically experienced long, harsh winters are now experiencing more uncertain cold periods (e.g., more mild winters on average that are shorter, resulting in longer summers, and experience more frequent freeze-thaw cycles during a single winter/spring season); however, these regions are still experiencing periods of extreme cold (i.e., < -20 °C) but perhaps not as often. For these reasons, bioretention and other Low Impact Development (LID) practices may be more financially feasible and incentivized for cold climate municipalities with evidence that these technologies can still function in these shifting climates.

The leading source of surface water degradation is from stormwater runoff in which the primary pollutants are sediment, nutrients, bacteria, and metals (USEPA 2000). Bioretention functions via sedimentation, filtration, physical and chemical adsorption and precipitation, microbial degradation, and vegetative uptake/evapotranspiration to treat these non-point source contaminants. TSS in stormwater have a broad range of sources and concentrations and can originate from road maintenance activities in winter, such as traction grit/sand application, the breakdown of vegetative and anthropogenic debris, and construction, demolition, and other land disturbing activities. Particles are also released from burning of materials and are later deposited on surfaces. Runoff TSS in surface water may reduce light penetration required for aquatic plant growth and sedimentation impacts bottom-dwelling aquatic species' habitat (USEPA 1999).

Fertilizers, animal/plant waste, sewage, and atmospheric deposition result in nutrient pollution in runoff (Weiss *et al.* 2008) in excess concentrations leading to algae blooms and possibly eutrophication, which is a major concern (Dodds *et al.* 2009). Severe enough algae blooms can lead to toxic cyanobacteria growth. Eutrophication is both a serious environmental problem and economic issue as it leads to decreased waterfront property value and impairs recreation, habitat, and drinking water treatment (Dodds *et al.* 2009).

Phosphorus in runoff is comprised of particulate and dissolved phosphorus. Particulate phosphorus is removed via sedimentation and filtration and is therefore typically removed well (Blecken *et al.* 2007). The more abundant form of phosphorus is dissolved and ranges from 45 to 90% of total phosphorus (Erickson *et al.* 2012). Of dissolved phosphorus,

the reactive form (i.e., orthophosphate) is the bioavailable form and therefore more likely to lead to eutrophication when in excess in runoff.

The two forms of nitrogen of most concern in stormwater runoff are the bioavailable nitrate (NO_3^-) and ammonia (NH_3) due to its rapid conversion to nitrate and toxicity at low concentrations to some aquatic organisms (Leisenring *et al.* 2010). Contaminants in snowmelt may be even more problematic to natural systems than in rainfall runoff due to their accumulation in snowpack over cold seasons leading to more concentrated releases over winter and spring runoff (LeFevre *et al.* 2009). During several freeze-thaw cycles throughout winter, dissolved contaminants are flushed from the snowpack to accumulate at its bottom which is subject to melting first in spring during the ‘first flush’. Winters in cold climates also experience higher concentrations of TSS from road sands applied for traction and of salts from application of ice melt products. These seasonal differences in contaminant loads are simulated in this research by elevating the concentrations of salt in winter runoff and all contaminants in spring runoff applied to the large bioretention columns.

This research aims to investigate low permeability soils and amendments suitable for use as bioretention media, evaluate the water quality improvement of typical stormwater runoff through bioretention for TSS, phosphate, ammonium, and nitrate, and determine the impact that long, extremely cold winters have on bioretention’s water quality improvement ability. This research also investigated the water quantity control of the same laboratory setup discussed in this paper and the results are provided in Li *et al.* (2021).

METHODOLOGY

Bioretention column configuration

The custom-designed and built bioretention columns, their media configuration, and the custom water distribution systems used in this study have been described elsewhere (Li *et al.* 2021). Two soil media were utilized: soil media A is loam soil (i.e., 50.8% sand, 29.4% silt, and 19.8% clay (w/w)) and soil media B is sandy loam soil (i.e., 67.2% sand, 19.6% silt, and 13.2% clay (w/w)). The two soil media types were evaluated to determine if the greater porosity of soil media B, which is recommended to achieve >10 cm/h hydraulic conductivity for operation in cold climates to prevent concrete frost from forming in freezing conditions and completely clogging the soil (Paus *et al.* 2016; Kratky *et al.* 2017), would hinder the ability of the bioretention columns to reduce stormwater contaminants as effectively as the less porous soil (as less porous soil has greater contact time and area for treatment). This research aims to prove that even with a higher sand content (i.e., soil media ‘B’ found in columns 2 and 4) and increased hydraulic conductivity, water quality improvement is not hindered.

Loam soil was used in columns 1 and 3 and sandy loam soil in columns 2 and 4. Detailed analysis of the hydraulics observed in this study is presented elsewhere (Li *et al.* 2021). All columns were first filled with a 25 cm thick bottom layer of rocks considered the ‘gravel layer’. These rocks were graded appropriately so that the overlaying soil would not fall through and exfiltrate the system (i.e., a 15 cm depth of 40 mm round rock was placed and then a 10 cm depth of 7 mm washed rock was placed above). All columns have a surface layer of mulch and 16 cm of soil media mixed with 20% compost to promote plant establishment and health. Columns 1 and 2 follow a conventional bioretention design and columns 3 and 4 are modified to enhance nutrient removal by the addition of a 20 cm deep layer amended with 0.5% (by weight) of steel wool to enhance phosphate removal and a 20 cm deep layer of 5% (by weight) woodchips of 2–20 mm size that are submerged to enhance nitrate removal. By comparing columns 1 and 2, the impact of soil porosity on water quality improvement can be determined. By comparing columns 3 and 4 with columns 1 and 2, the impact that steel wool has on phosphate removal and the impact of the denitrification layer on nitrate removal can be determined. All media used in this study was air-dried and mixed homogeneously. The media used in this study was freshly installed in columns 1, 3, and 4 prior to the first stage of operation. Prior to the first stage of operation, column 2 had approximately 1 years’ worth of Edmonton’s precipitation as tap water applied to measure hydraulic conductivity. The schematic of the media configuration in each column is shown in Figure 1. Each column was initially planted with vegetation (Heavy Metal Blue Switch Grass – *Panicum virgatum* ‘Heavy Metal’). However, the vegetation did not survive long enough, likely due to the frequency of the events applied, to have a recognizable impact on the study.

Each bioretention column is supported by a steel frame on wheels; the columns have two valved effluent outlets of 1.5” diameter at different elevations which can be used to form an anoxic zone or allow the system to drain completely. An

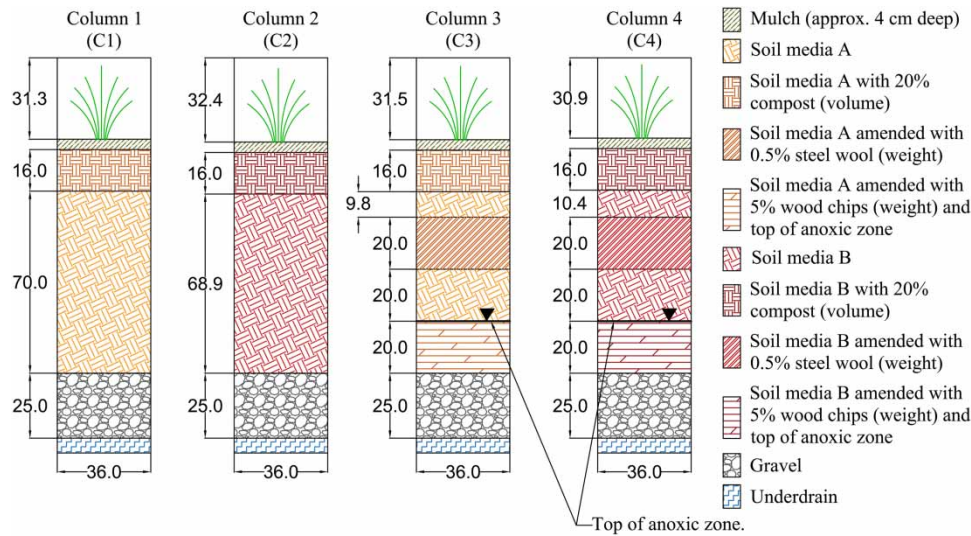


Figure 1 | Schematic of bioretention column compositions. Dimensions are in cm.

influent water distribution system was custom-designed and built to uniformly distribute a wide range of flow rates while not retaining significant amounts of TSS. A schematic of the columns is shown in Figure 2.

Synthetic stormwater

Synthetic stormwater was prepared in four separate buckets, one for each column, using tap water to meet target concentrations as described in Table 1 and allowed time to equilibrate with the experiment's temperature before application of an event. Peristaltic pumps pumped the influent synthetic stormwater into the top of the columns through the water distribution systems as described in Li *et al.* (2021).

The chemical composition of the synthetic stormwater was selected based on the review and compilation of local stormwater quality assessments based on literature values, residential land use, and sampling programs (CoE 2016a, 2017) and synthetic stormwater compositions used in numerous other, non-local stormwater studies (Hsieh & Davis 2003; Blecken *et al.* 2007, 2009, 2010; Denich *et al.* 2013; Soberg *et al.* 2017). This wealth of data was compiled and compared and the most practical values for each contaminant in Table 1 was selected for this research. Generally, a combination of either the mean or the mode values were selected depending on the contaminant.

This research assumed that the influent synthetic stormwater passed through some form of pretreatment prior to entering the large columns. Such pretreatment may consist of a settling basin with a weir and/or large rocks that slow influent flow rates and allow time for sedimentation of TSS before entering the bioretention facility. Pretreatment systems should prevent unnecessary amounts of sediment from entering the bioretention media and be easily and periodically cleaned out. Designing systems that incorporate some form of sediment pretreatment is vital to ensuring the extended lifetime of bioretention facilities by preventing premature clogging of the soil media pore spaces and consequential reduction of hydraulic conductivity of the soil media. This is especially required in regions with cold climates due to the major road maintenance throughout winter in which hundreds of thousands of tonnes of sand is applied (CoE 2016b). This is not an issue in non-cold climate regions and therefore makes the design of bioretention pretreatment systems even more important in cold climate regions.

Experimental approach

Experiments for this research were carried out concurrently with Li's (Li *et al.* 2021) research in order to collect both hydraulic performance and water quality improvement data. The five stages of operation conducted and a chronological list of events applied during the operation have been described previously in greater detail (Li *et al.* 2021). The stages of operation related to this water quality study were as follows:

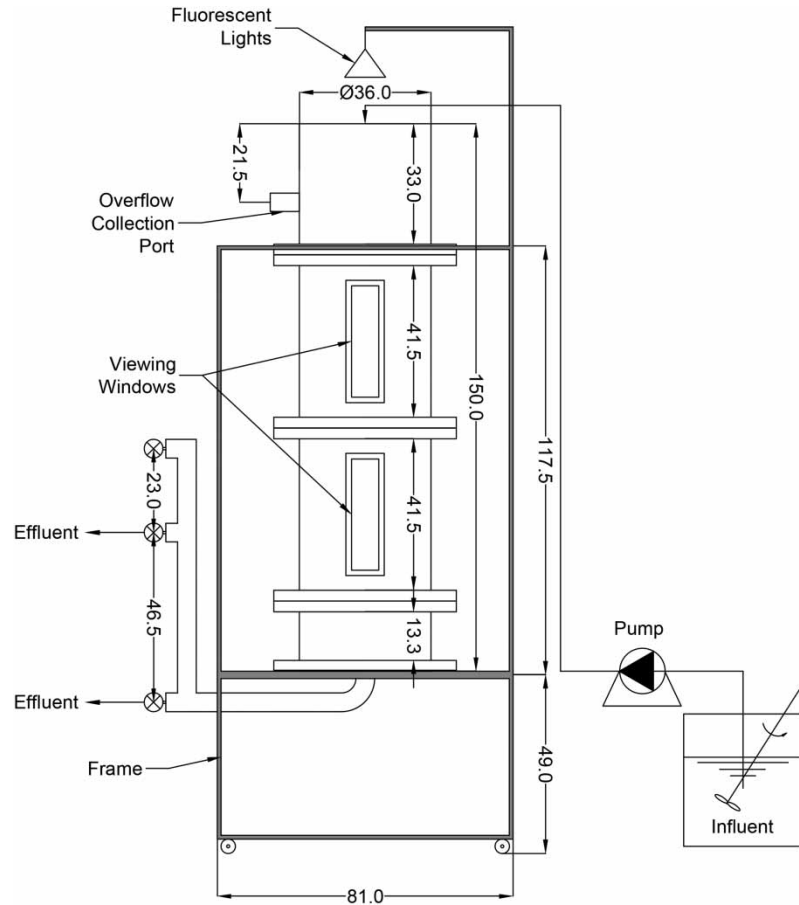


Figure 2 | Schematic of large bioretention columns. Dimensions are in cm.

Table 1 | Composition of simulated stormwater influent used in this study

Parameter	Source	Unit	Target concentration	Average actual concentration
TSS	Local topsoil <0.500 mm	mg/L	150	150
COD	Glucose	mg/L	40	45.04
Total Nitrogen (TN)	See below	mg/L	4	4.68
Ammonium (NH ₄ ⁺ -N)	NH ₄ Cl	mg/L	2	2.23
Nitrate (NO ₃ ⁻ -N)	KNO ₃	mg/L	1.5	2.04
Nitrite (NO ₂ ⁻ -N)	NaNO ₂	mg/L	0.5	0.41
Phosphate (PO ₄ ³⁻ -P)	KH ₂ PO ₄	mg/L	2	2.04
Chloride (Cl ⁻)	NaCl	mg/L	15 ^a 320 ^b 1,280 ^c	16.17 ^a 318.43 ^b 1,266.21 ^c
Cadmium (Cd)	Cd(NO ₃) ₂ ·4H ₂ O	µg/L	5	2.3
Copper (Cu)	CuSO ₄ ·5H ₂ O	µg/L	150	330
Lead (Pb)	Pb(NO ₃) ₂	µg/L	50	6.5
Zinc (Zn)	ZnSO ₄ ·7H ₂ O	µg/L	400	300

Note: All contaminants except chloride remained the same concentration during all stages of operation except for during the four times concentrated spring runoff event, in which contaminants other than COD were quadrupled.

^aDuring the summer operation.

^bDuring the winter operation and the major melt of spring runoff event.

^cDuring the four times concentrated spring runoff event.

- *1st summer operation*: includes 17 weekly, 1:2 year frequency events applied at room temperature (20 ± 2 °C). Columns 3 and 4 both contained an approximately 46.5 cm deep submerged zone (measured from the lowest effluent outlet). After these events, the submerged zone was drained prior to freezing the columns so that concrete frost would not form.
- *Winter operation*: includes four simulated, snowmelt events applied in the temperature-controlled room. The concentration of chloride was increased to represent road maintenance salts applied during cold climate winters. Synthetic snowmelt was only ever applied when the air temperature in the room was approximately 1–3 °C.
- *Spring runoff*: includes one high concentration (i.e., four times the winter operation concentration), low volume event to represent the *first flush* of accumulated pollutants at the base of packed snow. This was followed by one typical winter concentration, high volume event to represent the *major melt* of packed snow. Both events were applied at approximately 1–3 °C.
- *2nd summer operation*: includes 5 weekly, 1:2 year frequency events applied at room temperature. For the 1st event, the lowest effluent pipe valve was closed to re-form the submerged zone in columns 3 and 4.

Before winter and spring runoff, the submerged zone of columns 3 and 4 was drained and effluent was then allowed to flow out freely through the lowest effluent pipe. This process of draining bioretention facilities and reforming a submerged zone depending on the season may be slightly more challenging to implement in field applications but it is not impossible. For any system that contains perforated underdrains, those drainpipes could be connected to the outlet structures (e.g., a manhole) at a higher and a lower elevation by utilizing a vertical wye adaptor and blocking the lower drainpipe with a screw cap during the warmer season to form the submerged zone. Then, the bioretention facility could be drained by removing the screw cap during the last scheduled maintenance event before the temperatures are expected to drop for the season. LID facilities are typically maintained multiple times throughout the warm season and often with a clear checklist for the maintenance personnel to follow. This additional step to drain the submerged zone or recap the lower elevation drainpipe during the annual spring maintenance event could, therefore, easily be added to the maintenance scope with minimal additional cost and training requirements. After winter and spring runoff operation in this research, the bottom effluent pipe valve was closed, and the submerged zone was re-formed.

As events were conducted weekly, very little evaporation occurred and there was, therefore, consistently little volume reduction through evaporation and transpiration. For this reason, mass reduction was not evaluated and only the difference between influent and effluent contaminant concentrations was analyzed. The results and discussion will evaluate the difference in treatment capacity (i.e., change in influent to effluent concentration) between the four different column designs as well as the difference across stages of operation (i.e., seasonal changes). Columns 1 and 3 contain loam soil media (i.e., less porous) and columns 2 and 4 contain sandy loam soil media (i.e., more porous). However, it is worth noting that if these bioretention columns were outdoors and not subjected to weekly events or had healthy vegetation growth and therefore allowed time for evaporation and evapotranspiration of water in the columns, it is assumed that dissolved contaminants, such as nitrate, would have had improved removal efficiencies (Subramaniam *et al.* 2014; He *et al.* 2020).

The 1:2 year events all followed a 4-h Chicago distribution based on Edmonton's historical data (CoE 2014a). These influent hydrographs as well as the influent hydraulics of winter and spring runoff have been detailed elsewhere (Li *et al.* 2021). The flow rate was determined by assuming a 100% impervious catchment area 10 times the area of each bioretention column (CoE 2014b). An equivalent volume of 1.6 years' worth of Edmonton's precipitation was applied in 10 months and air temperatures were adjusted from 20 to -20 °C in a controlled environment to simulate Edmonton's seasonal temperature variations.

Over a period of 10 months, 778 liters (764.4 mm) of synthetic rainwater was applied to each bioretention column, which is the equivalent of 1.6 years' worth of volume of precipitation for Edmonton. The air temperature was varied as shown in Figure 3. The internal temperatures of the columns were also monitored, and it was observed that the exterior temperature matched the internal column temperature if the columns were given 1–3 days to adjust. It took about 5 days, however, when the exterior temperature was transitioning from negative to positive temperatures. Although the insulation of the laboratory columns may differ from that of field bioretention systems as the latter would have more natural insulation from surrounding soil, the design of the laboratory columns should result in conservative estimates on water quality improvement by bioretention systems during intermittent winter warming periods and spring runoff.

Leachate analysis

A period of large column media maturation occurred in the initial stage of operation in which certain contaminants leached considerably from the systems. To determine which component(s) of the columns could be contributing to this leachate, a soil media

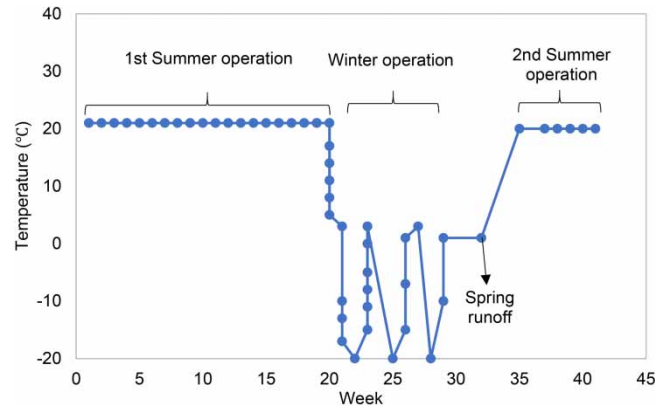


Figure 3 | External air temperature fluctuation during all four stages of the operation.

and amendment leachate analysis was conducted as follows. Soil media 'A' or loam soil, soil media 'B' or sandy loam soil, compost, and woodchips were the most likely sources of the leached contaminants and were, therefore, tested as follows. Eight Erlenmeyer flasks (i.e., two per media type) were used to contain fresh samples of the four media types and 180 mL of deionized water. Prior to weighing the appropriate aliquots to put into each Erlenmeyer flasks, all media was dried at 50 °C for 48 h.

Each media type was tested twice to determine the impact that contact time has on leaching of contaminants. One of the flasks for each media type had 8 h of contact time and the other flask had 1 week of contact time with the deionized water prior to sampling. The media was hand stirred in the water until all media appeared wet. After the respective contact time, samples were collected, immediately filtered with a 0.2 µm syringe filter, and stored at 4 °C until analyzed. These samples were analyzed for numerous contaminants, including $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$ by the same methods outlined in Sampling and analysis section below. The difference in values between the samples taken after 8 h and 1 week of contact were not considerably different so the average was taken for all parameters to calculate the contaminant concentrations and weight of contaminants per weight of media mixed.

Sampling and analysis

The entire effluent volume for each large column was collected up to 24 h following the start of each event conducted via one of the two effluent pipes connected to an underdrain. All effluent was collected out of the lower pipe except for columns 3 and 4 during summer operation, in which a submerged zone was present, and effluent was collected from the top pipe. The influent and effluent stormwater was held in 26.5 litre pails and all samples were taken from their total respective volumes. Magnetic stir plates were used to mix the water well while it was being pumped into the columns and for sampling purposes. Influent and effluent samples were collected to measure $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$ in duplicate. Effluent TSS samples were collected and analyzed in triplicate and influent TSS concentrations were simply calculated. The standard methods and HACH kits used to measure the concentrations in the samples collected are as follows:

- TSS (mg/L): APHA Standard Method 2540 D: Total Suspended Solids Dried at 103–105 °C.
- Nitrate (mg $\text{NO}_3^-\text{-N/L}$) and Orthophosphate (mg $\text{PO}_4^{3-}\text{-P/L}$): APHA Standard Method 4110 B: Ion Chromatography with Chemical Suppression of Eluent Conductivity.
- Ammonium (mg $\text{NH}_4^+\text{-N/L}$): HACH method 10205 for Ammonia TNTplus Vial Test, ULR (0.015–2.00 mg/L $\text{NH}_3\text{-N}$) Product #: TNT830-CA. This test kit prepares samples for analysis by distillation according to APHA Standard Method 4500- NH_3 B and is based off the principles of APHA Standard Method 4500- NH_3 F: Phenate Method.

Detailed descriptions of each method can be found in Standard Methods for the Examination of Water and Wastewater (APHA 2018) and online at www.ca.hach.com.

RESULTS AND DISCUSSION

Leachate analysis

Figures 4 and 5 provide a comparison of the nutrient concentrations measured during the leachate analysis test for the four fresh medias used in the large columns likely to be a contaminant source: soil media 'A' and 'B', compost, and woodchips.

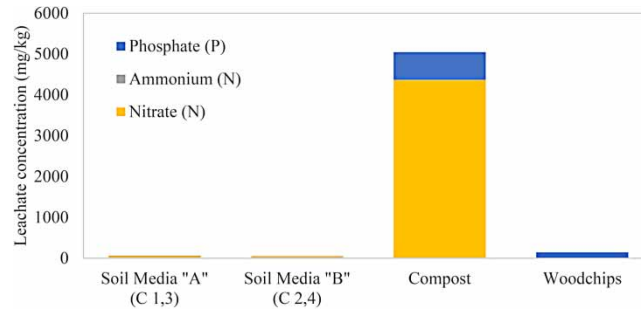


Figure 4 | Leachate concentration from the different soil media used as found in the leachate analysis.

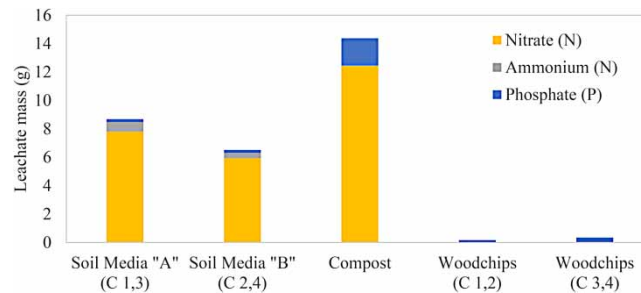


Figure 5 | Approximate leachate mass available in the large columns.

Table 2 | Mass of nutrients available to leach from each column

Nutrient	Column 1	Column 2	Column 3	Column 4
Phosphate (mg $\text{PO}_4^{3-}\text{-P}$)	2,277	2,277	2,448	2,448
Ammonium (mg $\text{NH}_4^+\text{-N}$)	706	401	707	402
Nitrate (mg $\text{NO}_3^-\text{-N}$)	20,255	18,392	20,256	18,393

Each source of leachate and their fate during the four stages of operation in this research are discussed in more detail in the results for Phosphorus and Nitrogen sections. This section is intended to serve as a summarized comparison of the media types. Figure 4 expresses the nutrients in terms of mg of contaminant per kg of media and Figure 5 shows the approximate mass of stormwater contaminants that are available in the large columns used in this research that could potentially leach into the effluent of the columns. These data are based on the approximate weights of soil media, compost, and woodchips that were installed in each large column. From this information, the mass of nutrients available to leach from each column was calculated as shown in Table 2 based on the approximate weights of soil, compost, and woodchips that were installed in each large column.

Total Suspended Solids

TSS removal by all columns throughout all stages of operation holds consistent with previous research at 95.3–99.5% concentration reduction (Blecken *et al.* 2007, 2009, 2010; Bratieres *et al.* 2008; Muthanna *et al.* 2007a; Roseen *et al.* 2009). The effluent TSS concentrations are also similar to those observed by Géhéniau *et al.* (2015), i.e., 4.1 mg/L in winter. The only exception is columns 3 and 4 during the 1st summer operation and during the major melt of spring runoff in which concentration reduction is 68.3–90.1%. The average percent concentration reductions of TSS and average effluent TSS concentrations can be seen in Figure 6.

By comparing TSS concentration reduction in columns 1 and 2, the difference in porosity between soil media 'A' (i.e., loam) and soil media 'B' (i.e., sandy loam), respectively, does not hinder TSS removal as all percent reductions are 95.3–97.1%.

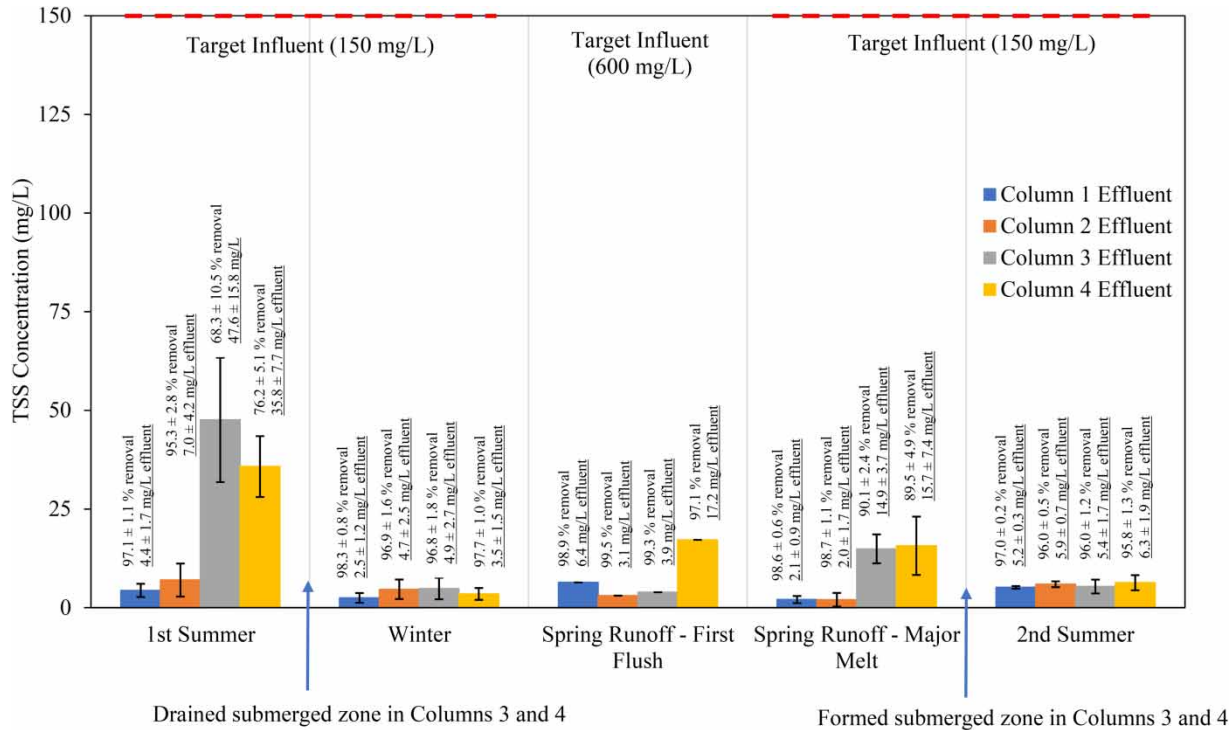


Figure 6 | TSS removal during the 1st summer, winter, spring runoff, and 2nd summer operation. \pm Values indicate standard deviations. The error bars represent the ranges in effluent TSS concentrations.

Despite column 2 being washed with a years' worth of precipitation as tap water prior to being put into operation, its effluent concentration is comparable to the effluent concentration in column 1, indicating that sediment washout from the media itself is quite minimal and that fresh bioretention systems implemented in the field that follow these columns' design and construction should not expect a stabilization period of poor performance for TSS removal as noted in Blecken *et al.* (2010) and Hsieh *et al.* (2007). Even the first 4 weeks of operation had a maximum effluent TSS concentration of 9.67 mg/L for column 1 and 16.05 mg/L for column 2, which still shows 94 and 89% reduction, respectively, and does not imply a significant washout of media fines.

It should also be noted that over a longer period of time than assessed in this research, smaller pore sizes may form as more TSS accumulates and blocks filtration pathways resulting in finer filtration capabilities. This may lead to an increase in TSS removal over time; however, due to the annual freeze-thaw cycles and because the bioretention media will experience root penetration in field applications, these complex mechanisms may counteract each other such that this finer filtration mechanism is not observed.

Summer (1:2 year events). The anomaly occurring in columns 3 and 4 during the 1st summer operation (i.e., higher effluent concentration than in columns 1 and 2 resulting in 68.3–76.2% concentration reduction) was not repeated during the 2nd summer after the submerged zone is re-formed. During the 2nd summer operation, the effluent TSS concentration for all the columns is quite similar, each with a concentration reduction of 95.8–97.0%. Therefore, the excess fine material originating from the ground woodchips in the submerged zone of columns 3 and 4 possibly contributed to the considerably higher levels of effluent TSS in columns 3 and 4 compared to columns 1 and 2 during the 1st summer operation and washout of these fines coincidentally completed after the 1st summer operation. Once stabilized, the highest average effluent concentration of all columns is still only 17.2 mg/L, as shown in Figure 6, for column 4 during the first flush of spring runoff.

Winter and spring runoff. During winter and spring runoff operation, all four columns underwent multiple periods of freezing at -20°C and thawing. Events were conducted at air temperatures between 1 and 3°C and infiltration rates were slower during these events than during room temperature operation. However, all volumes applied ultimately infiltrated

through each column within a few days without any overflow forming. During these stages of operation, concentration reduction remained between 96.8 and 99.5% for all columns, except during the major melt of spring runoff for columns 3 and 4, which was closer to 90% removal. Even with influent concentrations four times that of typical concentrations (i.e., 600 mg/L), TSS removal was 97.0–99.5%. Therefore, the capacity for TSS removal was not hindered by the cold temperatures, which was expected as TSS removal is a physical treatment process.

The ability to remove filterable contaminants, like TSS, so shortly after being frozen is an important bioretention capability. This implies that during intermittent warming periods throughout winter and during spring runoff, bioretention cells could have capacity to filter and retain TSS if warm temperatures (1–3 °C) last long enough to permit infiltration through the media. This is significant as road sediment concentrations are considerably higher in cold climates due to sanding conducted for winter road maintenance and bioretention could be a viable management technology for this source of pollution in cold climate regions; however, longer-term studies are needed to evaluate how the TSS loading, the freeze-thaw cycle, and vegetation growth over time will impact infiltration rates for a design period of 20 years.

Although this research shows excellent TSS reduction without a corresponding reduction in hydraulic conductivity (Li *et al.* 2021), only 1.6 years of typical, equivalent Edmonton precipitation volume was simulated. As smaller pore sizes become progressively blocked by influent TSS, flow pathways may become clogged. Vegetative root growth and the freeze-thaw cycle have the potential to reopen these blocked flow paths, but the timeline of this research cannot provide insight into this phenomenon. Long-term studies on the large columns in this research would be required to determine the impact of prolonged TSS application on infiltration and therefore water quality improvement capacities.

Phosphorus

This research is focused on phosphorus in the form of reactive phosphorus (i.e., orthophosphate) as it is the bioavailable form and therefore most problematic in leading to the eutrophication of surface waters when found in excess quantities in stormwater runoff. Particulate phosphorus was also not heavily focused on in this study because stormwater is typically characterized as having an average of 45% and sometimes more than 90% of total phosphorus as dissolved phosphorus (Erickson *et al.* 2012); particulate phosphorus is also removed via the same mechanisms as TSS, and therefore, its removal can be evaluated by TSS reduction results.

Phosphate removal by all columns throughout all stages of operation is 85.2–99.1% concentration reduction with average effluent concentrations <0.27 mg/L, as seen in Figure 7. These results are on par with other research such as Blecken *et al.* (2010) which observed >90% total phosphorus removal, especially compared with other research that has experienced significant phosphate export (Denich *et al.* 2013). However, these results are not quite as promising as Ding *et al.* (2019), in which ~98% of dissolved phosphate was captured, even after six consecutive freeze-thaw cycles increased pore spaces. It is important to note, however, that the media used in Ding *et al.* (2019) was from an active bioretention cell that had been amended with 3.1% by volume of iron and aluminum oxides. As determined in Landsman & Davis (2018), one reason for phosphate removal in this study may have been that sorption of dissolved phosphate onto the collected sediment occurred, rather than onto the bioretention media itself. Reasons for discrepancy in performance between this study and Denich *et al.* (2013) will be discussed below.

Summer (1:2 year events). By comparing effluent phosphate concentrations in columns 1 and 2 for the 1st and 2nd summer of operation, the difference in porosity between soil media 'A' (i.e., loam) and soil media 'B' (i.e., sandy loam), respectively, does not hinder phosphate removal as effluent concentrations were 0.07–0.18 mg/L. This research also shows that the vegetation used did not play an obvious factor in phosphate reduction; this is because healthy vegetation was present in each column during the 1st summer but did not grow back in the 2nd summer, yet phosphate reduction did not show a consistent increase or decrease between each column from the 1st to 2nd summer.

Winter and spring runoff. During this period, average effluent concentrations in all columns remained similarly low as in summer temperatures at 0.07–0.27 mg/L. The reason for the effluent concentration being slightly higher in column 2 is unknown. The comparable effluent concentrations in summer, winter, and spring runoff operation indicate that phosphate is being captured by the media or captured sediment via adsorption and/or precipitation mechanisms rather than biological degradation, which would likely be impacted by the cold temperatures. Other studies have also indicated that the main removal mechanism of phosphate is physical (Roseen *et al.* 2009).

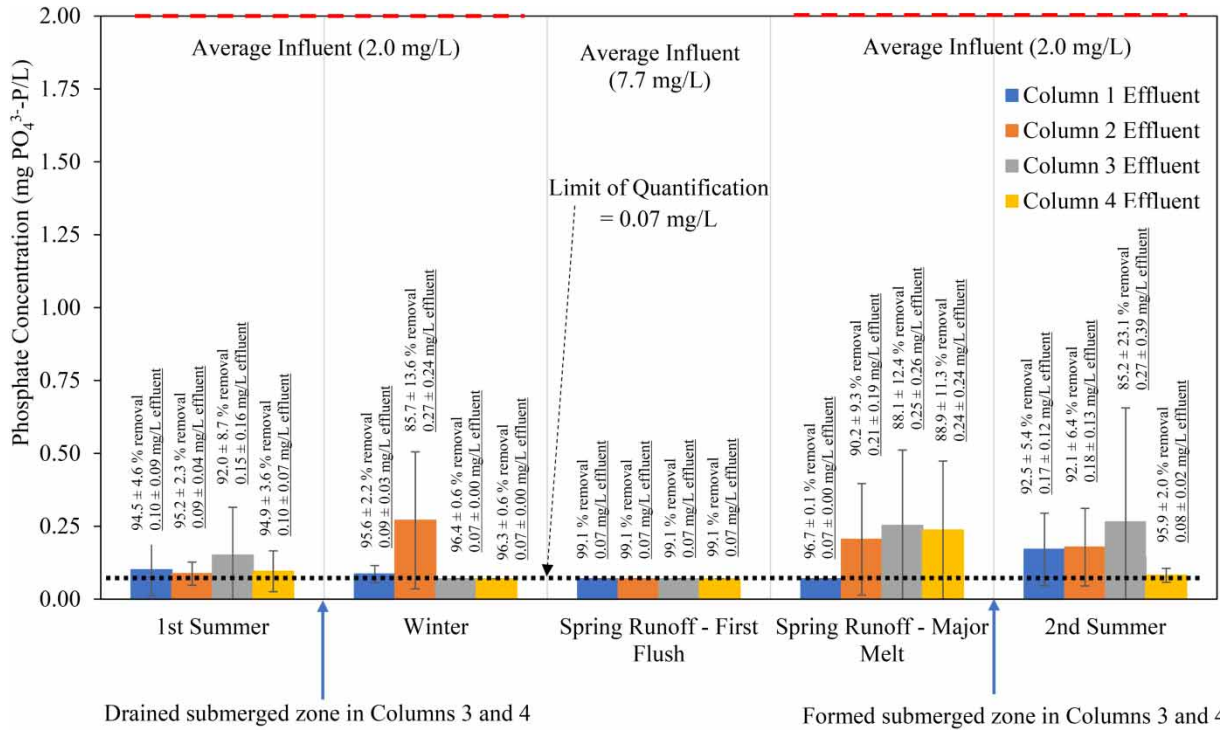


Figure 7 | Phosphate removal during the 1st and 2nd summer, winter, and spring runoff. ± Values indicate standard deviations. The error bars represent the ranges in effluent phosphate concentrations.

Much like TSS, the ability to retain phosphate shortly after being frozen and at near freezing temperatures is a valuable bioretention feature for application in cold climates. Such systems may still reduce phosphate during intermittent warming periods in winter and during spring runoff if air temperatures reach 1–3 °C and infiltration through the media occurs.

Table 3 shows the results from the leachate analysis described in the Methodology in which the different, fresh media types were soaked in water which was then analyzed for various parameters. These data are valuable to show practically what is occurring as water infiltrates through the large columns. Table 3 also shows the maximum phosphorus that is in the fresh media. From this information, the media can be ranked in terms of most likely to lead to phosphorus leaching to least likely: compost > woodchips > soil media ‘A’ (i.e., loam) > soil media ‘B’ (i.e., sandy loam).

Table 3 | Phosphorus leachate and maximum phosphorus extracted from different media types

Media	Soil Media ‘A’	Soil Media ‘B’	Compost	Woodchips	Media which experienced phosphorus leaching (Denich et al. 2013)
Phosphate Leachate (mg PO ₄ ³⁻ -P/L)	0.07	0.07	33.40	7.12	
Phosphate Leachate (mg PO ₄ ³⁻ -P/kg of soil)	1.44	1.45	667.99	142.39	
Available Phosphorus Extracted (mg P/kg of soil) (analyzed by APHA Method 4500-P D: Stannous Chloride Method (modified) (APHA 2018) after Modified Kelowna Extraction (Ashworth & Mrazek 1995)) ^a	16	14	2,100	250	2,235 ± 728
Phosphorus via acid extraction (mg P/kg of soil) (analyzed by APHA Method 3120 B: ICP (modified) (USEPA 1994) or US EPA Method 200.8 ICP-MS (modified) (BC Ministry of Environment 2009)) ^a	430	360	21,000	520	

mg/L leachate measurements utilized 180 mL of deionized water and approximately 9 g of media.

^aAs measured by third-party, commercial laboratory (i.e., Exova (www.exova.com)).

Although compost has the most available phosphorus per mass of media, its placement at the top of the column allows for media below the compost layer to adsorb or precipitate phosphate and grow bacteria that will degrade organic phosphorus to orthophosphate for subsequent physical removal. This benefit of layering compost on the top of a bioretention soil column has also been observed for nitrate and phosphate removal in other research (Lei 2018). Current local LID design guidelines (CoE 2014b) and numerous other cities recommend the use of compost to promote plant health or water holding capacity throughout the entire depth of the media; however, because compost acts as a fertilizer, it leaches phosphorus and nitrogen, not all of which can be taken up by plant roots. This research shows that compost placed as a surface layer only to the depth of current root growth will still have the capability of promoting plant health but will also have sufficient soil volume below the layer to capture phosphorus and nitrogen both physically and possibly, biologically. Also, by placing compost near the top of the bioretention cell, it can be more easily replenished through regular annual maintenance; thus, sparing quantities of compost can be applied to limit the potential for nutrient leaching while still ensuring vegetation has adequate access to nutrients.

Despite soil media 'A', 'B', compost, and woodchips having considerable phosphorus available to leach and migrate from the bioretention columns, they also have high levels of aluminum and iron, as indicated in Table 4, which have a high affinity to precipitate phosphate. Once precipitated, the high percentage of negatively charged clay and silt particles and high cation exchange capacity (CEC), also shown in Table 4, work to adsorb the now positively charged phosphate and/or filter the newly formed particles, much like the TSS removal mechanism. Table 4 also compares the soil characteristics in Denich *et al.*'s study which experienced significant phosphorus leaching from their bioretention columns (Denich *et al.* 2013). Although the aluminum, iron, and CEC values may be comparable to those of the media in this research, their media contained considerably higher levels of pre-existing phosphorus, as shown in Table 3. Based on the mass of phosphate available in the soil as determined by the leachate experiment (Leachate analysis section), columns 1 and 2 contained approximately 2,277 mg of phosphate and columns 3 and 4 contained approximately 2,448 mg of phosphate. The total mass of phosphate added to the columns from the synthetic stormwater throughout all stages of operation was approximately 1,322 mg and the average mass of phosphate released from the columns was approximately 65–107 mg, depending on the column. This results in each column storing approximately 3,500–3,700 mg of available phosphate over the lifetime of this research.

The results of this research show that even phosphorus and organic matter (that bacterially decomposed into orthophosphate that leached from the media) were well captured by the bioretention media. This research also did not show an obvious impact of the presence of steel wool in columns 3 and 4 enhancing phosphate removal, as was expected. The capacity of soil media 'A' and 'B', compost, and woodchips to retain phosphate appears to be sufficient for the time period of this research and steel wool did not appear to be needed yet. Perhaps in long-term operation, once the soil media adsorption capacity is exhausted, the steel wool will extend the bioretention columns adsorption lifetime. Further experiments are required to determine the impact of steel wool. The submerged zone incorporated into the design of columns 3 and 4 may also have an unanticipated benefit in terms of phosphate capture as phosphate adsorbed to aluminum within the submerged zone is less susceptible to desorption under anoxic conditions (Palmer *et al.* 2013).

Although good removal of phosphate through all stages of operation and of total phosphorus during select events has been observed in this research, only 1.6 years of equivalent Edmonton precipitation volume was simulated. As phosphate removal is primarily a physical mechanism via adsorption and/or precipitation, there is a soil capacity that will eventually be reached.

Nitrogen

This research focuses on the ammonium and nitrate species of nitrogen because ammonia is toxic to fish and nitrate is highly mobile through soil typically. Both these nitrogen species are also the bioavailable forms of nitrogen making them problematic in excess quantities in stormwater runoff as they can lead to eutrophication of surface waters.

Table 4 | Bioretention media characteristics that act to remove phosphorus from stormwater

Media	Soil Media 'A'	Soil Media 'B'	Compost	Woodchips	Media which experienced phosphorus leaching (Denich <i>et al.</i> 2013)
Aluminum (mg/kg Al)	5,900	4,370	9,370	1,150	5,035
Iron (mg/kg Fe)	14,100	7,900	16,300	1,800	7,215
Clay and Silt (% w/w)	49.2	32.8	–	–	8
CEC (meq/100 g)	16	12	25	56	21.9

Ammonium

Columns 1 and 2, which contain soil media 'A' (i.e., loam) and soil media 'B' (i.e., sandy loam), respectively, reduce the concentration of influent ammonium in all stages of operation by 83.2–99.8% to effluent concentrations of 0.02–0.36 mg/L, as shown in Figure 8. However, by only considering summer and winter operation, concentration reduction is 95.0–98.9%; this is comparative to Hunt *et al.* (2008), which showed effluent ammonium to be <0.1 mg/L, and Li & Davis (2014). This discrepancy was caused by the high concentrations applied during the first flush of spring runoff having an impact on ammonium reduction during the major melt phase. Ammonium was also removed through columns 3 and 4 (i.e., soil media 'A' and 'B', respectively, with denitrification enhancement amendment) throughout all stages of operation, but percent concentration reduction was much lower and more variable than in columns 1 and 2. Concentration reduction ranged on average from 21.1% (Column 3 during Spring Runoff – Major Melt) to 88.8% (Column 4 during Spring Runoff – First Flush) for columns 3 and 4 and had average effluent concentrations as high as 1.84 mg/L. It is likely that ammonium was reduced mainly via a combination of adsorption and nitrification (Dietz & Clausen 2005; Sharkey & Hunt 2005).

Summer (1:2 year events). By comparing effluent ammonium concentrations in columns 1 and 2 for the 1st and 2nd summer of operation, the difference in porosity between soil media 'A' (i.e., loam) and soil media 'B' (i.e., sandy loam), respectively, does not hinder ammonium reduction as effluent concentrations are 0.03–0.10 mg/L. While columns 3 and 4 still remove ammonium, their percent concentration reduction is on average 26.2% worse for column 3 and 27.9% worse for column 4 in the 1st summer, and 33.2% worse for column 3 and 14.7% worse for column 4 in the 2nd summer, as compared with the average removal by columns 1 and 2. The higher effluent concentration in column 3 in the 2nd summer as compared with the 1st summer may be due to an increase in infiltration rate from 1.6 to 6.1 cm/h (likely caused by the freeze-thaw cycle expanding media pore spaces (Li *et al.* 2021)) leading to shorter contact time between the influent ammonium and soil for adsorption to occur. Conversely, the lower effluent concentration in column 4 in the 2nd summer as compared with the 1st summer may be due to a decrease in infiltration rate from 11.6 to 9.7 cm/h (likely caused by the snowmelt compacting the pore spaces (Li *et al.* 2021)) increasing the contact time for ammonium adsorption. The higher sand content in column 4 allowed for greater compaction of the pore spaces as compared with column 3.

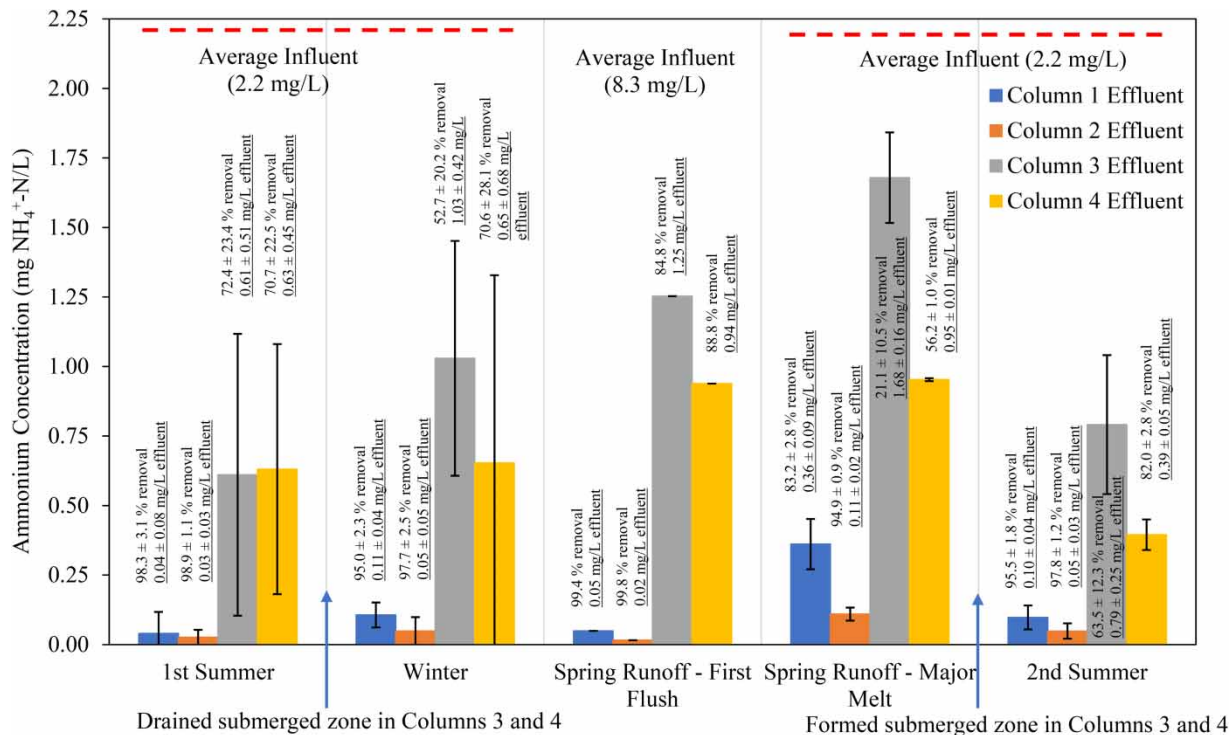


Figure 8 | Ammonium removal during the 1st and 2nd summer, winter, and spring runoff. ± Values indicate standard deviations. The error bars represent the ranges in effluent ammonium concentrations.

Winter and spring runoff. During this period, effluent concentrations in columns 1 and 2 remained similarly low as in summer temperatures at 0.02–0.11 mg/L, except for column 1 during the major melt of spring runoff, in which effluent concentrations reached as high as 0.36 mg/L on average. This is likely due to the higher average influent of 8.3 mg/L being applied during the first flush of spring runoff and being slightly delayed in its migration from column 1. Ammonium reduction was maintained in columns 1 and 2 to nearly the same level as in summer operation during cold temperatures (i.e., 1–3 °C) very shortly after the soil column was frozen and subsequently thawed; therefore, the dominant, short-term ammonium removal mechanism is physical adsorption of positive ammonium ions to negatively charged soil particles. Biological nitrification by nitrifying bacteria of ammonium to nitrite and then nitrate is also possible as this process has been observed by other research at temperatures as low as 2 °C (Blecken *et al.* 2010), but their columns were not frozen at –20 °C only 1–5 days prior to the stormwater application, as in this research. At –20 °C, nitrifying bacteria will go dormant and will need time to rebound to initial performance.

Although not evidently a dominant process, nitrification may still be occurring during room temperature operation as a slower process over the intermittent drying period between events (Stefanakis *et al.* 2014). Between events, accumulated ammonium is transformed to nitrate via aerobic autotrophic bacteria (Chen *et al.* 2006). As will be seen in the Nitrate results, nitrate is leached (i.e., more nitrate is found in the effluent than in the influent) in all situations in which a submerged zone is not present; this may be from a number of sources, one of which being nitrification of ammonium. During the event, ammonium is quickly sorbed to the soil media; once most of the water drains or evaporates from the soil, nitrifying bacteria have access to molecular oxygen and carry out the process of consuming ammonium sorbed to the soil particles and ultimately producing nitrate; this consequentially frees ammonium adsorption sites and regenerates the media to enable further ammonium adsorption.

This process could be evident by the increased effluent ammonium concentrations in columns 3 and 4 in winter and spring runoff as compared with summer operation. Reduced nitrification caused by low temperatures during this period could be leading to less conversion of sorbed ammonium to nitrate through nitrification, thus providing more ammonium available to desorb and migrate from the soil into the effluent. The higher sodium chloride concentration applied in winter and spring runoff may also be leading to higher effluent ammonium concentrations in columns 3 and 4 in winter and spring runoff as compared with summer as the sodium acts as a more preferred cation over ammonium on the media (Wasielewski *et al.* 2018). As this same increase in ammonium effluent concentration is also consistently non-visible in columns 1 and 2 when sodium chloride concentrations increased, perhaps the greater volume of soil capable of nitrification (due to the lack of an anoxic zone), allowed for more conversion of ammonium to nitrate during summer operation and thus, less available for subsequent desorption during winter. Another possible mechanism for ammonium reduction in all columns may be volatilization of ammonium to ammonia (Wang *et al.* 2015), however, without a nitrogen mass balance and soil coring, this would be difficult to definitively determine.

Much like TSS and phosphate, the ability to retain ammonium shortly after being frozen and at near freezing temperatures is a valuable feature as bioretention system in cold climate regions could still expect to experience ammonium capture during intermittent warming periods in winter and during spring runoff if air temperatures reach 1–3 °C and infiltration through the media is still occurring.

Based on the above analysis on the difference between ammonium reduction between the columns without ground woodchips and a submerged zone (i.e., columns 1 and 2) and columns with ground woodchips and a submerged zone (i.e., columns 3 and 4), the dominating, short-term ammonium reduction process is physical adsorption. Therefore, the reduced performance of columns 3 and 4 as compared with columns 1 and 2 is likely not due to the presence of the submerged zone decreasing the volume of aerobic soil available to carry out nitrification; more likely, the higher effluent concentrations in columns 3 and 4 as compared with columns 1 and 2 are due to the presence of woodchips within the submerged zone. This is also likely because draining the submerged zone for winter and spring runoff operation did not enhance ammonium removal.

Table 5 shows the results from the leachate analysis described under the Experimental approach section. These data are valuable to show practically what is occurring as water infiltrates through the large columns. Table 5 also shows the maximum possible ammonium, nitrate, and total nitrogen available in the fresh media used in this research. Although compost has the highest nitrogen levels compared with the other media, its placement at the top of the column allows for the most contact time in the media below for physical and biological treatment. Woodchips may have the lowest

Table 5 | Nitrogen leachate and maximum nitrogen extracted from different media types

Media	Soil Media 'A'	Soil Media 'B'	Compost	Woodchips
Ammonium leachate (mg NH ₄ ⁺ -N/L)	0.24	0.13	0.75	0.07
Ammonium leachate (mg NH ₄ ⁺ -N/kg of soil)	4.72	2.54	14.97	1.39
Nitrate leachate (mg NO ₃ ⁻ -N/L)	2.79	2.13	218.12	0.05
Nitrate leachate (mg NO ₃ ⁻ -N/kg of soil)	55.87	42.56	4,362.14	1.00
Total nitrogen leachate (mg N/L)	4.05	3.05	193.31	1.10
Total nitrogen leachate (mg N/kg of soil)	80.99	61.05	3,866.03	21.97
Ammonium extracted (mg NH ₄ ⁺ -N/kg of soil) (analyzed by APHA Method 4500-NH ₃ G: Automated Phenate Method (modified) (APHA 2018) after Method 6.2 – NO ₃ -N and NH ₄ -N extraction with 2.0 M KCl (modified) (Carter & Gregorich 2008)) ^a	5.80	2.90	42.60	9.50
Nitrate extracted (mg NO ₃ ⁻ -N/kg of soil) (analyzed by Method 6.3 – Determination of NO ₃ -N in 2.0 M KCl extracts by segmented flow analysis (cadmium reduction procedure) (Modified) after Method 6.2 – NO ₃ -N and NH ₄ -N extraction with 2.0 M KCl (modified) (Carter & Gregorich 2008)) ^a	53.00	23.00	3,700.00	<3

mg/L leachate measurements utilized 180 mL of deionized water and approximately 9 g of media.

^aAs measured by third-party, commercial laboratory (i.e., Exova (www.exova.com)).

levels of nitrogen available to leach, but due to their placement in the lowest soil layer (i.e., the submerged zone), any ammonia leached from woodchips may be physically adsorbed to the media but will not experience aerobic conditions for nitrification to convert the ammonium to nitrate. This is also the case for soil media 'A' or 'B' that are in the submerged zone and have even higher ammonia levels than in woodchips that may leach from the system. Without aerobic conditions that may regenerate the adsorption media, the soil in the submerged zone will ultimately reach its adsorption capacity and be unable to sorb more ammonium and be prone to desorption, especially in the presence of higher salt concentrations.

Not only do woodchips and soil media 'A' and 'B' contain ammonium in the submerged zone that could leach from the system, but they may also contain organic nitrogen which, through biological conversion known as ammonification, organic nitrogen is converted to ammonia through hydrolysis; this process can occur in both aerobic and anaerobic conditions, such as in the submerged zone (Stefanakis *et al.* 2014).

Nitrate

An anoxic zone (i.e., submerged zone) and supplemental carbon (i.e., woodchips) are required to reduce nitrate via denitrification, as indicated by columns 1 and 2 consistently exporting nitrate and columns 3 and 4 consistently reducing nitrate when a submerged zone is present and also shown by Igielski *et al.* (2019) and Lucas & Greenway (2011). Figure 9 shows the percent concentration reduction of nitrate by columns 3 and 4 only while a submerged zone is formed (i.e., during the 1st and 2nd summer) and the effluent concentrations for all columns during the same period of operation.

During the 1st summer of operation, all columns experienced a period of initial leaching in which effluent nitrate concentrations were as high as 150 mg NO₃⁻-N/L. After the first three events applied to each column, these high concentrations dropped and stabilized. Therefore, these first three data points were omitted from the data in Figure 9 and the following analysis to discuss the systems once matured. Similarly, the 2nd summer experienced two initial weeks of effluent nitrate concentrations being higher than influent concentrations in columns 3 and 4 in which time the denitrifying bacteria came out of dormancy and rebounded to almost initial performance. Therefore, these first two data points were also omitted from Figure 9 and the following analysis. These two initial weeks of nitrate leaching may have been caused by three mechanisms: influent nitrate, potentially still from the higher influent concentrations applied during the first flush of spring runoff, leached from the media itself (leachate potential can be seen in Table 5), and/or ammonium nitrified to nitrate; this may indicate that nitrification rebounds more quickly than denitrification after winter conditions leading to nitrate formation without subsequent denitrification.

While the columns without denitrification (i.e., columns 1 and 2) export nitrate to sometimes double the influent concentrations, which is consistent with other conventional bioretention systems (Hunt *et al.* 2006; Landsman & Davis 2018),

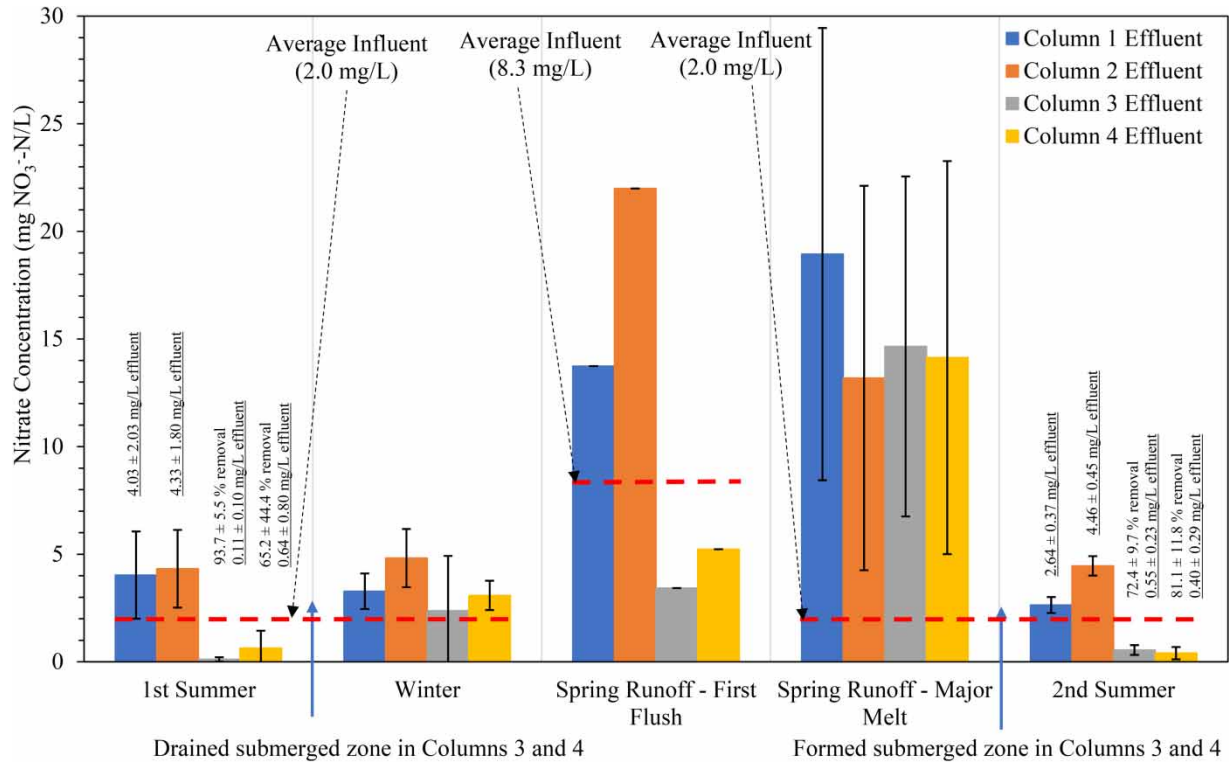


Figure 9 | Nitrate removal and leaching during the 1st and 2nd summer, winter, and spring runoff. Omitted weeks of maturation in the 1st and 2nd summer (i.e., weeks 1, 2, and 3 (columns 1 and 2), weeks 4, 5, and 6 (columns 3 and 4), and weeks 37 and 38). \pm indicates standard deviations. The error bars represent the ranges in effluent nitrate concentrations.

columns 3 and 4 carry out denitrification and reduce concentrations by 65.2–93.7% on average while an anoxic zone is present.

Summer (1:2 year events). Columns 1 and 2, which contain soil media ‘A’ (i.e., loam) and soil media ‘B’ (i.e., sandy loam), respectively, export nitrate in concentrations ranging between averages of 2.64 and 4.46 mg/L during the summer operation. Columns 3 and 4 (i.e., loam and sandy loam soil, respectively, with the denitrification layer) reduce average nitrate concentrations to 0.11–0.64 mg/L. By comparing effluent nitrate concentrations in columns 3 and 4 for the 1st and 2nd summer of operation, the difference in porosity between soil media ‘A’ (i.e., loam) and soil media ‘B’ (i.e., sandy loam), respectively, does not hinder nitrate reduction as concentration reductions are 65.2–93.7% and do not show either column 3 or 4 performing consistently better than the other.

Higher nitrate reduction of 82% has been observed in another study (Peterson *et al.* 2015) that used a submerged zone, hardwood woodchips (i.e., Willow Oak), and a 0.8-day retention time; this research utilized softwood woodchips (i.e., Cedar) for a supplemental carbon source and approximately 1-week retention time. Although the performance of columns 3 and 4 in this research is acceptable as most traditionally designed bioretention columns (i.e., no submerged zone) export high levels of nitrate, further analysis would be useful to determine if a different type of supplemental carbon or varying contact time could enhance nitrate reduction in the media designed for use in cold climate regions. Regardless, this research shows that conditions that promote denitrification are a requirement to obtain nitrate reduction rather than nitrate leaching. The presence of nitrate in bioretention media is from both soil media ‘A’, ‘B’, and compost, which are unavoidable components in bioretention design. Therefore, if nitrate is of concern at a specific site, denitrification conditions must be incorporated into the design to prevent nitrate leaching into the effluent.

This research also shows that the vegetation used did not play a visible role in nitrate reduction; this is because healthy vegetation was present in each column during the 1st summer but did not grow back in the 2nd summer, yet effluent nitrate concentrations did not show a consistent increase or decrease between columns from the 1st to 2nd summer operation for all four columns.

Winter and spring runoff. In the first flush of spring operation, nitrate was reduced in columns 3 and 4 by 58.2 and 37%, respectively, but this was likely just a delayed reaction to the four times concentrated stormwater applied because the effluent concentrations for columns 3 and 4 during the major melt phase are approximately seven times that of the influent. The other interesting observation during spring runoff is the high effluent concentrations of columns 1 and 2. During the first flush, columns 1 and 2 effluent concentrations are on average 5.4 and 13.7 mg/L, respectively, higher than the influent. During the major melt, columns 1 and 2 effluent concentrations are on average 16.9 and 11.2 mg/L, respectively, higher than the influent. Because it is unlikely that this large amount of nitrate was suddenly leached from the media, this may be an indication that the higher concentrations of ammonium applied during the first flush (i.e., 8.3 mg/L), which was reduced, underwent nitrification to nitrate without subsequent denitrification and was released during the first flush and major melt in elevated concentrations.

Ultimately, nitrate is exported from every column when denitrifying conditions are not present. There are three sources of this nitrate leachate that were listed above: influent nitrate, leachate from the media itself, and/or ammonium nitrification to nitrate.

As explained in the Ammonium results, during an event, ammonium is quickly sorbed to the soil media; once most of the water drains or evaporates from the soil, nitrifying bacteria have access to molecular oxygen and carry out the process of consuming ammonium sorbed to the soil particles and ultimately producing nitrate; this consequentially frees ammonium adsorption sites and regenerates the media to enable further ammonium adsorption and subsequent nitrification. However, due to the complexity of the large bioretention columns used in this study and the inability to isolate the confounding factors such as the woodchips and the submerged zone, it is difficult to confirm whether, or to what extent, nitrogen was removed via physical or biological mechanisms. It is recommended that further research, including microbiological monitoring and experimenting on more bioretention columns such that controls can be established, is conducted to better understand these mechanisms.

From an approximate mass balance based on the leachate experiment (Leachate analysis section), influent contaminants applied throughout all stages of operation, and average effluent masses, the mass of ammonium and nitrate retained in each column for the duration of this research was determined. Columns 1 and 3 contained approximately 700 mg of ammonium and 20,250 mg of nitrate and columns 2 and 4 contained approximately 400 mg of ammonium and 18,300 mg of nitrate. The total mass of ammonium and nitrate added to the columns from the synthetic stormwater was approximately 1,445 and 1,322 mg, respectively. Based on the average mass of ammonium released over the lifetime of this research, columns 1, 2, 3, and 4 retained approximately 2,100, 1,800, 1,650, and 1,450 mg of available ammonium, respectively. Similarly, columns 1, 2, 3, and 4 retained approximately 13,110, 12,750, 16,700, and 16,000 mg of nitrate, respectively.

In the absence of a submerged zone and sufficient carbon, nitrate will leach from bioretention systems designed with the media in this research, especially when designed with the use of compost; as seen from the leachate experiment and Table 5, compost has 77–101 times the level of nitrate available to leach compared with soil media 'A' and 'B'. Careful selection and placement of compost is necessary to minimize nitrate leachate in the field. This research used columns 0.36 m in diameter with an entire surface layer of compost; as the vegetation used in this research filled almost the whole diameter of the column, this amount of compost was necessary. In the field, it should be considered to put a carefully calculated quantity of compost either only on the surface (like in this research) or only in and surrounding vegetation root balls. This will heavily depend on the vegetation design.

The vegetation in this research did not survive winter and spring runoff operation; therefore, the above-discussed compost application recommendation needs further experimental confirmation. However, based on the presence of phosphate and nitrate in the effluent of each column (without an anoxic zone), the lack of plant regrowth is unlikely the result of insufficient nutrients.

CONCLUSION

In both the 1st summer and 2nd summer of simulated operation with an influent concentration of 150 mg TSS/L, 2 mg $\text{PO}_4^{3-}\text{-P/L}$, and 2 mg $\text{NH}_4^+\text{-N/L}$, each contaminant was reduced by all four media compositions and column configurations tested in this research. During this operation, the columns with soil media 'A' (i.e., loam soil) and soil media 'B' (i.e., sandy loam) and no nutrient removal amendment layers (i.e., columns 1 and 2, respectively) had removal efficiency of TSS, phosphate, and ammonium $\geq 90\%$. These results indicate that the difference in porosity between the soils used in this research (i.e., loam and sandy loam) did not hinder these contaminants' removal efficacy, confirming the original hypothesis.

TSS removal in columns 3 and 4 (soil media 'A' (loam) and 'B' (sandy loam), respectively, both with nutrient amendments) improved from the 1st summer to the 2nd summer of simulated operation, likely due to fines from woodchips completing washout from the media. Ammonium reduction in columns 3 and 4 was not as effective as in columns 1 and 2 likely due to ammonium leaching from the woodchips in the submerged zone or organic nitrogen from the woodchips and submerged zone media undergoing ammonification. Phosphate was comparably removed in columns 3 and 4 as in columns 1 and 2 for the 1st and 2nd summer by being $\geq 85\%$ removed. The steel wool amendment in columns 3 and 4 did not show enhanced phosphate removal during this experiment, likely due to the existing capacity of the soil media to adsorb/precipitate phosphate and the limitations to the experiment timeline; further, long-term studies would be required to determine the impact of steel wool on phosphate removal.

Nitrate reduction due to denitrification was observed in the columns with an anoxic zone and supplemental carbon (i.e., columns 3 and 4) in both the 1st summer and 2nd summer of simulated operation. During this stage, an influent concentration of 1.5 mg NO_3^- -N/L was reduced to an average concentration ≤ 0.64 mg/L in both columns 3 and 4. Columns without an anoxic zone and supplemental carbon (i.e., columns 1 and 2) leached nitrate consistently (i.e., higher nitrate concentrations in the effluent than in the influent) due to the nutrient content of the fresh media and from nitrification of sorbed ammonium to nitrate during the drying period between simulated events.

If infiltration of snowmelt and runoff occurs during cold temperatures, physical removal of TSS, phosphate, and ammonium can still be achieved, even only days after the complete freezing (and subsequent thawing) of bioretention media at -20°C . During one winter and one spring runoff event at an air temperature between 1 and 3°C and influent concentrations of 150 and 600 mg TSS/L, 2 and 8 mg PO_4^{3-} -P/L, and 2 and 8 mg NH_4^+ -N/L, each contaminant was reduced by all four columns. All columns showed $>89.5\%$ removal on average of TSS and $>85.7\%$ removal on average of phosphate during winter and spring runoff. Columns 1 and 2 also showed the removal of ammonium in winter and spring runoff $>83\%$; however, much like during summer operation, although still reduced, columns 3 and 4 exhibited worse performance of ammonium reduction due to woodchips in the anoxic zone.

Once the submerged zones in columns 3 and 4 were drained in preparation for winter operation and spring runoff, denitrification ceased and nitrate leached from the columns similarly to columns 1 and 2, which did not contain a submerged zone and supplemental carbon. However, after winter and spring runoff operation and once the submerged zone was reformed in columns 3 and 4, denitrifying bacteria rebounded within only 2 weeks to almost original nitrate reduction performance.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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