REMOVAL OF METALS FROM HIGHWAY STORMWATER RUNOFF USING ENHANCED FILTRATION MEDIA AMENDMENTS

by

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ABSTRACT

KAITLYNN J. BRYAN-SCAGGS. Removal of Metals from Highway Stormwater Runoff Using Enhanced Filtration Media Amendments. (Under the direction of DR. DAVID VINSON)

Stormwater runoff can introduce contaminants including heavy metals, chloride, and phosphorus compounds, which can have negative impacts on receiving waters. Stormwater filtration systems can offer successful and cost-effective reduction of stormwater contaminants. The objective of this research is to evaluate cost-effective filtration media amendments in column experiments, quantifying contaminant removal under different simulated field conditions. For this research project, field-collected stormwater was spiked at common contaminant levels, buffered for pH, and filtered through sand and Stalite (an expanded slate aggregate) filtration columns amended with biochar or zero-valent iron. The simulated field conditions include baseline flow, alternating contaminant concentrations, antecedent drought, de-icing agents and cold temperature (phase 4.4), and media aging (phase 4.5). Dissolved metals aluminum, chromium, copper, manganese, lead, and zinc were analyzed in phases 4.1 through most of phase 4.4; However, total recoverable metals were also analyzed in samples from the end of phase 4.4 and throughout phase 4.5 due to the relationship between solid particles and metals. Laboratory and statistical analyses showed that aluminum was significantly removed by the Stalite + biochar stormwater filtration system throughout most phases of the project. For example, influent aluminum was 113-450 µg/L during phase 4.3, while effluent through Stalite + biochar exhibited aluminum concentrations less than ~50 µg/L. Chromium was not significantly removed by any of the stormwater filtration systems; however, Stalite and Stalite + biochar displayed lower effluent concentrations than the other stormwater filtration systems throughout most phases. For example, influent chromium was ~0.1-2 µg/L during phase 4.3 while effluent through Stalite + biochar exhibited chromium concentrations below ~0.5 µg/L. Copper was significantly removed by both the Stalite + biochar and Stalite + biochar + iron stormwater filtration systems throughout most phases of the project. For example, influent copper was ~1-7 µg/L, while effluent through Stalite + biochar exhibited copper concentrations less than ~2.5 µg/L. Manganese was significantly removed by the Stalite + iron and Stalite + biochar + iron stormwater filtration systems throughout most phases of the project. For example, influent manganese was 53.2-104 µg/L while effluent through Stalite + biochar + iron exhibited concentrations less than ~5 µg/L. Lead was significantly removed by both the Stalite + biochar and Stalite + biochar + iron stormwater filtration systems throughout most phases of the project. For example, influent lead was ~0-16 µg/L while effluent from Stalite + biochar + iron exhibited concentrations less than ~5 µg/L. Zinc was significantly removed by both the Stalite + biochar and Stalite + biochar + iron stormwater filtration systems throughout all phases of the project. For example, influent zinc was 106-217 µg/L while effluent through Stalite + biochar was less than ~20 µg/L. The Stalite base displayed the most effective removal of metals as opposed to sand. Statistical analyses showed that Stalite + biochar stormwater filtration amended system displayed the most effective overall metals removal, except for chromium.

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1. INTRODUCTION

1.1 Stormwater Contaminants

Stormwater runoff from urban areas across impervious paved surfaces can discharge contaminants into nearby streams, creeks, or stormwater remediation structures. These contaminants include dissolved and particulate contaminants such as suspended solids, nutrients (phosphorus), metals, and chloride in high concentrations (McKenzie & Irwin, 1983; Kayhanian et al., 2012; Maniquez-Redillas and Kim, 2016). These contaminants, specifically metals, can negatively impact these nearby water bodies (Reddy et al., 2013; Galfi et al., 2017).

The sources of the contaminants found in stormwater runoff vary from runoff near industrial sites, domestic households, agricultural lands, and urbanized areas (U.S. EPA, 2017). Runoff from urban areas is largely due to the increased overland flow from impervious surfaces such as construction surfaces, buildings, sidewalks, and highways, all of which are commonly found in urban areas and are characterized as non-point source pollution. Contaminant concentrations in runoff can be impacted by precipitation, seasonal variation, flow path, and other environmental factors of the drainage area (Maniquez-Redillas and Kim, 2016). Contaminant concentrations in runoff can also be impacted by chemical parameters including pH, oxidation-reduction potential (ORP), and turbidity. These chemical parameters can influence the chemical reactivity of water and can allow speciation of metals (Martinez et. al, 2014). Several million miles of highways in the U.S. focus non-point source pollution into streams (Trenouth and Gharabaghi, 2015). While highways typically account for 5-8% of an urban catchment area, highways contribute stormwater contaminants disproportionate to their area. Highway runoff can contribute up to 50% of the total suspended solids (TSS), 16% of total hydrocarbons, and 35-75% of the total metal concentrations to receiving streams close to major road (Ellis et al., 1987; 1994). When stormwater contaminants reach receiving waters, the aquatic ecosystem can be disrupted. For example, excess nutrients can cause an increase in algal growth in surface water bodies, which can then impact the surrounding ecosystem and possibly drinking water quality (Reddy et al., 2013). Another example is that excess metals can are not biodegradable and can accumulate in soils and water bodies, causing long-term negative impacts on water quality such as death to freshwater organisms, and acute and chronic toxicity to humans (Genç-Fuhrman et al., 2007; Hassaan et al., 2016). Contaminants in stormwater runoff should be studied simultaneously as they can have large influences on one another in natural and experimental settings. For example, increasing chloride concentrations can mobilize metals in soils, allowing the metals to enter freshwater systems where they can negatively impact the environment (Schuler & Relyea, 2018). Also, soluble phosphate and ammonium has been shown to chemically react with multivalent cations, such as metal cations, to form insoluble metal phosphate salts similar to what is found in naturally occurring environments (Nzihou & Sharrock, 2010).

Metals that were studied for this project include aluminum, chromium, copper, manganese, lead, and zinc. Stormwater runoff in urbanized areas is known to accumulate metals (Maniquez-Redillas and Kim, 2016). Metals do not generally degrade naturally, and their concentrations can continue to accumulate in a variable pattern based on the source, location, and availability of the specific metal. This accumulation can come from sources such as vehicles, construction materials, industrial materials, atmospheric deposition, as well as many other point and non-point sources of pollution (Reddy et al., 2014). Some metals, such as copper, selenium and zinc, are essential for the function of the human metabolism at low levels; however, metal accumulation from contaminated drinking water or intake via the food chain can become toxic and/or poisonous (Hassaan et al., 2016). Table 1 shows a list of metals, including the metals that were observed in this project, and their common sources of contamination.

Table 1. Common metal contaminants, contamination source, and environmental impact.

	Common Contamination Source	Contaminant Effect on Environment	Reference
Aluminum	Naturally occurring, construction materials	Aquatic exposure	Claytor and Schueler, 1996
Chromium	Industrial waste, automobile exhaust and vehicular ware	Toxic, carcinogenic, environmentally persistent	Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008; Reddy et al., 2014
Copper	Industrial waste, automobile exhaust and vehicular ware	Toxic, carcinogenic, environmentally persistent	Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008; Inyang et al., 2013; Reddy et al., 2014
Manganese	Naturally occuring	Regulation of heavy metals, transformation of organic substrates	Remucal & Ginder-Vogel, 2014
Lead	Automobile exhaust and vehicular ware	Toxic, carcinogenic, aquatic exposure, environmentally persistent	Rangsivek & Jekel, 2005; Inyang et al., 2013; Reddy et al., 2014; Trenouth & Gharabaghi, 2015
Zinc	Industrial waste, automobile exhaust and vehicular ware	Aquatic exposure, environmentally persistent	Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008; Reddy et al., 2014; Trenouth & Gharabaghi, 2015
Cadmium	Industrial waste, automobile exhaust and vehicular ware	Toxic, carcinogenic, environmentally persistent	Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008; Inyang et al., 2013; Reddy et al., 2014
Arsenic	Industrial waste	Toxic	Genç-Fuhrman et al., 2008

Metals including aluminum, manganese and zinc are commonly found in higher concentrations than lead, chromium and copper. Aluminum, manganese and zinc are commonly used in the production of vehicle structures, construction materials, and drainage systems/pipes that transport stormwater from roadways. Some of these toxic metals can also be found in fuel additives, fertilizers, and pesticides that could be collected in stormwater runoff (Hasaan et al., 2016). The reactivity and ubiquitous nature of these metals can result in speciation concurrent with other contaminants at significant rates, impacting the contaminant form and strength (Ellis et al., 1987). Metals can be considered contaminants in their dissolved form and their particulate form, as the uptake of both chemical forms can be toxic in the environment.

1.2 Current Contaminant Regulations

The Environmental Protection Agencies (EPA) National Pollutant Discharge Elimination System (NPDES) program requires that municipal transportation authorities be responsible for any stormwater runoff management (US EPA, 2015). In North Carolina, the Department of Environmental Quality (NCDEQ) regulates stormwater runoff discharges through the National Pollutant Discharge Elimination System (NPDES) by issuing permits to different sectors, including stormwater runoff from construction, industrial facilities, and other areas of interest that could potentially introduce contaminants into receiving waters. By regulating stormwater runoff through permits, state officials are aware of the quality of the stormwater that is being discharged by observing different qualitative parameters such as pH, total suspended solids, and odor. The stormwater is also analyzed in an analytical laboratory for contaminants based on the environmental concern, including metals. These metals can range from lightweight metals such as aluminum, which is generally not toxic, to chromium, which is generally toxic in small amounts. The NCDEQ also helps to regulate stormwater management including detailing minimum design criteria recommendations and water supply watershed protection rules (NCDEQ, n.d.).

The North Carolina Department of Transportation (NCDOT) Highway Stormwater Program encompasses management of stormwater runoff. NCDOT details many programs and tools that perform contaminant removal from stormwater runoff (NCDOT, n.d.). However, removal of contaminants other than TSS is not primarily achieved with the current stormwater runoff filtration media mixture. Therefore, it is beneficial for the NCDOT to consider different management criteria, including different filter media mixtures, to optimize contaminant removal as well as stormwater runoff management.

1.3 Stormwater Treatment by Filtration

Various stormwater control measures have been developed including wet ponds, wetlands, infiltration trenches and wells, rain gardens, bio-retention areas, riparian buffers, sand filters, etc. The removal of stormwater contaminants through filtration is a useful remediation technique. Current stormwater filtration systems include media filters, green infrastructure, and bioretention basins (Claytor and Schueler, 1996). Currently, sand filtration is commonly used for physical sieving of particulate pollutants smaller than the sand pore size, and filtered water is delivered to receiving waters or a treatment plant (Erickson et al., 2007). Sand filters may be composed of one type of media or a combination of media amendments, including vegetation, activated carbon, calcite, zeolite, iron filings, and/or other reactive filtration materials (Reddy et al., 2014; Wu et al., 1998; Prabhukumar, 2013). These media-based filtration systems can be implemented above ground in the form of physical barriers that stormwater must flow through before reaching its drainage point or in the form of below ground systems that allow stormwater to filter through soil and plant systems as well (Lenhart et al., 2019). Green infrastructure is a cost-effective, resilient stormwater treatment technique commonly designed to mimic natural processes of vegetation, as opposed to grey infrastructure such as drainage pipes and water treatment systems (EPA, 2019). Green infrastructure includes technologies such as green roofs, permeable pavement, and vegetation channels to accomplish physical and chemical objectives (NCDEQ, 2017). Physical objectives of green infrastructure include infiltration and slowing the stormwater flow off of impervious surfaces, while chemical objectives include contaminant filtration and treatment. Bioretention basins are shallow planted depressions in which stormwater is retained before infiltration or downstream discharge. In recent years, bioretention basins have become increasingly popular as this technique for stormwater management can be installed at various scales, and they have shown to effectively remove pollutants and reduce the volume of stormwater runoff from an area. Bioretention basins may be more costly when compared to other filtration practices. However, a smaller amount of infrastructure is required for the construction of these basins. A reduced amount of infrastructure can offset the long-term costs and management of bioretention basins (Clark & Acomb, 2008). Due to metal accumulation in the environment, filtration systems to remove heavy metals and other contaminants simultaneously are becoming more popular as states try to meet regulatory compliances. However, systems that are cost-effective and efficient are challenging to develop. This project will place emphasis on the filtration of metals from stormwater runoff using a range of materials suited for use in North Carolina as determined through discussions with NCDOT.

1.4 Stormwater Filtration Media

Filtration media amendments can replace or add to current stormwater filtration media. By adding different media amendments, the most effective stormwater filtration system can be identified and implemented.

Media bases include a sand base or a Stalite base, as each is cost-effective, useful, and easily applied filter media. Stalite is a lightweight aggregate material that is mainly composed of slate. Sand and Stalite can both successfully remove some amount of organic and inorganic contaminants; however, successful media amendments should help influence hydraulic conductivity and adsorption/ion exchange capacity. Optimal hydraulic conductivity is characterized by a 1-2 inch/hour flow rate as specified by the NCDOT and measured following Standard Method ASTM D2434-19. Optimal adsorption/ion exchange includes an abundance of sites for physical and chemical deposition, or oxidation of heavy metals. Suitable microbial colonization is required for complete nitrogen removal, as an anoxic saturated zone within the mixture should facilitate microbial denitrification. Optimal plant growth is characterized by supporting water retention capacity and organic matter content when the filtration media is simultaneously present in the field. The media bases and amendments will be discussed in further detail below, including their composition, physical characteristics, and removal efficiency.

Sand is a natural material with a variable composition mainly composed of silicon dioxide (SiO_2) assuming that the sand consists of quartz (Reddy et al., 2014). Sand filtration has been proven to remove stormwater contaminants including TSS and heavy metals (NCDEQ, 2017). These filters can be placed above or below ground, making them appealing for urban areas with limited surface space. Although sand filters typically have low cost, high hydraulic conductivity, and high removal of suspended solids, they are characterized by poor removal of other contaminants due to the lack of chemical affinity for adsorption. Removal efficiency for sand is usually low, and due to contaminants co-existing in urban stormwater, a combination of filter media with sand would be required for contaminant removal (Haile and Fuerhacker, 2018).

Stalite is a processed structural lightweight aggregate of slate produced in North Carolina. The deposit from which the raw slate is collected is located in the foothills of the

Uwharrie Mountains of North Carolina. The unprocessed rock is mainly composed of metamorphosed hardened clay particles originating from volcanic activity. After being heated at approximately 1000°C, the gases in the rock expand, creating a lightweight granular ceramic material (Stalite Environmental, 2014). Stalite MS16, the crushed version of the expanded slate, can contribute to the remediation of urban stormwater contaminants by retention of stormwater, as well as adsorption of contaminants and cation exchange of anionic compounds. While Stalite has the same durability as sand, it has a lower bulk density. Stalite also resists clogging during extreme rainfall events, while sand clogs quickly during extreme events. This is due to the material's high hydraulic conductivity, porous surface area, and its ability to resist deterioration. With these filtration qualities, the material has shown to be effective in removing common stormwater contaminants (Stalite Environmental, 2014). For example, studies have shown that the MS16 Stalite can remove 70% of nitrogen and 65% of phosphorus in column tests with synthetic stormwater in an anoxic environment with organic matter present as a carbon source for bacteria (Pledger et al., 2012). Also, one study determined that the pore network within Stalite is largely unconnected, with interior and exterior pores only connected by microcracks, allowing for the increased adsorption capacity of suspended solids (Stalite Environmental, 2014). This gives the lightweight aggregate a higher adsorption capacity than normal weight aggregates but lower adsorption capacity than materials with linked pore networks (Stalite Environmental, 2014). Also, initial toxicity analyses of Stalite have shown that concentrations of metals within the raw material were orders of magnitude below the EPA regulatory limits (Stalite Environmental, 2014). While these initial tests show that Stalite does not add metal contaminants to the filtrate, the material has not yet been tested for its ability to remove metal contaminants in stormwater runoff and could represent a favorable alternative to typical sand filtration.

Media amendments can be used to enhance contaminant filtration of a media type like sand or Stalite (Erikson et al., 2007; Bock et al., 2015) One media amendment that was used in this project was biochar. Biochar is a carbon-rich material that is produced when plant-based biomass is heated through pyrolysis, gasification, or hydrothermal carbonization in an oxygen deficient environment. The cost of biochar is significantly less than that of activated carbon, a commonly used filtration material. Pores formed within the heated biomass give the biochar a large surface area for contaminant adsorption (Reddy et al., 2014; Prabhukumar, 2013; Inyang et al., 2012). Biochar has been widely investigated as a soil amendment to improve soil characteristics and remove bacteria, nutrients, inorganic and organic pollutants. Various environmental factors may increase the contaminant removal capabilities of biochar, including aerobic vs. anoxic conditions. Effectiveness of biochar in metal immobilization can depend on both metal and biochar type, as different biochar products have shown significantly different metal removal rates (Inyang et al., 2012). Adsorption is an important capability of biochar; however, the media can also serve a reactive species, in which a chemical reaction like precipitation can aid in contaminant removal. One study found that lead removal occurred due to the surface complex formation between lead and the oxygenated functional groups present on the biochar surface (Reddy et al., 2014). Another study found that high lead concentrations led to the full consumption of alkali ions released by the biochar, confirming an important surface precipitation mechanism of metal removal (Inyang et al., 2012).

Another media amendment that was used in this project was zero-valent iron, also known as iron filings, which is produced commercially or acquired as a byproduct of the milling, filing, or grinding of iron materials. The term zero-valent iron accurately describes the elemental form of iron - the outer valence level of each atom of iron is filled, producing a zero charge for each atom. Zero-valent iron acts as a reducing agent when exposed to a chemically reactive environment, donating electrons to positively charged species while becoming a positively-charged iron species itself (Tiwari and Nayak, 2016). Iron-based products are currently used in stormwater best management practices (BMPs) as they have high porosity, high hydraulic conductivity, and the ability to remove dissolved phosphorus, an important stormwater contaminant (Erickson et. al, 2007). Contaminant removal by iron filings is dependent on hydraulic contact time, initial dissolved oxygen, and initial pH (Prabhukumar, 2013). Iron filings have been shown to be successful in achieving 95-100% removal of copper, lead and zinc, and 100% removal of chromium (Reddy et al., 2014; Trenouth and Gharabaghi, 2015). However, the oxidation-reduction reaction within the filter media has the potential to release soluble iron back into the filtered stormwater, serving as a contaminant source itself (Tiwari and Nayak, 2016).

1.5 Results of Previous Batch Tests

The initial tasks of the overall NCDOT-supported project began in 2018 and is summarized here as background. Previously, a literature review was conducted to determine viable filter media amendments. The literature review identified media that was effective in removing different contaminants simultaneously, performing successfully under different field conditions, and mixing well with other media.

Batch tests were performed on the selected media from the literature review. This was used as a fast-screening test to determine which media had high contaminant removal rates to finalize options for the following column tests. In the first batch test, seventeen different media amendments were tested for their contaminant removal rates. Results from the first batch test showed that while activated carbon was the most successful contaminant filter media, biochar was a close competitor. Batch test two was used to determine removal capacity of the best 6 performers from batch test one (activated carbon, 2 different biochar media, vermiculite, and 2 different iron media) and the two baseline materials (sand and Stalite). Three sequential media tests were completed in batch 2 – batch test 2.1, 2.2 and 2.3. Based on results from batch test two, two filter amendments were chosen to be mixed with sand and Stalite in the bench-scale column tests: biochar and zero-valent iron (Table 2).

Table 2. Contaminant Removal Percentages from Batch Test 2

(Highlighted media represent media chosen for column tests; Percentages represent removal of the listed contaminant by the associated filter media)

Media	**Batch**	**Phosphate**	**Nitrite**	**Nitrate**	**DOC**	**Total P**	**Cr**	**Mn**	**Pb**	**Zn**
Activated Carbon	2.1	3%	9%	19%	4%	15%	-1%	6%	-8%	10%
	2.2	85%	76%	53%	15%	-6%	19%	9%	9%	16%
	2.3	54%	11%	2%	11%	84%	20%	17%	-31%	13%
Biochar 1	2.1	-1%	1%	6%	7%	19%	3%	17%	12%	33%
	2.2	76%	76%	53%	10%	-3%	4%	11%	10%	24%
	2.3	53%	22%	100%	0%	77%	17%	39%	14%	33%
Biochar 2	2.1	-16%	-4%	4%	0%	14%	-7%	-9%	5%	6%
	2.2	24%	20%	-4%	4%	-10%	6%	6%	-2%	12%
	2.3	-11%	-32%	4%	23%	5%	-3%	-49%	-191%	-73%
Vermiculite	2.1	-6%	-5%	0%	-14%	7%	-12%	-10%	-28%	6%
	2.2	23%	18%	-4%	-1%	-3%	5%	5%	-12%	13%
	2.3	-6%	-16%	2%	19%	18%	-10%	-66%	-268%	-100%
Iron 1	2.1	62%	6%	1%	-3%	59%	12%	-10%	5%	23%
	2.2	72%	14%	0%	8%	46%	26%	-14%	29%	41%
	2.3	37%	5%	4%	23%	26%	-5%	-92%	-193%	-33%
Iron 2	2.1	62%	3%	1%	-8%	58%	8%	-10%	-6%	22%
	2.2	70%	15%	3%	7%	29%	23%	-23%	21%	32%
	2.3	20%	-7%	7%	18%	19%	-10%	-81%	-241%	-57%
Stalite	2.1	-12%	-5%	0%	-5%	10%	10%	1%	6%	2%
	2.2	82%	69%	56%	-2%	-3%	14%	7%	1%	12%
	2.3	55%	1%	100%	-16%	83%	6%	0%	-22%	-3%
Sand	2.1	-9%	-2%	0%	-14%	7%	-22%	-1%	-53%	-15%
	2.2	26%	16%	-1%	-2%	-6%	4%	7%	-9%	5%
	2.3	-8%	-4%	0%	19%	-2%	-11%	-75%	-236%	-102%

During task 2, spiked stormwater was used during both batch tests so that removal rates could be measured. Spiking was done to introduce a higher concentration of metals, nutrients, and organic substances.

In task 3, mixing ratios of filter media were determined for suitable water infiltration. To satisfy specific stormwater filtration guidelines and specifications set by NCDOT, porosity and hydraulic conductivity of the media mixtures were measured and adjusted based on media cost. Media were mixed with sand or Stalite at a ratio of 5% by weight of the base used, allowing for suitable water infiltration and a reasonable stormwater management cost. Based on results from task 3, eight media mixtures for bench-scale column filtration were selected and were given a unique ID (Table 3).

Table 3. Column Compositions for Filter Media Tests

Column	Column Contents Description
Sand	100% sand
Sand + biochar	95% sand, 5% biochar
Sand + iron	95% sand, 5% zero-valent iron
Sand + biochar + iron	90% sand, 5% biochar, 5% zero-valent iron
Stalite	100% Stalite
Stalite + biochar	95% Stalite, 5% biochar
Stalite + iron	95% Stalite, 5% zero-valent iron
Stalite + biochar + iron	90% Stalite, 5% biochar, 5% zero-valent iron

1.6 Objectives

NCDOT's current stormwater media filter BMP does not optimize simultaneous removal of multiple contaminants within stormwater runoff filtration media. Therefore, the primary objective of the overall NCDOT-supported project is to evaluate cost-effective engineered media amendments and optimize their compositions in stormwater filtration systems for contaminant removal. Multiple contaminants should be removed simultaneously under various field conditions. These contaminants include suspended solids, phosphorus, and metals (lead, zinc, manganese, copper, chromium, and aluminum). The addition of media amendments will help NCDOT comply with their National Pollutant Discharge Elimination System permits, as well as other current and future regulations on contaminants in stormwater runoff. Discussion of metal adsorption of Stalite in this project will be the first of its kind, and discussion of metal adsorption of the different media mixtures will contribute to the current knowledge of contaminant removal. A discussion of field suitability will be beneficial in aiding NCDOT in making a confident decision about which filter media mixture to implement for best contaminant removal, as well as other researchers. Within this scope, the objective of this M.S. thesis research is to quantify the removal of the metals aluminum, chromium, copper, manganese, lead and zinc over time and over different simulated field conditions for the media amendments biochar and zero-valent iron to sand and Stalite. This will be done using simulated filtration columns and influent stormwater with field-acquired chemical composition and realistic contaminant concentrations.

1.7 Hypotheses

The two base stormwater filtration media studied in this project have similar physical qualities; however, they may differ in chemical properties of contaminant removal. Additionally, the two stormwater filtration media amendments are expected to have different chemical properties of contaminant removal. Stormwater filtration is also subject to differ under different field conditions, such as precipitation occurrence, contaminant amounts, temperature, and drought conditions. Four hypotheses were developed to address the concerns of differing chemical properties from the different media types and the multiple field conditions that the media could be exposed to:

- Stalite will significantly outperform sand as a stormwater filtration media base for metals removal because of the previously mentioned increased pore space and adsorption capacity.
- The different chemical properties of the stormwater filtration media bases and amendments will impact contaminant removal differently for some contaminants and similarly for other contaminants.

- Exposing the stormwater filtration media to different field conditions over an extended period of time will impact contaminant removal.

This project will aid in the knowledge of stormwater contaminant removal using different filtration media. These hypotheses will increase the understanding of stormwater filtration media and how filtration media perform in different scenarios of media mixture and field conditions. By analyzing influent and effluent contaminant concentrations of different media mixtures in different field conditions, these hypotheses will be explored. Metal removal methods will be discussed in detail to conclude the most likely metals removal method in the different stormwater filtration media.

2. MATERIALS AND METHODS

2.1 Stormwater Collection

Shortly after high-intensity rain events, stormwater runoff was collected under the bridge (GPS coordinates 35°19'06.2"N 80°44'15.1"W) located on the North Tryon Street in Charlotte, NC (Figure 1). This site is directly adjacent to Highway 29, which is a recognized NCDOT highway. Stormwater was collected from a piping network that channels stormwater directly from the highway to Mallard Creek and Toby Creek, which are both parts of the Mallard Creek watershed. This is the largest watershed in Mecklenburg County with a drainage area of 20.7 km^2 and flows into the Yadkin-Pee Dee River. Stormwater was collected in multiple 5-gallon polypropylene containers and stored in a laboratory refrigerator at approximately 8°C for later analysis. Collection occurred approximately once a month or after all of the collected stormwater was used, whichever came first. Collected stormwater was brought to room temperature, shaken and spiked to common contaminant concentrations using stock chemical solutions before column filtration to ensure that contaminant levels in different collection batches were approximately consistent.

Figure 1. Stormwater Collection Site

2.2 Column Media

Based on preliminary batch tests, two filter media amendments were chosen for this project: biochar and zero-valent iron. Acquired from Stormwater biochar (Oregon, U.S.), the biochar product ‘biochar Basic’ is produced by mixing Stormwater biochar and Stormwater Shale, an activated ceramic. The zero-valent iron product selected for this study was Zero-Valent iron aggregate from Peerless Metal Powder (Melvindale, MI). The product is furnace produced, dried, mechanically ground and precision sized. Sand and Stalite were chosen for this project as filter media bases. The sand chosen for this project was a type II fine aggregate provided by Stalite Environmental in Salisbury, North Carolina (Hedrick Industries sand was used in previous project phases). Stalite is a lightweight aggregate, and the manufactured MS16 gradation of Stalite used for this project is similar to the size, hardness and chemical composition of sand (Table 4). All media were rinsed with deionized water to remove any soluble impurities prior to use.

2.3 Column Setup

Before the beginning of the column tests, plastic columns were selected for stormwater filtration purposes (Figure 2). The height of the chosen columns is approximately 3m and the inner diameter of the columns is approximately 10cm. The tops of the columns were open to air, while the bottoms of the columns had connected valves that could open and close for effluent collection. The stormwater was filtered by downward gravity flow, in which effluent was drawn for approximately 15-17 hours before collection. The plastic columns were covered with a thin, black plastic material shortly after the beginning of the column filtration tests to prevent any light from reaching the media, which could possibly aid in biochemical reactions unlikely to take place in field conditions.

Table 4. Aggregate Media Gradations for Type 2 Sand and MS16 Stalite.

Percentage (%) of Total by Weight Passing		
Sieve Size	**Type 2 Sand** (Hedrick Industries)	**MS16 Stalite** (Stalite Environmental)
3/8" (9.5mm)	100	100
#4 (4.75mm)	95-100	85-100
#16 (1.18mm)	45-95	40-80
#50 (300µm)	5-30	5-35
#100 (150µm)	0.010	5-25

Figure 2. Stormwater Filtration Column Setup

2.4 Stormwater Spikes

Stormwater was spiked within common stormwater contaminant concentration ranges to ensure that measurable concentrations of contaminants would be present in the influent solution. For the baseline and media aging testing conditions, stormwater was spiked at the high end of common contaminant ranges (Table 5). For the alternating concentration testing condition, high end concentrations were approximately three times the concentration of the baseline flow test. For the low-end concentrations, the stormwater was not spiked and any contaminants that were present in the stormwater served as the low-end concentrations (Table 5). For the cold weather and deicing agent testing condition, all contaminants other than chloride were spiked at the high end of the corresponding common stormwater contaminant concentration range. For this condition, chloride concentrations were spiked according to relevant literature at approximately 500 mg/L using sodium chloride (Snodgrass et al., 2017; Burgis et al., 2020).

Table 5. Common Stormwater Contaminant Concentrations – Estimate concentrations used as guidance for stormwater spikes and phase 4.2 (alternating contaminant concentrations).

Stormwater Spike Compounds	**Common Stormwater Concentration Range**	**Approximate Stormwater Spike Concentration**[1]	**Phase 4.2 Approximate Low Spike Concentration**[1]	**Phase 4.2 Approximate High Spike Concentration**[1]
Dissolved Organic Carbon (mg/L)	5.1 – 24 (Lopes et al., 2000)	24	<LOQ[2]	72
Phosphate as P (mg/L)	0.1 – 0.4 (Kayhanian et al., 2012)	0.4	<LOQ[2]	1.2
Chloride (mg/L)	0 – 45 (Chang, 2009)	45	<LOQ[2]	135
Al (µg/L)	20 – 160 (Kayhanian et al., 2012)	160	<LOQ[2]	480
Cr (µg/L)	0.03 – 1.4 (Kayhanian et al., 2012)	1.4	<LOQ[2]	4.2
Cu (µg/L)	1.7 – 3.36 (Kayhanian et al., 2012)	3.36	<LOQ[2]	10.1
Pb (µg/L)	0.3 – 10.2 (Kayhanian et al., 2012)	10.2	<LOQ[2]	30.6
Mn (µg/L)	3.37 – 128 (Kayhanian et al., 2012)	128	<LOQ[2]	384
Zn (µg/L)	35.3 – 416 (Kayhanian et al., 2012)	416	<LOQ[2]	1,240

[1]Approximate stormwater spike concentrations for phases 4.1, 4.3, 4.4 and 4.5; Concentrations are total contaminant concentration estimates after spiking occurred.

[2]LOQ – Limit of Quantification – Estimate phase 4.2 low-end concentrations are likely to be below the instruments limit of quantification.

2.5 Chemical Analyses

All influent and effluent stormwater samples from the column tests were tested for pH, turbidity and Total Suspended Solids (TSS), Oxidation-Reduction Potential (ORP), and pathogen indicators immediately after collection and before vacuum filtration. The remaining volume of the samples were filtered using Whatman 0.45 μm glass microfiber filters for other chemical analysis. Influent and effluent stormwater samples from the column tests were measured for UV-254 absorbance immediately after filtration. Anion samples were first filtered and then frozen in 50 mL polypropylene centrifuge tubes until further analysis. Samples collected for DOC and total nitrogen (TN) were refrigerated at 8°C in 40 mL amber glass vials that were acid-washed and oven-baked at 425°C with Teflon-lined caps and preserved with hydrochloric acid until further analysis. Samples collected for metals analysis and total phosphorus (TP) were refrigerated at 8°C in 50 mL polypropylene centrifuge tubes and preserved with nitric acid and sulfuric acid, respectively, until further analysis. Samples were brought to room temperature before analysis.

Before vacuum filtration, pH was measured immediately using EPA method 415.3, "The Determination of Total Organic Carbon and Specific Absorbance at 254 nm in Source Water and Drinking Water." TSS was also measured immediately using Standard Method 2540, "Solids in Water." ORP was measured for all baseline, influent, effluent stormwater samples using a multi-meter electrode that produced readings in millivolts (mV). Pathogen indicator tests were conducted immediately upon column filtration using Enterolert and Colilert-18 test kits for total coliforms, fecal coliforms, enterococci and *E. coli*. Pathogen indicators were analyzed using IDEXX Quanti-Trays, in which IDEXX trays were filled with 100 mL of the column effluent and incubated at 35 ± 0.5 °C for approximately 24 hours for total coliform and *E. coli*, 44.5 ± 0.2 °C for approximately 24 hours for fecal coliform, and 35°C for approximately 18 hours for enterococci. After incubation, total coliform and fecal coliform IDEXX trays were observed for positive tray wells, in which positive means that the tray well reacted and turned yellow.

Enterococci and *E. coli* IDEXX trays were observed for positive tray wells, in which positive means that the tray well reacted and fluoresced under UV light. These trays were then used to calculate an observed most probable number (MPN) of the different bacteria, ranging from 1 to 2419.6 MPN/100 mL. After filtration, UV-254 absorbance was measured using EPA method 415.3, "The Determination of Total Organic Carbon and Specific Absorbance at 254 nm in Source Water and Drinking Water."

Within 48 hours of being at room temperature or after being stored frozen, anions including chloride, nitrate, nitrite, and phosphate were measured using EPA method 300.1, the Determination of Inorganic Anions in Drinking Water by Ion Chromatography. Instrument calibration was completed using 1000 mg/L standards of sodium nitrate, sodium nitrite, potassium dihydrogen phosphate and sodium chloride. Within two weeks of sample collection, DOC and TN were measured using EPA method 415.3 and ASTM Method D8083-16, Standard Test Method for Total Nitrogen in Water by High Temperature Catalytic Combustion and Chemiluminescence Detection, respectively. Instrument calibration was completed using 1000 mg/L standard of purchased organic carbon and laboratory made sodium nitrate. TKN was estimated by subtracting the nitrate-nitrogen and nitrite-nitrogen from the TN measurement using the following equation:

$$TKN = TN - [(NO_3\text{-}N) + (NO_2\text{-}N)] \quad (1)$$

Also, within two weeks of sample collection, total phosphorus was measured using HACH method 8190, the Acid Persulfate Digestion Method, which is accepted by the EPA as an alternative to Standard Methods 4500-P E. This method measures all phosphorus species, including orthophosphate, polyphosphates, and organic phosphates. Within 6 months of sample storage, trace metals including aluminum, copper, chromium, lead, manganese, and zinc were measured using EPA method 200.7, the Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry. Instrument calibration was completed using diluted concentrations of purchased standards. Two separate procedures were conducted, one to determine the concentrations of dissolved metals that underwent vacuum filtration, and the other for concentrations of total recoverable metals that did not undergo vacuum filtration. These two methods are referred to as the determination of dissolved metals and the determination of total recoverable metals, respectively. Unfiltered and filtered samples were preserved using concentrated nitric acid; however, unfiltered samples were digested in acid to dissolve metals that might be present in solid particles. Quality assurance (QA) and quality control (QC) data were collected for all sets of data, including method blanks, check standards, matrix spikes, duplicates, and continuing calibration verification standards. Due to the usage of instruments such as the Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES), Ion Chromatograph (IC) and Total Organic carbon (TOC) analyzer, specific limits of detection (LOD) or instrument detection limits (IDL) were determined. These limits are not necessarily quantified as an exact value but display the lowest amount of an analyte that can be detected on a specific instrument. This limit is determined for each individual analyte by calculating the standard deviation between a minimum of seven blank values and multiplying this value by 3.

2.6 Statistical Analyses

All statistical analyses were completed using JMP® Pro 15 (JMP®, Version 15, 1989-2021). JMP provides many options for using and viewing statistical analyses. For this project, a students t-test was used for the significance comparison of stormwater column influent to individual column effluent, as well as the comparison of an individual column effluent to another column effluent. All stormwater filtration column influent was compared to each individual column effluent and all column effluent were compared to each other for significant differences. A connecting letters report was utilized for viewing these statistical analyses. For this project, the connecting letters report is displayed as a table with the influent and stormwater filtration columns along the left-most table column and the observed parameter in the top-most table row. For one specific parameter, if two or more stormwater filtration columns (or the influent) shared the same letter, those stormwater filtration columns did not display a significantly different parameter value. To help visualize which stormwater filtration columns displayed significantly greater, similar, or significantly lower values, figures are provided directly before or directly after each connecting letters report. Significant difference was quantified by a p-value of less than 0.05 ($p<0.05$) unless otherwise specified.

In the discussion of metal removal over time, bed volume was calculated using the following equation:

$$\text{Bed Volume} = \frac{Cumulative\ Volume\ of\ Water}{Volume\ of\ Column\ Media} = \frac{i\ m^3}{\pi \times r^2 \times h} \times 10^3 \tag{2}$$

Where i = 0.001 m^3 through 0.044 m^3, π = 3.14159, r = 0.05 m, and h = 3 m.

3. RESULTS AND DISCUSSION

3.1 Unspiked Stormwater Baseline Analyses

3.1.1 pH, ORP, Turbidity, TSS

Parameters including pH, ORP, Turbidity and TSS were analyzed in stormwater to determine background quality of the collected stormwater (Table 6). Analyses were conducted immediately or soon after stormwater collection on August 31, 2020, September 29, 2020, November 30, 2020, January 5, 2021, and February 1, 2021. This thesis focuses primarily on metal analysis, and therefore other contaminant results (pathogen indicators, UVA, SUVA, and dissolved organic carbon) are reported in the appendix and not discussed further.

Little pH variation was observed in stormwater, which remained near neutral (Table 6). Adsorption potential of a stormwater filtration system increases when pH is near neutral or alkaline (Claytor & Schueler, 1996). Since spiked stormwater was buffered, pH should not be an environmental variable that hinders the stormwater filtration system. Little ORP variation was observed as well, which is expected for aerated waters. Turbidity varied slightly throughout the stormwater collection period, which was likely due to antecedent precipitation, stormwater collection practices and/or local construction activities. TSS measurements also expressed significant variation with measurements being higher during the summer and lower during the winter (Table 6). Dissolved and suspended particles that increase turbidity and TSS can trap and adsorb metal pollutants with chemical and physical reactions (Prabhukumar, 2013). Therefore, during times like August of 2020 when turbidity and TSS are higher, we can expect higher total metal concentrations to be greater as well, as metals are likely present in the suspended solids.

Table 6. Unspiked Stormwater Baseline Concentrations - pH, ORP, Turbidity and TSS measurements.

Date	pH	ORP (mV)	Turbidity (NTU)	TSS (mg/L)
August 31, 2020	NA	NA	139	506.67
September 29, 2020	7.35	NA	34.1	35.00
November 30, 2020	7.94	NA	90.5	74.28
January 5, 2021	7.40	232	60.9	14.58
February 1, 2021	7.55	193	70.7	15.00

*NA – Results are not available.

3.1.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations in stormwater were analyzed (Table 7) immediately or soon after stormwater collection on August 31, 2020, September 29, 2020, November 30, 2020, January 5, 2021, and February 1, 2021. Phosphate as P results are not available for August 2020 and February 2021.

Total phosphorus concentrations are representative of all dissolved inorganic and organic forms of phosphorus in the stormwater samples. Total phosphorus and phosphate as P follow a similar pattern of high concentrations in stormwater in summer months and lower concentrations in winter months; However, phosphate as P had a slightly lower concentration than total phosphorus (Table 7). This indicates that there are other phosphorus species in the collected stormwater runoff, e.g., organic phosphorus. It is possible that a portion of the inorganic forms of detected phosphorus are metal-phosphate minerals that have dissociated into phosphate and the corresponding metal. This dissociation could be due to pH, ORP or other metal speciation controlling factors (Martinez et. al, 2014).

Table 7. Unspiked Stormwater Baseline Concentrations - Total phosphorus and phosphate as P.

Date	Total Phosphorus (mg/L)	Phosphate as P (mg/L)
August 31, 2020	0.16	NA
September 29, 2020	0.31	0.179
November 30, 2020	0.08	0.064
January 5, 2021	0.04	0.062
February 1, 2021	0.05	NA

*NA – Results are not available.

3.1.3 Chloride

Background concentrations of chloride were measured in stormwater (Table 8) soon after stormwater collection on September 29, 2020, November 30, 2020, and January 5, 2021.

Chloride in highway stormwater runoff is relatively common since it is a mostly conservative ion and does not readily interact with other chemical constituents (Burgis et al., 2020). However, concentrations will likely vary due to the surrounding environment. In summer months, chloride in stormwater runoff can be attributed to evaporation and/or shallow groundwater mixing. In winter months, higher chloride concentrations can be attributed to de-icing agents such as sodium chloride and potassium chloride being applied to roads and highways when needed (Kaushal et al., 2005; Burgis et al., 2020). De-icing agents are only applied when an ice/snow event is expected to occur. In North Carolina, this is not common until the colder winter months. Therefore, if no ice/snow is expected, baseline chloride concentrations in North Carolina stormwater runoff will likely be low.

Table 8. Unspiked Stormwater Baseline Concentrations – Chloride.

Date	Chloride (mg/L)
September 29, 2020	4.79
November 30, 2020	1.66
January 5, 2021	3.44

3.1.7 Metals

Background concentrations of metals aluminum, chromium, copper, manganese, lead and zinc were measured in stormwater (Table 9) soon after stormwater collection on August 31, 2020, September 29, 2020, November 30, 2020, January 5, 2021, and February 1, 2021.

There could be multiple factors influencing the unspiked stormwater baseline metals data, including domestic, industrial, agricultural, and/or technological usage in the surrounding area (Hassan et al., 2016). Many metals are also naturally occurring and could be present due to the sample location site geology. Since the sample collection location is located in an urban area nearby a main highway and continuous construction, it is difficult (if not impossible) to determine the sources of these metals in the unspiked stormwater.

Table 9. Unspiked Stormwater Baseline Concentrations – Aluminum, copper, manganese, chromium, lead, zinc.

Date	Aluminum (µg/L)	Chromium (µg/L)	Copper (µg/L)	Manganese (µg/L)	Lead (µg/L)	Zinc (µg/L)
August 31, 2020	84.01	<LOD[1]	9.96	4.42	0	12.84
September 29, 2020	689.56	0.56	3.56	14.59	0.34	8.76
November 30, 2020	229.82	1.29	2.72	5.12	<LOD[1]	12.9
January 5, 2021	121.76	<LOD[1]	0.65	73.62	9.9	5.13
February 1, 2021	166.87	<LOD[1]	2.17	35.72	0	2.02

[1]<LOD – The measured value was below the limit of detection or the lowest calibration point.

3.2 Spiked Stormwater Column Analyses – Phase 4.1

Phase 4.1 represents the stormwater column filtration baseline phase, in which stormwater was spiked within common stormwater contaminant ranges to ensure that measurable concentrations were present in the stormwater effluent. A total of 8 bed volumes were filtered for baseline stormwater filtration through the engineered media filtration columns. Influent samples were refrigerated at 8°C while the filter effluent was collected over a 15-17 hour period for complete drainage by gravity. All spiked stormwater influent samples for phase 4.1 were collected from August 13, 2020 to September 6, 2020.

3.2.1 Influent Analysis

3.2.1.1 pH, ORP, Turbidity, Total Suspended Solids

pH, ORP, Turbidity and TSS were analyzed in the spiked stormwater column influent (Table 10). pH ranged from 6.75 to 7.50, indicating that the influent spiked stormwater was chemically neutral for most influent solutions. ORP ranged from approximately 100 mV to 170 mV. It is possible that these values were lower than the unspiked stormwater baseline due to a lower oxygen concentration and more chemical reactivity within the spiked stormwater, indicating a large temperature difference, or oxygen consumption between stormwater collection time and column loading time. Turbidity ranged from approximately 15 to 40 NTU, which was slightly lower than what was measured for the unspiked stormwater. This slightly lower turbidity could be due to insufficient mixing of the sample before measurement. Total suspended solids ranged from slightly higher than 0 to approximately 400 mg/L. This range was similar to what was measured for the unspiked stormwater.

Table 10. Phase 4.1 spiked stormwater influent concentrations – pH, ORP, Turbidity and TSS.

	Minimum	Median	Maximum
pH	5.62	6.50	7.59
ORP (mV)	105	139	169
Turbidity (NTU)	16.1	22.0	200.
TSS (mg/L)	10.77	134.09	383.33

3.2.1.2 Total Phosphorus and Phosphate

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column influent (Table 11). Total phosphorus concentrations ranged higher than phosphate at 0.3 to 0.6 mg/L versus 0.05 to 0.2 mg/L, respectively. This indicated that other phosphorus species were present in the spiked stormwater, as they were in most of the unspiked stormwater samples.

Table 11. Phase 4.1 spiked stormwater influent concentrations – Total phosphorus and phosphate as P.

	Minimum	Median	Maximum
Phosphate as P (mg/L)	0.041	0.087	0.46
Total Phosphorus (mg/L)	0.31	0.42	0.83

3.2.1.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column influent (Table 12). Chloride concentrations in spiked stormwater range from 5 to 30 mg/L, which is approximately 3X the concentration observed in unspiked stormwater. This higher concentration is due to the added chloride spike.

Table 12. Phase 4.1 spiked stormwater influent concentrations – Chloride.

	Minimum	Median	Maximum
Chloride (mg/L)	4.32	16.4	28.4

3.2.1.4 Metals

Metal concentrations of aluminum, copper, manganese, chromium, lead and zinc were analyzed in the spiked stormwater column influent (Table 13). Concentrations of aluminum ranged from approximately 60 to 100 µg/L, copper ranged from undetectable to 9 µg/L, and chromium concentrations ranged from approximately 0 to 1.5 µg/L, which is similar to what was measured in unspiked stormwater (Table 9). Manganese concentrations ranged from approximately 50 to 150 µg/L, which is approximately 2X higher than unspiked stormwater manganese concentrations. Lead concentrations ranged from undetectable to 4 µg/L, which is similar and slightly higher than what was measured in unspiked stormwater. Zinc concentrations ranged from approximately 130 to 220 µg/L, which is approximately 10X higher than unspiked stormwater zinc concentrations. Higher concentrations are due to the added metals spikes.

Table 13. Phase 4.1 spiked stormwater influent concentrations – Aluminum, copper, manganese, chromium, lead, zinc.

	Minimum	Median	Maximum
Aluminum (µg/L)	60.6	76.3	98.0
Copper (µg/L)	0.541	3.51	8.65
Manganese (µg/L)	43.3	95.0	150
Chromium (µg/L)	<LOD[1]	0.830	1.49
Lead (µg/L)	<LOD[1]	1.06	4.49
Zinc (µg/L)	131	176	218

[1]<LOD – The measured value was below the limit of detection or the lowest calibration point.

3.2.2 Effluent Analysis

3.2.2.1 pH, ORP, Turbidity, Total Suspended Solids

pH, ORP, turbidity, and total suspended solids were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure 3). For phase 4.1, all columns displayed a significantly different pH from the influent. pH ranged from ~6-10 in the column effluent while pH ranged from 5.62-7.59 in the column influent. All columns displayed a significantly different ORP from the influent other than sand, Stalite, and Stalite + biochar. For all other columns, ORP ranged from ~0-200 mV in the effluent while ORP ranged from 105-169 mV in the influent. Sand + biochar + iron and sand + iron effluent displayed significantly greater TSS and turbidity values than the influent. This indicates that leaching of suspended solids occurred in these columns.

A significant difference was observed between the filtration columns for turbidity and TSS. Sand + biochar and sand + biochar + iron displayed significant leaching of suspended solids, while all other columns performed significantly greater removal of suspended solids. Other than the two leaching columns, no significant differences were observed between the remaining filtration columns (Table 14).

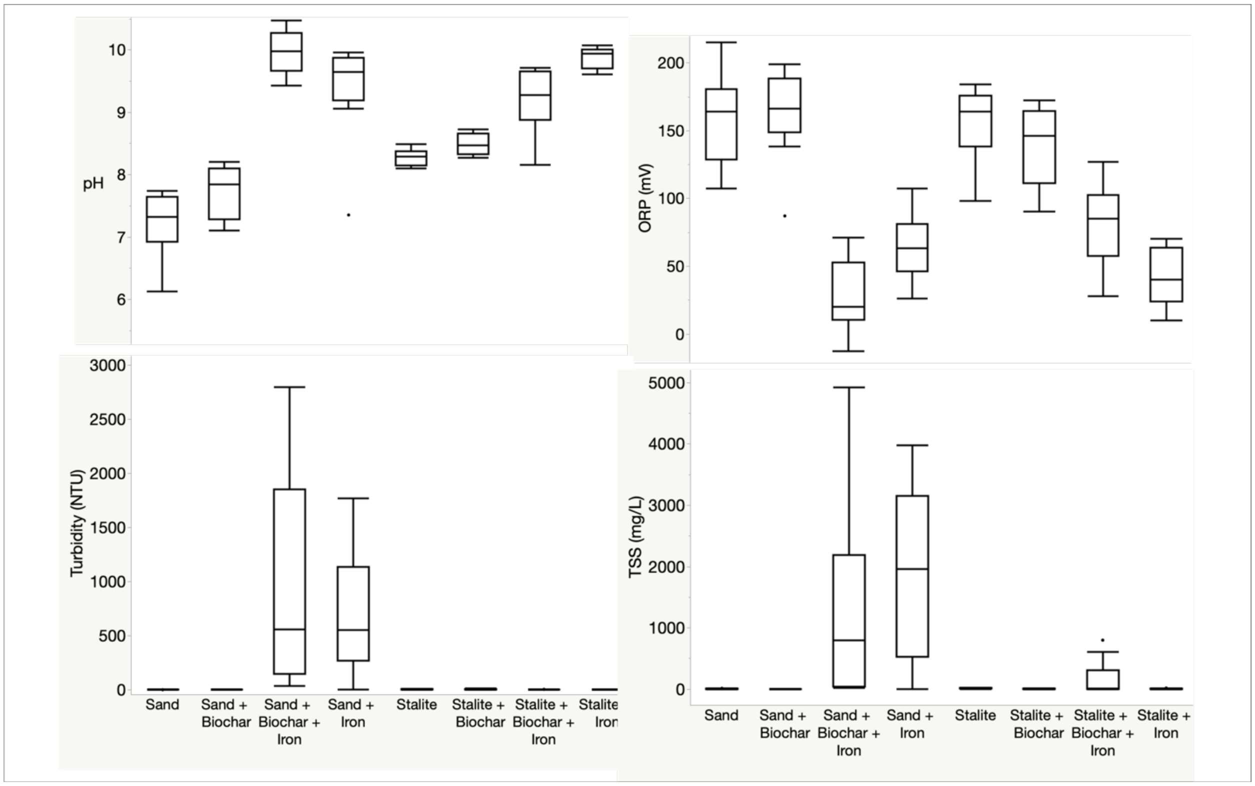

Figure 3. Phase 4.1 spiked stormwater effluent - pH, ORP, turbidity and TSS.

Table 14. Phase 4.1 spiked stormwater effluent connecting letters report – pH, ORP, turbidity and TSS.

	pH						ORP					Turbidity		TSS	
Influent						F		B					B		B
Sand					E		A	B					B		B
Sand + biochar				D			A						B		B
Sand + biochar + iron	A										E	A		A	
Sand + iron		B							C	D		A		A	
Stalite			C				A	B					B		B
Stalite+ biochar			C					B					B		B
Stalite + biochar + iron		B							C				B		B
Stalite + iron	A									D	E		B		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.2.2.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure 4). For phase 4.1, all columns displayed significant total phosphorus and phosphate as P removal from the influent ($p<0.01$).

For total phosphorus, significantly different removal was observed between most of the filtration columns (Table 15). Notably, sand + biochar effluent displayed significantly higher concentrations of total phosphorus than all other filtration columns ($p<0.01$). Sand and Stalite + biochar + iron displayed the lowest average concentrations of total phosphorus; however, they are not significantly different from each other. For phosphate as P, a significant difference was observed between sand + biochar and sand, as well as sand + biochar and sand + iron, as the sand + biochar effluent exhibited significantly greater phosphate as P concentrations than the sand and sand + iron column ($p<0.05$). All other filtration columns displayed similar phosphate as P removal and were not significantly different from each other (Table 15).

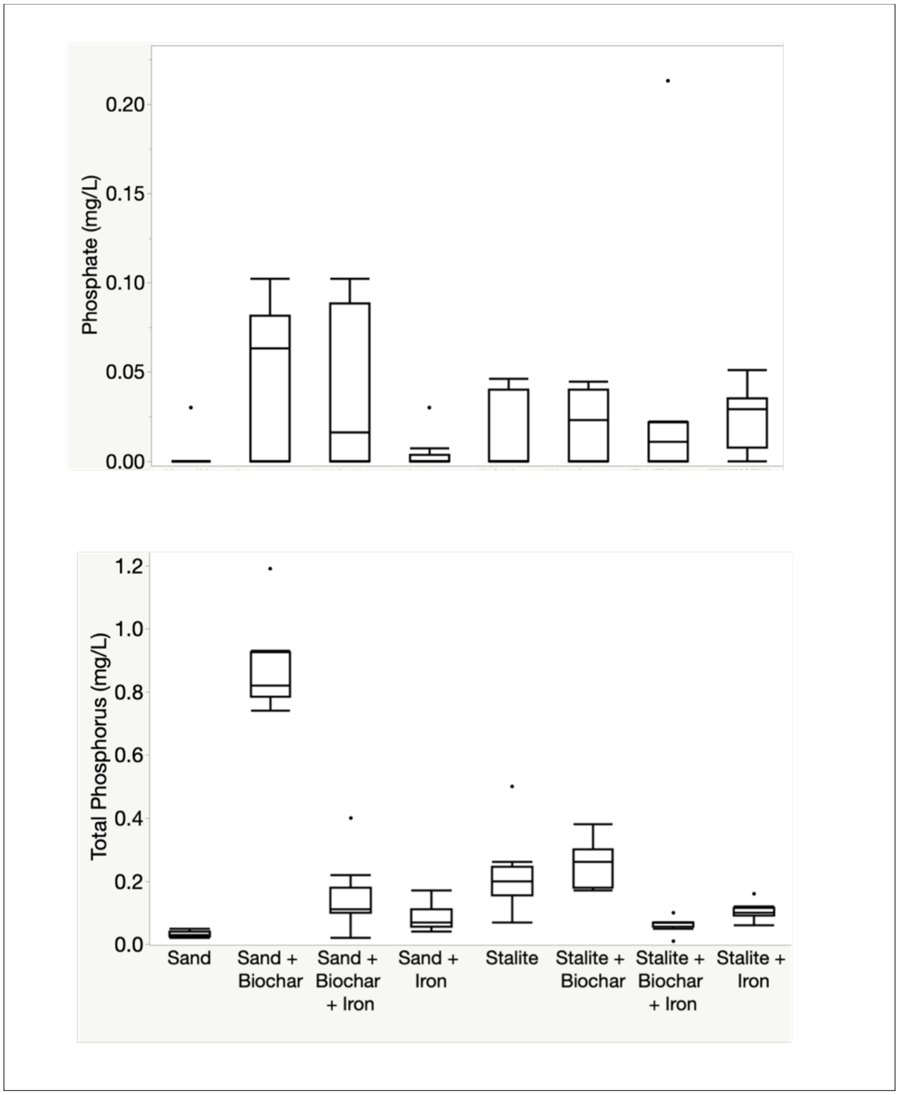

Figure 4. Phase 4.1 spiked stormwater effluent - Total phosphorus and phosphate as P.

Table 15. Phase 4.1 spiked stormwater effluent connecting letters report – Total phosphorus and phosphate as P.

	Total Phosphorus						Phosphate as P		
Influent		B					A		
Sand						F			C
Sand + biochar	A							B	
Sand + biochar + iron				D	E			B	C
Sand + iron					E	F			C
Stalite			C	D				B	C
Stalite + biochar			C					B	C
Stalite + biochar + iron					E	F		B	C
Stalite + iron					E	F		B	C

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.2.2.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column effluent to for comparison to high chloride concentrations in phase 4.4 (de-icing agents and cold temperature) (Figure 5). For phase 4.1, none of the stormwater filtration columns significantly removed chloride from the spiked stormwater influent. There was no significant difference observed between the stormwater filtration columns for chloride removal (Table 16). It appears that sand + biochar + iron had the lowest median removal, as well as the smallest range of removal, meaning that there was less deviation from the median (Figure 16). However, these are not statistically significant observations.

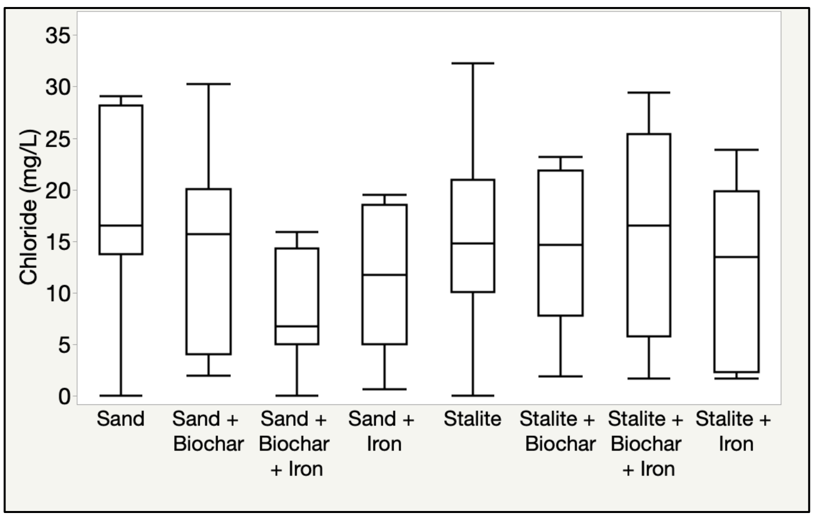

Figure 5. Phase 4.1 spiked stormwater effluent – Chloride.

Table 16. Phase 4.1 spiked stormwater effluent connecting letters report – Chloride.

	Chloride
Influent	A
Sand	A
Sand + biochar	A
Sand + biochar + iron	A
Sand + iron	A
Stalite	A
Stalite + biochar	A
Stalite + biochar + iron	A
Stalite + iron	A

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.2.2.4 Metals

Metal concentrations of aluminum, copper, manganese, chromium, lead and zinc were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure 6). For phase 4.1, significant manganese removal from the spiked stormwater influent was observed for all columns except the sand + biochar + iron and sand + iron columns. Significant zinc removal from the spiked stormwater influent was also observed for all columns (Table 17). The stormwater filtration columns did not display significant aluminum, chromium, copper, or lead removal from the spiked stormwater influent.

For aluminum, a significantly greater leaching was observed from the sand + iron column, the Stalite + biochar + iron column, and the Stalite + iron column, while the remaining stormwater filtration columns showed similar effluent concentrations. For copper, sand + biochar + iron displayed the greatest amount of leaching into the stormwater filtration column effluent, while the other columns displayed significantly different levels of copper leaching. For manganese, significant leaching was observed for the sand + biochar + iron and sand + iron stormwater filtration columns. For chromium, significantly greater leaching was observed for the sand + biochar column versus the other columns. The remaining stormwater filtration columns displayed significantly different levels of chromium leaching. For lead, a significant difference was observed for the sand, sand + biochar + iron, and Stalite + biochar + iron stormwater filtration columns versus the remaining columns. For zinc, the stormwater filtration columns all displayed similar removal.

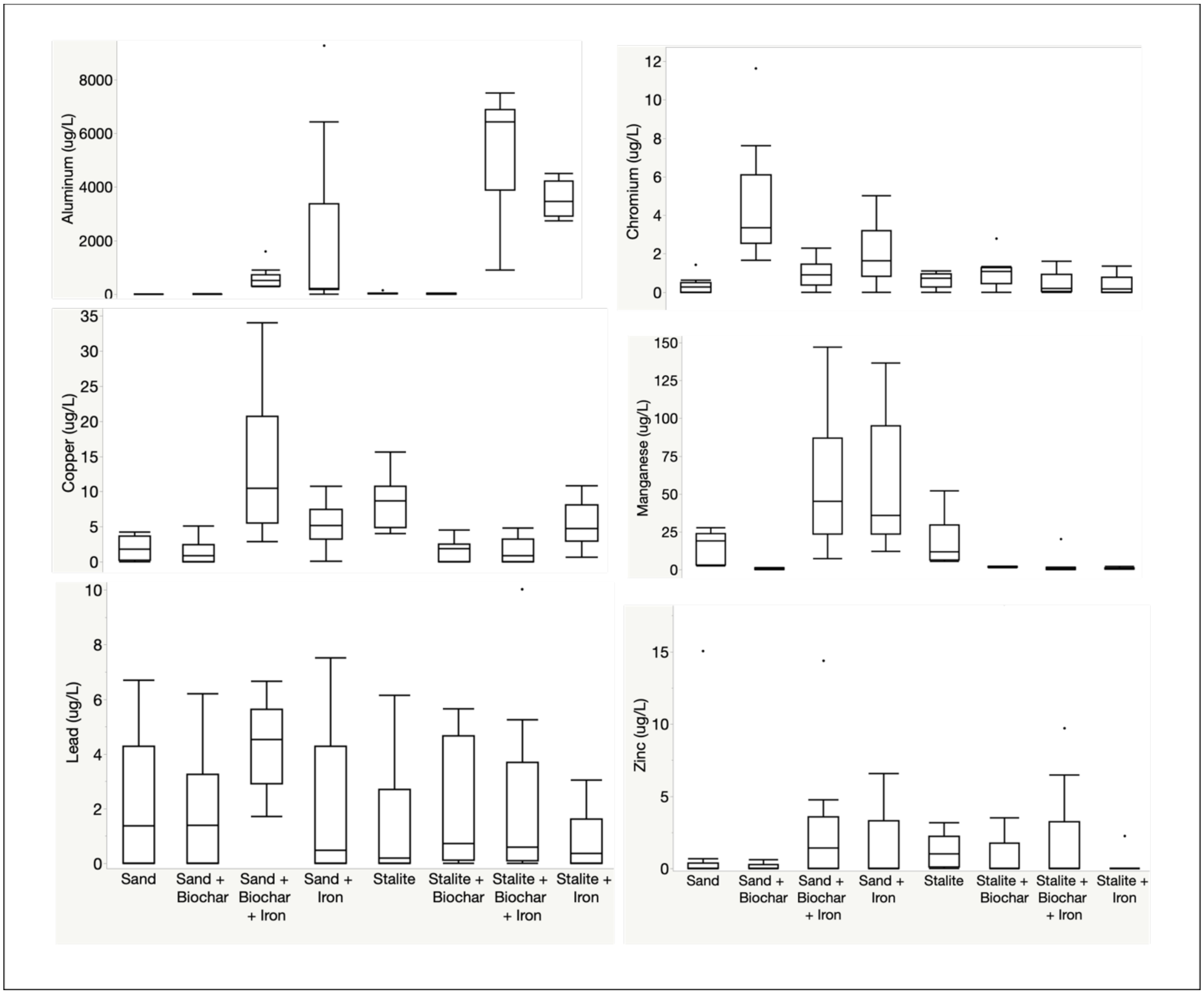

Figure 6. Phase 4.1 spiked stormwater effluent - aluminum, copper, manganese, chromium, lead and zinc.

Table 17. Phase 4.1 spiked stormwater effluent connecting letters report – Aluminum, copper, manganese, chromium, lead and zinc.

	Aluminum				Copper				Manganese			Chromium			Lead		Zinc	
Influent				D			C	D	A				B	C		B	A	
Sand				D			C	D			C			C	A	B		B
Sand + biochar				D				D			C	A				B		B
Sand + biochar + iron				D	A					B			B	C	A			B
Sand + iron			C			B	C	D		B			B			B		B
Stalite				D		B					C			C		B		B
Stalite+ biochar				D			C	D			C		B	C		B		B
Stalite + biochar + iron	A							D			C			C	A	B		B
Stalite + iron		B				B	C				C			C		B		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.3. Spiked Stormwater Column Analyses – Phase 4.2

Phase 4.2 represents the stormwater column filtration alternating contaminant concentrations phase, in which stormwater was spiked with low stormwater contaminant concentrations and high stormwater contaminant concentrations to determine the leaching effect, if any, on the stormwater filtration columns from the high-end spike. A total of 7 bed volumes of stormwater were loaded through the engineered media filtration column, as the sand + biochar + iron column was discontinued due to significant clogging and almost no seepage by gravity. Influent samples were refrigerated at 8°C while the filter effluent was collected over a 15-17 hour period. All spiked stormwater influent samples for phase 4.2 were collected from September 20, 2020 to October 20, 2020. Spiked contaminants include DOC, nutrients (nitrate, nitrite, phosphate, chloride), and metals (aluminum, chromium, copper, manganese, lead, and zinc).

3.3.1 Influent Analysis

3.3.1.1 pH, ORP, Turbidity, Total Suspended Solids

Parameters pH, ORP, Turbidity and TSS were analyzed in the spiked stormwater column influent (Table 18).

Table 18. Phase 4.2 spiked stormwater influent concentrations - pH, ORP, Turbidity and TSS.

	Minimum	Median	Maximum
pH Low Spike	6.87	7.24	7.43
pH High Spike	6.54	6.69	6.94
ORP (mV) Low Spike	152	174	261
ORP (mV) High Spike	143	197	286
Turbidity (NTU) Low Spike	24.5	34.6	162
Turbidity (NTU) High Spike	54.2	61.3	89.0
TSS (mg/L) Low Spike	10.4	110	435
TSS (mg/L) High Spike	193	213	291

3.3.1.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate concentrations were analyzed in the spiked stormwater column influent (Table 19).

Table 19. Phase 4.2 spiked stormwater influent concentrations - Total phosphorus and phosphate as P.

	Minimum	Median	Maximum
Phosphate as P (mg/L) Low Spike	0.077	0.16	0.19
Phosphate as P (mg/L) High Spike	<LOD	0.53	0.87
Total Phosphorus (mg/L) Low Spike	0.20	0.28	2.1
Total Phosphorus (mg/L) High Spike	1.42	1.85	2.12

3.3.1.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column influent (Table 20).

Table 20. Phase 4.2 spiked stormwater influent concentrations - Chloride.

	Minimum	Median	Maximum
Chloride (mg/L) Low Spike	2.31	3.96	19.1
Chloride (mg/L) High Spike	<LOD	30.7	33.0

3.3.1.4 Metals

Aluminum, chromium, copper, lead, manganese and zinc concentrations were analyzed in the spiked stormwater column influent (Table 21).

Table 21. Phase 4.2 spiked stormwater influent concentrations – Metals.

	Minimum	Median	Maximum
Aluminum (µg/L) Low Spike	81.2	529	1680
Aluminum (µg/L) High Spike	407	529	1140
Chromium (µg/L) Low Spike	<LOD	0.560	0.920
Chromium (µg/L) High Spike	<LOD	1.53	3.58
Copper (µg/L) Low Spike	<LOD	3.97	10.5
Copper (µg/L) High Spike	0.180	2.39	11.2
Lead (µg/L) Low Spike	3.04	7.64	10.7
Lead (µg/L) High Spike	8.11	13.5	239
Manganese (µg/L) Low Spike	5.44	7.99	80.4
Manganese (µg/L) High Spike	15.5	191	209
Zinc (µg/L) Low Spike	10.8	12.0	199
Zinc (µg/L) High Spike	542	615	664

3.3.2 Effluent Analysis

3.3.2.1 pH, ORP, Turbidity, Total Suspended Solids

Parameters pH, ORP, turbidity, and total suspended solids were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during high and low contaminant concentration periods (Figure 7). For phase 4.2, stormwater contaminant concentrations were alternated between low and high concentrations, as described in the methods section.

When stormwater influent had low or high contaminant concentrations, all stormwater filtration effluent displayed significantly higher pH than the influent (Table 22 and Table 23). With low contaminant concentrations, all stormwater filtration columns displayed significantly different pH from other filtration columns, except for Stalite + biochar and Stalite + biochar + iron, which were not significantly different from each other. With high contaminant concentrations, sand + iron displayed a significantly greater pH from all stormwater filtration columns except for the Stalite + iron column, sand displayed a significantly lower pH from all stormwater filtration columns except for the sand + biochar column, and Stalite displayed a significantly different pH from all stormwater filtration columns except for the Stalite + biochar column. Stalite + biochar + iron displayed a significantly different pH from all stormwater columns when stormwater was spiked with high contaminant concentrations., with an average around pH 8.5.

When stormwater influent had low contaminant concentrations, ORP was not significantly different from any stormwater filtration column effluent except for sand + iron, which was significantly lower than the influent (Table 22). When stormwater influent had high contaminant concentrations, ORP was not significantly different from any of the stormwater filtration column effluent other than sand + iron (Table 23). With low contaminant concentrations, ORP for sand + iron was significantly lower than all other filtration columns, and sand + biochar and Stalite + iron were significantly different. With high contaminant concentrations, ORP for sand + iron was significantly lower than all other filtration columns.

When stormwater influent had low contaminant concentrations, turbidity for sand and sand + iron were significantly greater than the influent, while all other filtration columns were not significantly different from the influent (Table 22). When stormwater influent had high contaminant concentrations, turbidity for sand and sand + iron were significantly greater than the influent, while all other filtration columns were not significantly different from the influent (Table 23). With low and high contaminant concentrations, turbidity for sand was significantly greater than all other filtration columns, and all other filtration columns were not significantly different from each other, other than sand + iron, which was significantly greater than the remaining stormwater filtration columns.

When stormwater influent had low contaminant concentrations, TSS influent concentrations were significantly greater than the filtration column effluent for all columns except sand and sand + iron (Table 22). When stormwater influent had high contaminant concentrations, TSS influent concentrations were significantly greater than the filtration column effluent for all columns (Table 23). With low and high contaminant concentrations, TSS for sand and sand + iron was significantly greater than all other filtration columns, and all other filtration columns were not significantly different from each other.

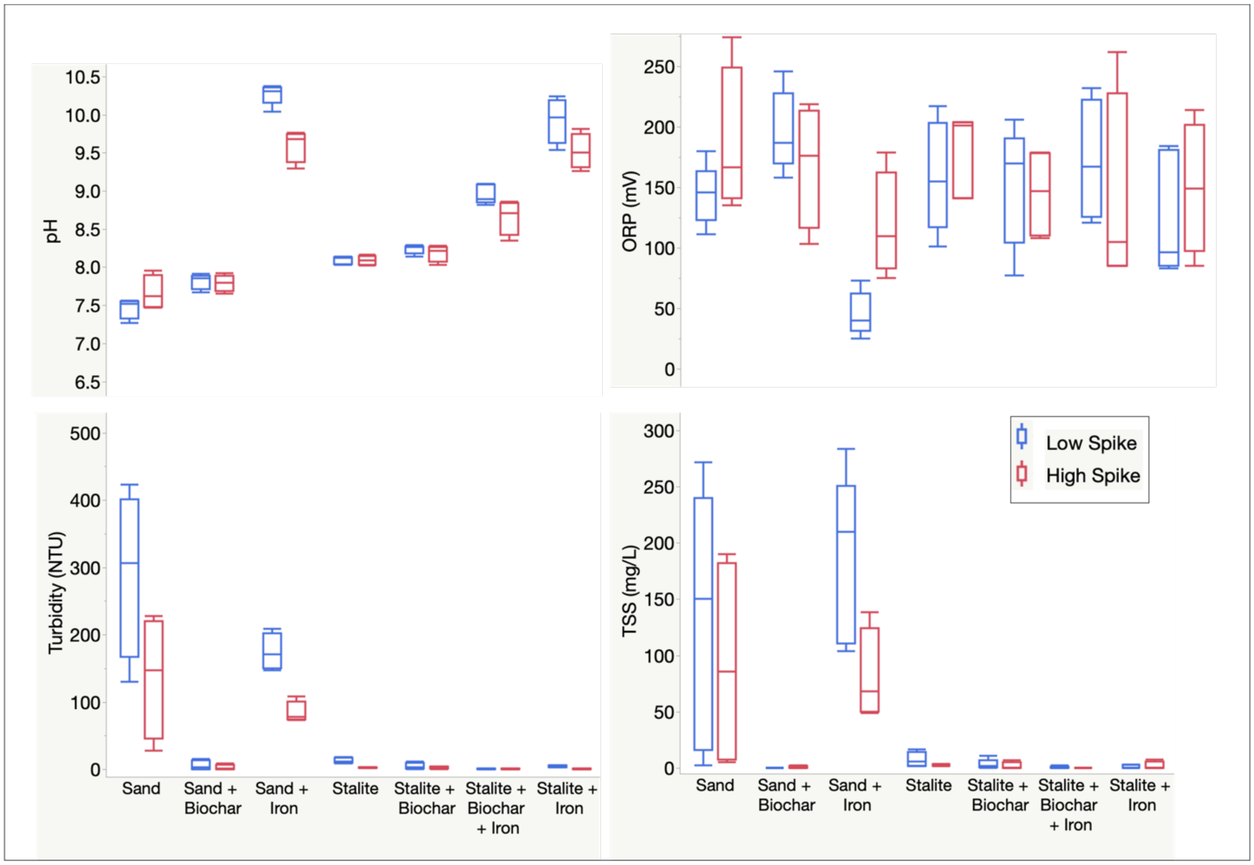

Figure 7. Phase 4.2 spiked stormwater effluent – pH, ORP, turbidity, and TSS.

Table 22. Phase 4.2 low-spiked stormwater effluent connecting letters report – pH, ORP, turbidity and TSS.

	pH							ORP			Turbidity			TSS	
Influent							G	A					C	A	
Sand						F		A	B		A			A	
Sand + biochar					E			A					C		B
Sand + iron	A									C		B		A	
Stalite				D				A	B				C		B
Stalite+ biochar				D				A	B				C		B
Stalite + biochar + iron			C					A	B				C		B
Stalite + iron		B							B				C		B

Levels not connected by the same letter are significantly different (p<0.05).

Table 23. Phase 4.2 high-spiked stormwater effluent connecting letters report – pH, ORP, turbidity and TSS.

	pH					ORP		Turbidity			TSS		
Influent					E	A				C	A		
Sand				D		A	B	A				B	
Sand + biochar				D		A	B			C			C
Sand + iron	A						B		B			B	
Stalite			C			A	B			C			C
Stalite+ biochar			C			A	B			C			C
Stalite + biochar + iron		B				A	B			C			C
Stalite + iron	A					A	B			C			C

Levels not connected by the same letter are significantly different ($p<0.05$).

3.3.2.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during high and low contaminant concentration periods (Figure 8).

When stormwater influent had low contaminant concentrations, sand and sand + biochar effluent displayed significantly higher phosphate as P than the influent and the remaining stormwater filtration columns did not significantly remove phosphate as P from the influent (Table 24). With low contaminant concentrations, filtration columns containing sand and sand + biochar displayed significantly greater phosphate as P from the remaining filtration columns. With high contaminant concentrations, sand + biochar displayed significantly greater phosphate as P than the influent while the remaining stormwater filtration columns significantly removed phosphate as P from the influent. (Table 25). With high contaminant concentrations, the sand and sand + biochar filtration columns did not display significantly different phosphate as P removal; however, the remaining columns did display significantly greater phosphate as P removal than sand + biochar.

When stormwater influent had low contaminant concentrations, sand and sand + biochar effluent displayed similar total phosphorus to the influent and the remaining stormwater filtration columns significantly removed total phosphorus from the influent (Table 24). With low contaminant concentrations, the sand and sand + biochar filtration columns did not display significantly different total phosphorus removal; however, the remaining columns did display significantly greater phosphate removal than sand + biochar. With high contaminant concentrations, all stormwater filtration columns significantly removed total phosphorus from the influent (Table 25). With high contaminant concentrations, the sand + biochar filtration column displayed significantly lower total phosphorus removal than the remaining filtration columns, followed by sand, and then followed by Stalite. Total phosphorus removal from the Stalite filtration column was not significantly different from the remaining filtration columns.

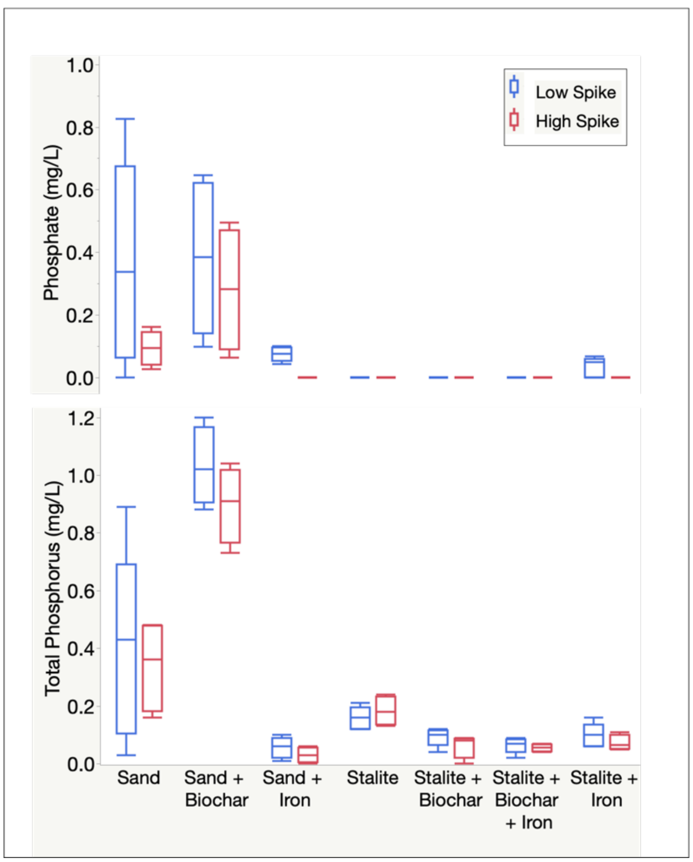

Figure 8. Phase 4.2 spiked stormwater effluent – Phosphate as P and total phosphorus.

Table 24. Phase 4.2 low-spiked stormwater effluent connecting letters report – Phosphate as P and total phosphorus.

	Phosphate as P		Total Phosphorus		
Influent		B	A	B	
Sand	A			B	C
Sand + biochar	A		A		
Sand + iron		B			C
Stalite		B			C
Stalite+ biochar		B			C
Stalite + biochar + iron		B			C
Stalite + iron		B			C

Levels not connected by the same letter are significantly different ($p<0.05$).

Table 25. Phase 4.2 high-spiked stormwater effluent connecting letters report – Phosphate as P and total phosphorus.

	Phosphate as P			Total Phosphorus			
Influent	A			A			
Sand		B	C			C	
Sand + biochar	A	B			B		
Sand + iron			C				D
Stalite			C			C	D
Stalite+ biochar			C				D
Stalite + biochar + iron			C				D
Stalite + iron			C				D

Levels not connected by the same letter are significantly different ($p<0.05$).

3.3.2.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column effluent for comparison to high chloride concentrations in phase 4.4 (de-icing agents and cold temperature) (Figure 9).

When stormwater influent had low contaminant concentrations, influent chloride concentrations were not significantly different from sand, sand + biochar, sand + iron, and Stalite stormwater filtration column effluent (Table 26). The remaining filtration columns displayed significantly higher chloride concentrations than the influent. With low contaminant concentrations, sand and sand + iron displayed similarly low chloride concentrations while the remaining stormwater filtration column effluent displayed greater chloride concentrations that were mostly similar. With high contaminant concentrations, influent chloride concentrations were not significantly different from sand, sand + biochar, and sand + iron filtration column effluent (Table 27). The remaining filtration column effluents had significantly lower chloride concentrations than the influent chloride concentration. With high contaminant concentrations, stormwater filtration column effluent did not display significantly different concentrations between filtration columns.

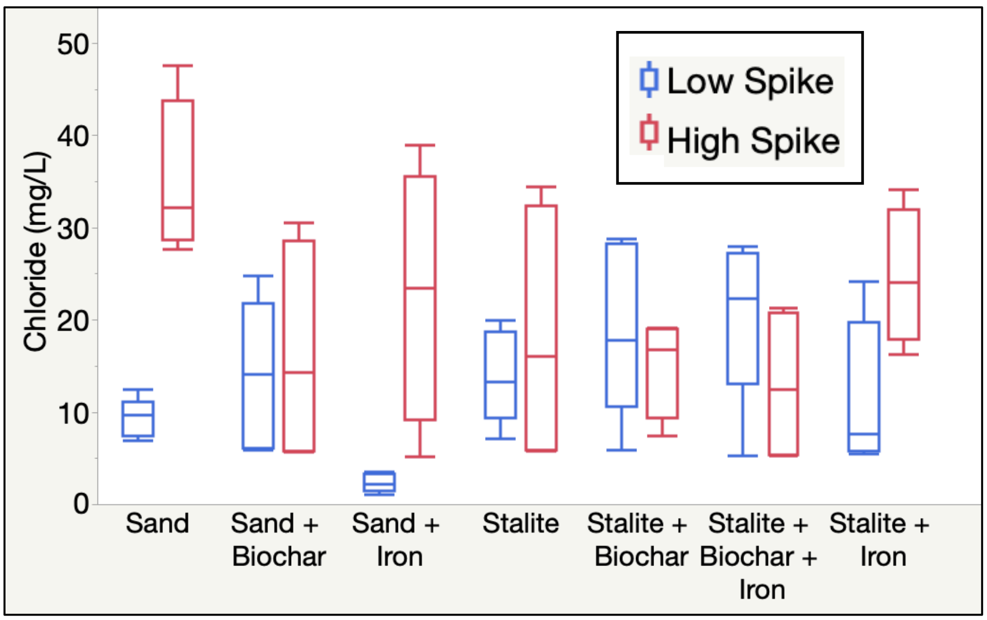

Figure 9. Phase 4.2 spiked stormwater effluent – Chloride.

Table 26. Phase 4.2 low-spiked stormwater effluent connecting letters report –Chloride.

	Chloride		
Influent		B	C
Sand		B	C
Sand + biochar	A	B	
Sand + iron			C
Stalite	A	B	
Stalite+ biochar	A		
Stalite + biochar + iron	A		
Stalite + iron	A	B	

Levels not connected by the same letter are significantly different ($p<0.05$).

Table 27. Phase 4.2 high-spiked stormwater effluent connecting letters report – Chloride.

	Chloride	
Influent	A	
Sand	A	B
Sand + biochar	A	B
Sand + iron	A	B
Stalite		B
Stalite+ biochar		B
Stalite + biochar + iron		B
Stalite + iron		B

Levels not connected by the same letter are significantly different ($p<0.05$).

3.3.2.4 Metals

Metal concentrations including aluminum, chromium, copper, lead, manganese and zinc were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during high and low contaminant concentration periods (Figure 10).

When stormwater influent had low contaminant concentrations, sand + biochar and Stalite + biochar stormwater filtration columns displayed significantly lower aluminum concentrations from the influent (Table 28). The remaining stormwater filtration effluent displayed greater aluminum concentrations similar to the influent. With low contaminant concentrations, stormwater filtration column effluent had significantly lower aluminum concentrations for sand + biochar and Stalite + biochar than the remaining filtration columns. When stormwater influent had high contaminant concentrations, influent aluminum concentrations were significantly different from sand + biochar, Stalite, and Stalite + biochar (Table 29). With high contaminant concentrations, stormwater filtration column effluent had significantly lower aluminum concentrations for sand + biochar, Stalite, and Stalite + biochar.

When stormwater influent had low contaminant concentrations, sand and sand + biochar stormwater filtration column effluent displayed significantly higher chromium concentrations than the influent, and the remaining filtration column effluent was lower and similar to the influent (Table 28). With low contaminant concentrations, sand and sand + biochar stormwater filtration column effluent displayed significantly higher chromium concentrations than the remaining filtration column effluent. With high contaminant concentrations, influent chromium concentrations were significantly different from Stalite + biochar filtration column effluent (Table 29). With high contaminant concentrations, stormwater filtration column effluent was mostly significantly different and Stalite + biochar effluent displayed the lowest chromium concentrations.

When stormwater influent had low contaminant concentrations, influent copper concentrations were similar to sand filtration column effluent (Table 28). With low contaminant concentrations, sand, sand + biochar, Stalite + biochar, and Stalite + biochar + iron effluent displayed similarly low copper concentrations while the remaining filtration column effluent displayed similarly high copper concentrations. With high contaminant concentrations, copper concentrations in the Stalite column effluent were significantly greater than the influent copper concentration and the remaining stormwater filtration columns were similar to the influent copper concentration (Table 29). With high contaminant concentrations, stormwater filtration column effluent was mostly significantly different and Stalite effluent displayed the highest copper concentrations.

With low contaminant concentrations, manganese concentrations in the sand + iron column effluent were significantly greater than the influent manganese concentration and the remaining stormwater filtration columns were similar to the influent manganese concentration (Table 28). With high contaminant concentrations, manganese concentrations were significantly lower in all stormwater filtration column effluent from the influent (Table 29). With high contaminant concentrations, all stormwater filtration columns similar manganese concentrations while Stalite + biochar + iron displayed the lowest manganese concentrations and Stalite displayed the highest manganese concentrations.

When stormwater influent had low contaminant concentrations, influent lead concentrations were not significantly different from any filtration column effluent lead concentrations (Table 28). With low contaminant concentrations, the filtration column effluent was not significantly different between any columns, and sand + iron filtration column effluent displayed higher manganese concentrations than the remaining filtration column effluent. With high contaminant concentrations, influent lead concentrations were significantly different from all filtration column effluent except for sand + iron, Stalite, and Stalite + iron (Table 29). With high contaminant concentrations, sand + iron, Stalite, and Stalite + iron stormwater filtration column lead concentrations were significantly different from the remaining stormwater filtration column lead concentrations.

When stormwater influent had low contaminant concentrations, influent zinc concentrations were significantly different from all filtration column effluent except for sand column effluent (Table 28). With low contaminant concentrations, the sand filtration column effluent zinc concentrations were significantly greater for the sand column than the remaining stormwater filtration columns. With high contaminant concentrations, influent zinc concentrations were significantly different from all filtration column effluent (Table 29). With high contaminant concentrations, zinc concentrations in the filtration column effluent were similar.

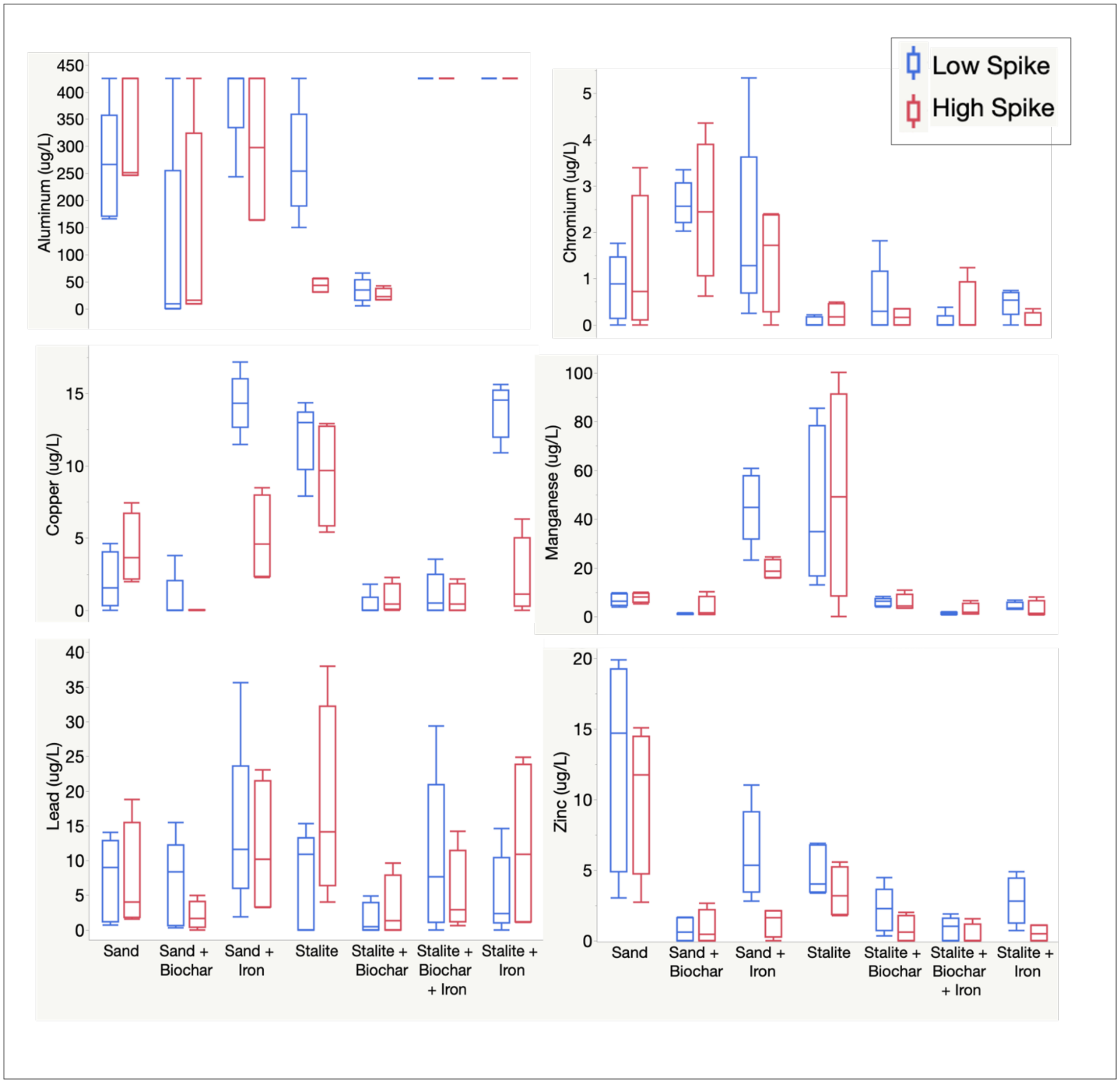

Figure 10. Phase 4.2 spiked stormwater effluent – Aluminum, chromium, copper, manganese, lead and zinc.

Table 28. Phase 4.2 low-spiked stormwater effluent connecting letters report – Aluminum, chromium, copper, manganese, lead and zinc.

	Aluminum			Chromium		Copper			Manganese		Lead		Zinc	
Influent	A	B			B		B			B	A	B	A	
Sand		B			B		B	C		B	A	B	A	B
Sand + biochar			C	A				C		B	A	B		B
Sand + iron	A	B		A		A			A		A			B
Stalite		B			B	A			A		A	B		B
Stalite+ biochar			C		B			C		B		B		B
Stalite + biochar + iron	A				B			C		B	A	B		B
Stalite + iron	A				B	A				B	A	B		B

Levels not connected by the same letter are significantly different ($p<0.05$).

Table 29. Phase 4.2 high-spiked stormwater effluent connecting letters report – Aluminum, chromium, copper, manganese, lead and zinc.

	Aluminum		Chromium			Copper				Manganese		Lead		Zinc	
Influent	A		A	B			B	C	D	A		A		A	
Sand	A		A	B	C		B	C			B		B		B
Sand + biochar		B	A						D		B		B		B
Sand + iron	A		A	B	C		B				B	A	B		B
Stalite		B		B	C	A					B	A	B		B
Stalite+ biochar		B		B	C			C	D		B		B		B
Stalite + biochar + iron	A			B	C			C	D		B		B		B
Stalite + iron	A				C		B	C	D		B	A	B		B

Levels not connected by the same letter are significantly different ($p<0.05$).

3.4 Spiked Stormwater Column Analyses – Phase 4.3

Phase 4.3 represents the stormwater column filtration antecedent drought phase, in which stormwater withheld from the filtration columns for a drought period of one month. Stormwater was then spiked within common stormwater contaminant ranges to determine the effect of a simulated drought on the stormwater filtration columns. A total of 7 bed volumes were loaded to the engineered media filtration column. The sand + biochar + iron column was discontinued due to significantly clogging and almost no seepage by gravity. Influent samples were refrigerated at 8°C while the filter effluent was collected over a 15-17 hour period. All spiked stormwater influent samples for phase 4.3 were collected from December 3, 2020 to January 14, 2021.

3.4.1 Influent Analyses

3.4.1.1 pH, ORP, Turbidity, and TSS.

Parameters pH, ORP, turbidity and TSS were analyzed in the spiked stormwater column influent (Table 30). pH ranged from 6.58 to 6.97, indicating that the influent spiked stormwater was chemically neutral for most influent solutions. ORP ranged from approximately 210 mV to 299 mV. This value indicates a high oxygen concentration within the spiked stormwater. Turbidity ranged from approximately 30.8 to 107 NTU. Total suspended solids ranged from slightly higher than 20 to approximately 320 mg/L.

Table 30. Phase 4.3 spiked stormwater influent concentrations – pH, ORP, Turbidity and TSS.

	Minimum	Median	Maximum
pH	6.58	6.69	6.97
ORP (mV)	210	249	299
Turbidity (NTU)	30.8	78.6	107
TSS (mg/L)	20.0	124	320

3.4.1.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column (Table 31). Total phosphorus concentrations ranged higher than phosphate at 0.28 to 0.48 mg/L versus 0.67 to 0.349 mg/L, respectively. This indicates that other phosphorus species are present in the spiked stormwater.

Table 31. Phase 4.3 spiked stormwater influent concentrations – Total phosphorus and phosphate as P.

	Minimum	Median	Maximum
Phosphate as P (mg/L)	0.0670	0.148	0.349
Total Phosphorus (mg/L)	0.280	0.375	0.480

3.4.1.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column influent (Table 32). Influent chloride concentration ranged from approximately 8.1 to 17.3 mg/L.

Table 32. Phase 4.3 spiked stormwater influent concentrations –Chloride.

	Minimum	Median	Maximum
Chloride (mg/L)	8.12	13.2	17.3

3.4.1.4 Metals

Metal concentrations of aluminum, chromium, copper, manganese, lead and zinc were analyzed in the spiked stormwater column influent (Table x). Influent aluminum concentrations ranged from approximately 113 µg/L to 450 µg/L, influent chromium concentrations ranged from approximately 0.1 µg/L to 2 µg/L, influent copper concentrations ranged from approximately 1 µg/L to 7 µg/L, influent manganese concentrations ranged from approximately 53 to 105 µg/L, influent lead concentrations ranged from <LOD to 16 µg/L, and influent zinc concentration ranged from approximately 106 to 217 µg/L.

Table 33. Phase 4.3 spiked stormwater influent concentrations – Aluminum, chromium, copper, manganese, lead, and zinc.

	Minimum	Median	Maximum
Aluminum (µg/L)	113	144	450
Chromium (µg/L)	0.060	0.855	2.09
Copper (µg/L)	1.11	3.12	6.86
Manganese (µg/L)	53.2	66.0	104
Lead (µg/L)	<LOD	4.96	16.2
Zinc (µg/L)	106	189	217

3.4.2 Effluent Analyses

3.4.2.1 pH, ORP, Turbidity, and Total Suspended Solids

Parameters pH, ORP, turbidity and total suspended solids were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal after an antecedent drought (Figure 11). All stormwater filtration columns displayed significantly different pH from the influent and between each other, except for Stalite and Stalite + biochar pH, which were similar at a pH of approximately 8 (Table 34).

All stormwater filtration columns displayed significantly different ORP from the influent. Sand + iron and Stalite + iron filtration column effluent displayed the lowest ORP among the stormwater filtration columns while the remaining stormwater filtration columns displayed significantly greater ORP values.

Stormwater filtration columns sand + biochar and sand + iron displayed similar turbidity to the influent. Sand filtration column effluent displayed significantly greater turbidity while the remaining filtration columns displayed significantly low turbidity compared to sand effluent.

All stormwater filtration columns displayed significant TSS removal from the influent. Between columns, the sand filtration column effluent displayed the greatest TSS while the remaining filtration columns displayed significantly low TSS compared to sand effluent.

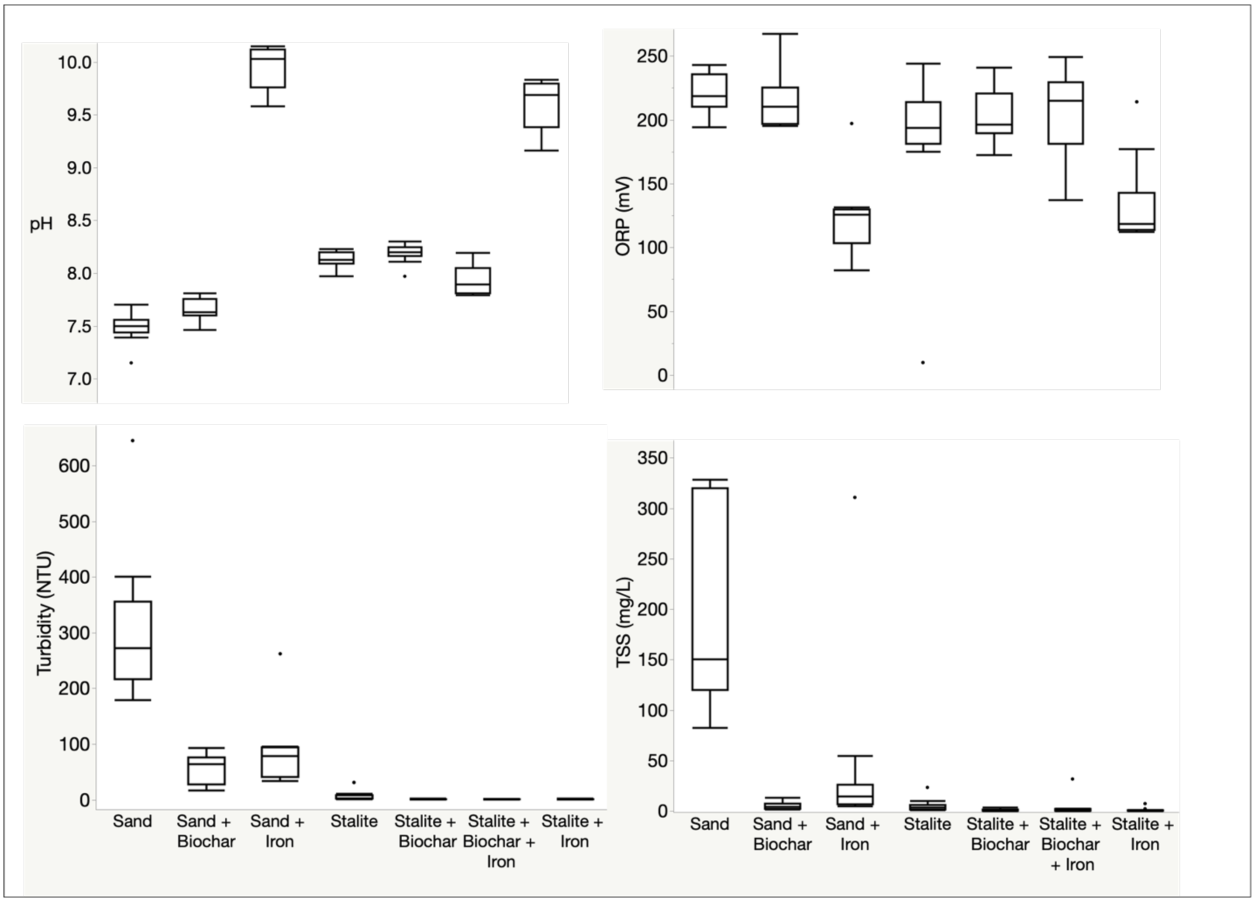

Figure 11. Phase 4.3 spiked stormwater effluent – pH, ORP, turbidity and TSS.

Table 34. Phase 4.3 stormwater effluent connecting letters report – pH, ORP, turbidity and TSS.

	pH							ORP				Turbidity			TSS		
Influent							G	A					B		A		
Sand						F			B			A				B	
Sand + biochar					E				B				B				C
Sand + iron	A										D		B				C
Stalite			C							C				C			C
Stalite+ biochar			C						B	C				C			C
Stalite + biochar + iron				D					B	C				C			C
Stalite + iron		B									D			C			C

Levels not connected by the same letter are significantly different ($p<0.05$).

3.4.2.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal after an antecedent drought (Figure 12). All stormwater filtration columns displayed significantly different total phosphorus than the influent except for the sand filtration column effluent, which was similar to the influent total phosphorus concentration. Sand + biochar column effluent displayed significantly greater total phosphorus than the remaining column effluent, which displayed significantly lower total phosphorus concentrations (Table 35).

Stormwater filtration column effluent for sand, Stalite, and Stalite + biochar displayed similar phosphate as P to the influent. Sand + iron filtration column effluent also displayed similar phosphate as P to the influent, however it displayed significantly lower phosphate as P concentrations from sand, Stalite, and Stalite + biochar. The remaining stormwater filtration columns displayed significantly greater phosphate as P concentrations than the influent and the remaining stormwater filtration.

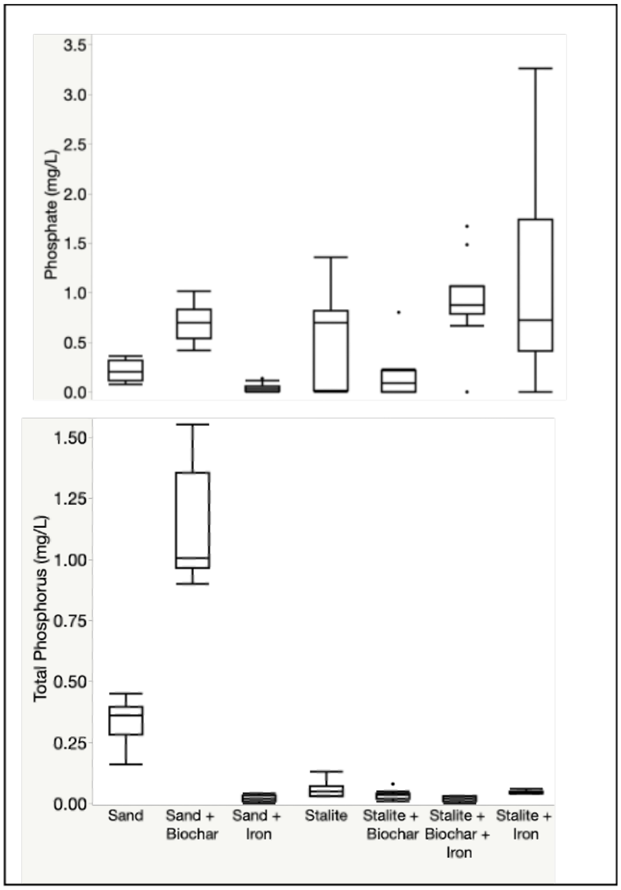

Figure 12. Phase 4.3 spiked stormwater effluent – Total phosphorus and phosphate as P.

Table 35. Phase 4.3 spiked stormwater effluent connecting letters report – Total phosphorus and phosphate as P.

	Total phosphorus			Phosphate as P			
Influent		B				C	D
Sand		B				C	D
Sand + biochar	A			A	B		
Sand + iron			C				D
Stalite			C		B	C	
Stalite + biochar			C			C	D
Stalite + biochar + iron			C	A	B		
Stalite + iron			C	A			

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.4.2.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column effluent for comparison to high chloride concentrations in phase 4.4 (de-icing agents and cold temperature) (Figure 13). Sand, sand + biochar, and sand + iron stormwater filtration columns displayed similar chloride concentrations to the influent while the remaining filtration columns displayed significantly higher concentrations than the influent (Table 36). Most stormwater filtration column effluent displayed similar chloride concentrations. The Stalite + biochar + iron stormwater filtration column effluent displayed a significantly greater chloride concentration than the remaining filtration columns, while sand + iron displayed a significantly lower chloride concentration than the remaining filtration columns.

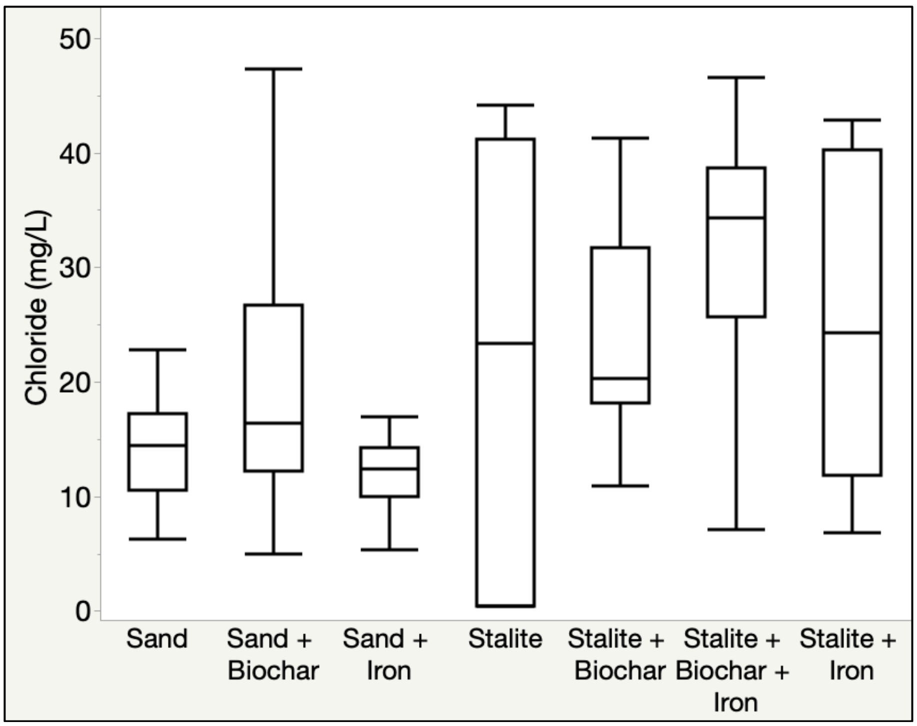

Figure 13. Phase 4.3 spiked stormwater effluent – Chloride.

Table 36. Phase 4.3 spiked stormwater effluent connecting letters report – Chloride.

	Chloride			
Influent			C	D
Sand			C	D
Sand + biochar		B	C	D
Sand + iron				D
Stalite	A	B	C	
Stalite + biochar	A	B		
Stalite + biochar + iron	A			
Stalite + iron	A	B		

*Levels not connected by the same letter are significantly different (p<0.05).

3.4.2.4 Metals

Metal concentrations of aluminum, chromium, copper, lead, manganese, and zinc were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal after an antecedent drought (Figure 14).

For aluminum, sand and sand + biochar, Stalite, and Stalite + biochar + iron filtration column effluent displayed similar concentrations to the influent (Table 37). The Stalite + iron stormwater filtration column displayed significantly greater aluminum concentrations than the influent while Stalite + biochar displayed significantly lower aluminum concentrations than the influent. Between filtration columns, Stalite + iron displayed the greatest aluminum concentrations and Stalite + biochar displayed the lowest concentrations. The remaining stormwater filtration columns displayed aluminum concentrations between Stalite + biochar and Stalite + iron concentrations.

For chromium, most stormwater filtration columns displayed similar concentrations to the influent. Sand + biochar effluent displayed significantly greater aluminum concentrations than the influent and Stalite + biochar and Stalite + iron effluent displayed significantly lower aluminum concentrations than the influent. Between stormwater filtration columns, sand + biochar displayed the greatest chromium concentrations while stalite + biochar displayed the lowest chromium concentrations.

For copper, sand, sand + iron, and Stalite + iron filtration column effluent displayed similar concentrations to the influent. The Stalite filtration column displayed significantly greater copper concentrations than the influent while sand + biochar and Stalite + biochar displayed significantly lower copper concentrations. Between columns, Stalite displayed the greatest copper concentrations while Stalite + biochar displayed the lowest copper concentrations.

For manganese, all stormwater filtration columns displayed significantly lower concentrations than the influent. Between filtration columns, sand + iron displayed significantly greater manganese concentrations than the remaining filtration columns.

For lead, all stormwater filtration columns displayed similar concentrations to the influent. Between filtration columns, Stalite + biochar + iron displayed the lowest lead concentrations while sand displayed the greatest lead concentrations.

For zinc, all stormwater filtration columns displayed significantly lower concentrations than the influent. Between filtration columns, all columns displayed similarly low zinc concentrations.

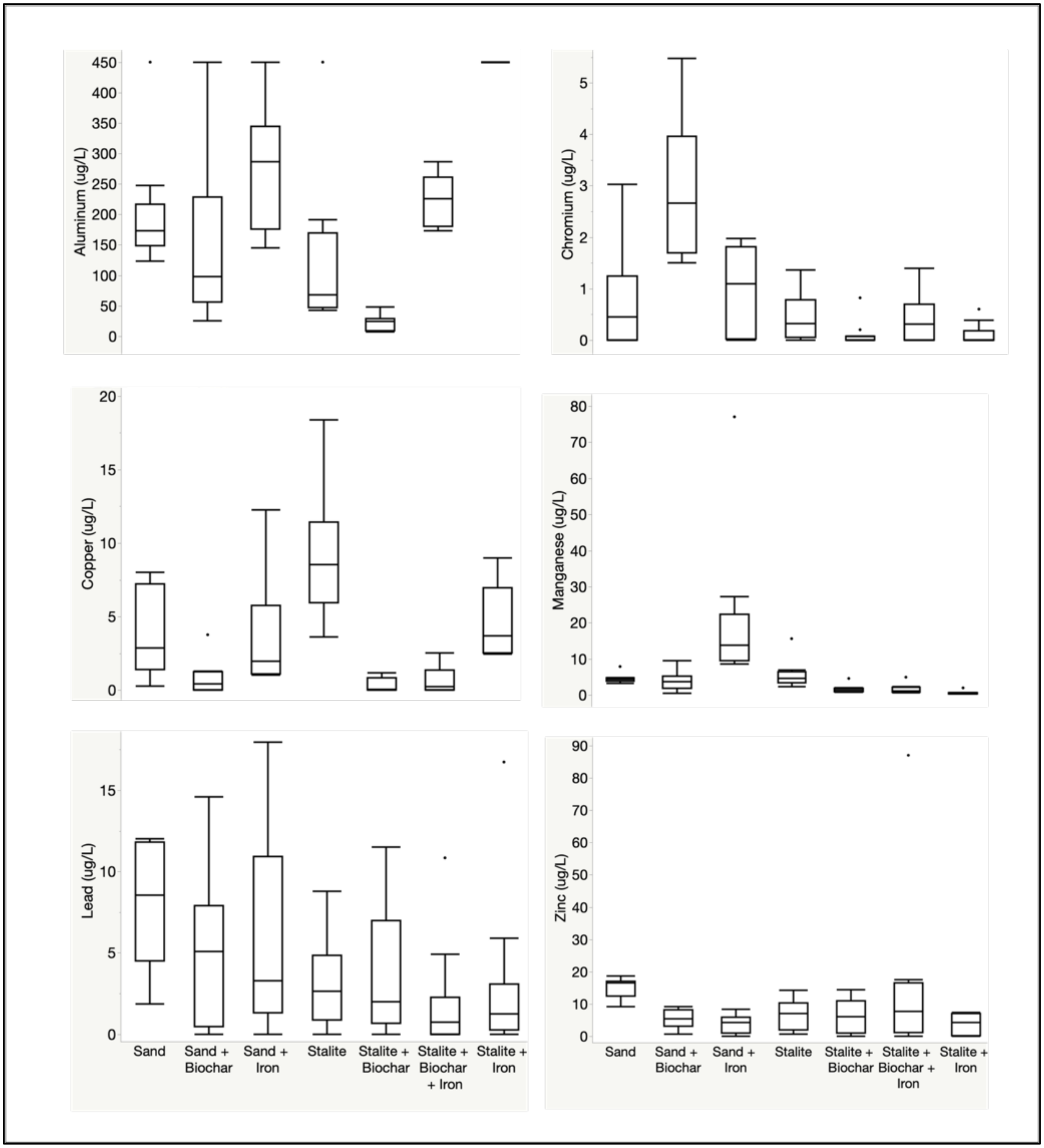

Figure 14. Phase 4.3 spiked stormwater effluent – Aluminum, chromium, copper, manganese, lead, and zinc.

Table 37. Phase 4.3 stormwater effluent connecting letters report – Aluminum, chromium, copper, manganese, lead, and zinc.

	Aluminum					Chromium			Copper			Manganese			Lead		Zinc	
Influent			C	D			B			B		A			A	B	A	
Sand		B	C	D			B	C		B				C	A			B
Sand + biochar			C	D		A					C			C	A	B		B
Sand + iron		B					B			B			B		A	B		B
Stalite				D			B	C	A					C		B		B
Stalite+ biochar					E			C			C			C	A	B		B
Stalite + biochar + iron		B	C				B	C			C			C		B		B
Stalite + iron	A							C		B				C		B		B

Levels not connected by the same letter are significantly different ($p<0.05$).

3.5 Spiked Stormwater Column Analyses – Phase 4.4

Phase 4.4 represents the stormwater column filtration cold weather and de-icing agent phase, in which stormwater was spiked within common stormwater contaminant ranges and high chloride concentrations to determine the leaching effect on the stormwater filtration columns. The columns were moved outdoors during January to February 2021, in which the temperature ranged from -4.3°C to 22.5°C. A total of 7 column volumes were performed for the cold weather and de-icing agent stormwater filtration through the engineered media filtration columns, as the sand + biochar + iron column was discontinued due to significant clogging observed. Influent samples were refrigerated at 8°C while the filter effluent was collected over a 15-17 hour period. All spiked stormwater influent samples for phase 4.4 were collected from January 21, 2021 to February 23, 2021.

3.5.1 Influent Analyses

3.5.1.1 pH, ORP, Turbidity, and Total Suspended Solids

Chemical parameters pH, ORP, Turbidity and TSS were analyzed in the spiked stormwater column influent (Table 38). pH ranged from 6.69 to 7.17. ORP ranged from approximately 211 mV to 291 mV. Turbidity ranged from approximately 46.8 to 67.4 NTU. Total suspended solids ranged from approximately 5 mg/L to approximately 34 mg/L.

Table 38. Phase 4.4 spiked stormwater influent concentrations – pH, ORP, Turbidity and TSS.

	Minimum	Median	Maximum
pH	6.69	6.81	7.17
ORP (mV)	211	240	291
Turbidity (NTU)	46.8	60.1	67.4
TSS (mg/L)	5.00	11.5	33.8

3.5.1.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column influent (Table 39). Total phosphorus concentrations ranged higher than phosphate as P at 0.32 to 0.42 mg/L versus 0.08 to 0.25 mg/L, respectively. This indicates that other phosphorus species are present in the spiked stormwater as they were in most of the unspiked stormwater samples. This includes organic phosphorus, which is found from the decomposition of plants/animals.

Table 39. Phase 4.4 spiked stormwater influent concentrations – Total phosphorus and phosphate as P.

	Minimum	Median	Maximum
Phosphate as P (mg/L)	0.0872	0.136	0.259
Total Phosphorus (mg/L)	0.320	0.355	0.420

3.5.1.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column influent (Table 40). Influent concentrations ranged from approximately 131 to 478 mg/L, which is similar to chloride concentrations reported by previous literature when de-icing agents are used (Snodgrass et al., 2017; Burgis et al., 2020). In one study, chloride concentrations ranged from 0 to 1000 mg/L in shallow groundwater and approximately 80 mg/L in adjacent streams (Snodgrass et al., 2017). In another study, chloride concentrations ranged from 10 to approximately 10,000 mg/L (Burgis et al., 2020).

Table 40. Phase 4.4 spiked stormwater influent concentrations – Chloride.

	Minimum	Median	Maximum
Chloride (mg/L)	131	235	478

3.5.1.4 Metals

Metals concentrations of aluminum, chromium, copper, manganese, lead and zinc were analyzed in the spiked stormwater column influent (Table x). Influent aluminum concentrations ranged from approximately 168 µg/L to 298 µg/L, influent chromium concentrations ranged from approximately <LOD to 0.65 µg/L, influent copper concentrations ranged from approximately 1.3 µg/L to 2.6 µg/L, influent manganese concentrations ranged from approximately 51 to 70 µg/L, influent lead concentrations ranged from approximately 1.4 to 3.9 µg/L, and influent zinc concentration ranged from approximately 195 to 231 µg/L.

Table 41. Phase 4.4 spiked stormwater influent concentrations – Aluminum, copper, manganese, chromium, lead, zinc.

	Minimum	Median	Maximum
Aluminum (µg/L)	169	205	298
Chromium (µg/L)	<LOD	0.125	0.650
Copper (µg/L)	1.25	1.71	2.62
Manganese (µg/L)	50.9	61.6	70.2
Lead (µg/L)	1.44	3.29	3.88
Zinc (µg/L)	195	207	231

3.5.2 Effluent Analyses

3.5.2.1 pH. ORP, Turbidity, and Total Suspended Solids

Parameters pH, ORP, turbidity, total suspended solids were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during an increase in chloride concentrations and cold weather (Figure 15). For pH, all stormwater filtration columns displayed significantly different pH from the influent except for sand. Between filtration columns, sand + iron column effluent displayed the greatest pH, while sand and sand + biochar column effluent displayed the lowest pH (Table 42.)

For ORP, all stormwater filtration column effluent displayed significantly lower values from the influent except for sand and sand + biochar effluent, which displayed similar ORP values to the influent. Between columns, sand and sand + biochar filtration column effluent displayed the greatest ORP values while the sand + iron filtration column effluent displayed the lowest ORP values.

For turbidity, sand and sand + iron displayed significantly greater values than the influent and the remaining columns. Between columns, sand + iron and sand and sand + iron filtration column effluent displayed the greatest turbidity values while the remaining filtration column effluent displayed significantly lower values.

For TSS, sand displayed significantly greater TSS than the influent and the remaining columns. The remaining stormwater filtration columns displayed similarly TSS concentrations, which were similar to the influent.

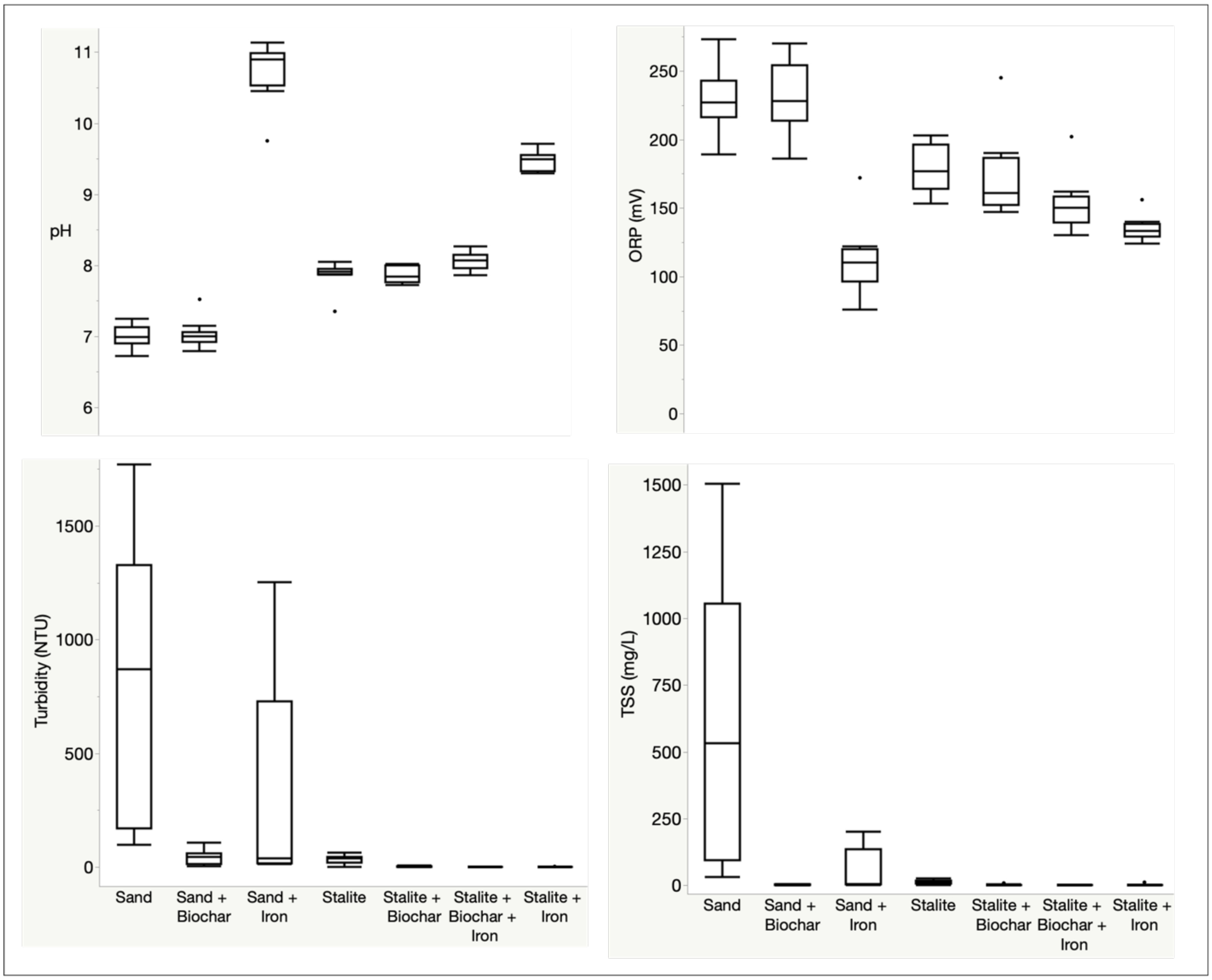

Figure 15. Phase 4.4 spiked stormwater effluent – pH, ORP, turbidity and TSS.

Table 42. Phase 4.4 spiked stormwater effluent connecting letters report – pH, ORP, turbidity, and TSS.

	pH						ORP				Turbidity			TSS	
Influent						F	A						C		B
Sand					E	F	A				A			A	
Sand + biochar					E		A						C		B
Sand + iron	A									D		B			B
Stalite				D				B					C		B
Stalite + biochar				D				B					C		B
Stalite + biochar + iron			C						C				C		B
Stalite + iron		B							C				C		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.5.2.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during an increase in chloride concentrations and cold weather (Figure 16). For total phosphorus, stormwater filtration column effluent displayed significantly different concentrations from the influent (Table 43). Sand and sand + biochar displayed significantly greater total phosphorus concentrations than the influent while the remaining filtration columns displayed significantly lower total phosphorous concentrations than the influent. Between columns, sand displayed the greatest total phosphorus concentrations and Stalite + biochar + iron displayed the lowest total phosphorus concentrations.

For phosphate as P, the sand stormwater filtration column displayed similar concentrations to the influent. Sand + biochar displayed significantly greater phosphate as P concentrations than the influent while the remaining stormwater filtration columns displayed significantly lower phosphate as P concentrations than the influent. Between columns, sand +

biochar displayed the greatest phosphate as P concentrations and sand + iron, Stalite + biochar, Stalite + biochar + iron, and Stalite + iron displayed the lowest phosphate as P concentrations.

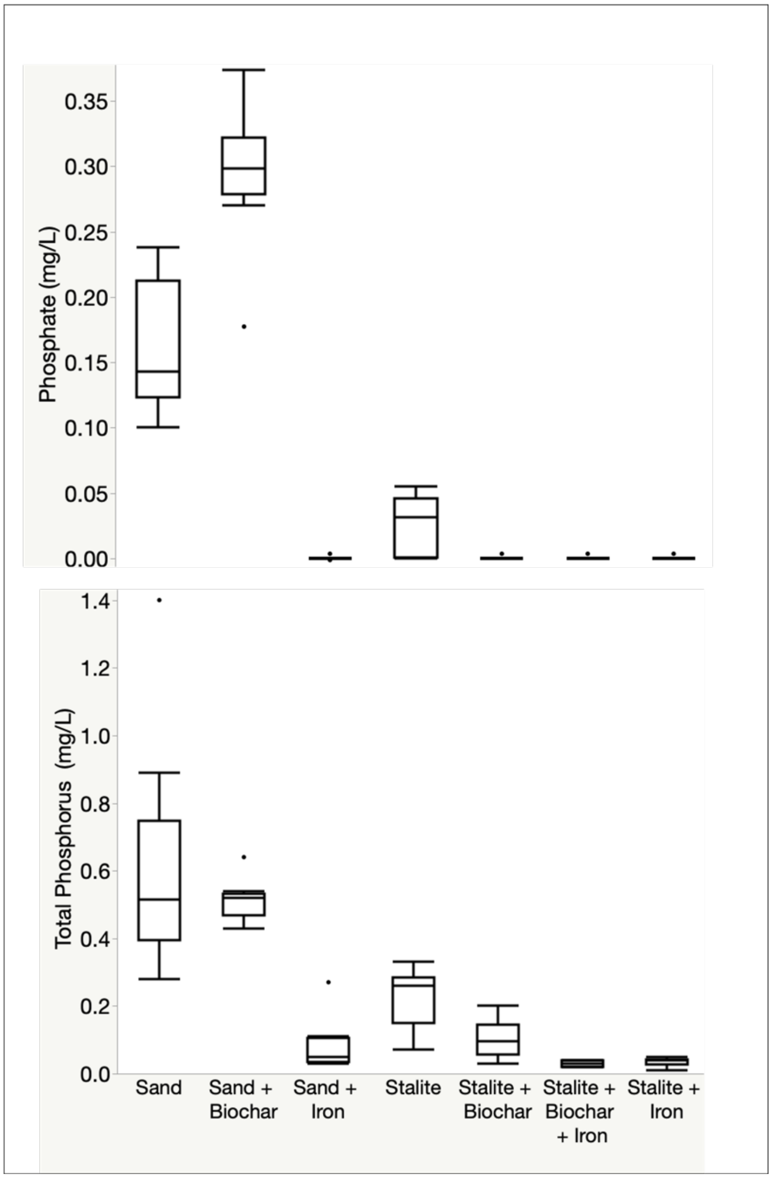

Figure 16. Phase 4.4 spiked stormwater effluent – Total phosphorus and phosphate as P.

Table 43. Phase 4.4 spiked stormwater effluent connecting letters report – Total phosphorus and phosphate as P.

	Total Phosphorus				Phosphate as P		
Influent		B				B	
Sand	A					B	
Sand + biochar	A				A		
Sand + iron				D			C
Stalite			C				C
Stalite + biochar				D			C
Stalite + biochar + iron				D			C
Stalite + iron				D			C

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.5.2.3 Chloride

Chloride concentrations were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during an increase in chloride concentrations and cold weather (Figure 17). Effluent concentrations ranged between approximately 100 mg/L chloride to approximately 500 mg/L chloride, while sand + iron displayed overall lower chloride concentrations than the remaining filtration columns. All stormwater filtration column effluent displayed similar chloride concentrations to the influent chloride concentration. Between columns, effluent chloride concentrations were not significantly different from each other (Table 44).

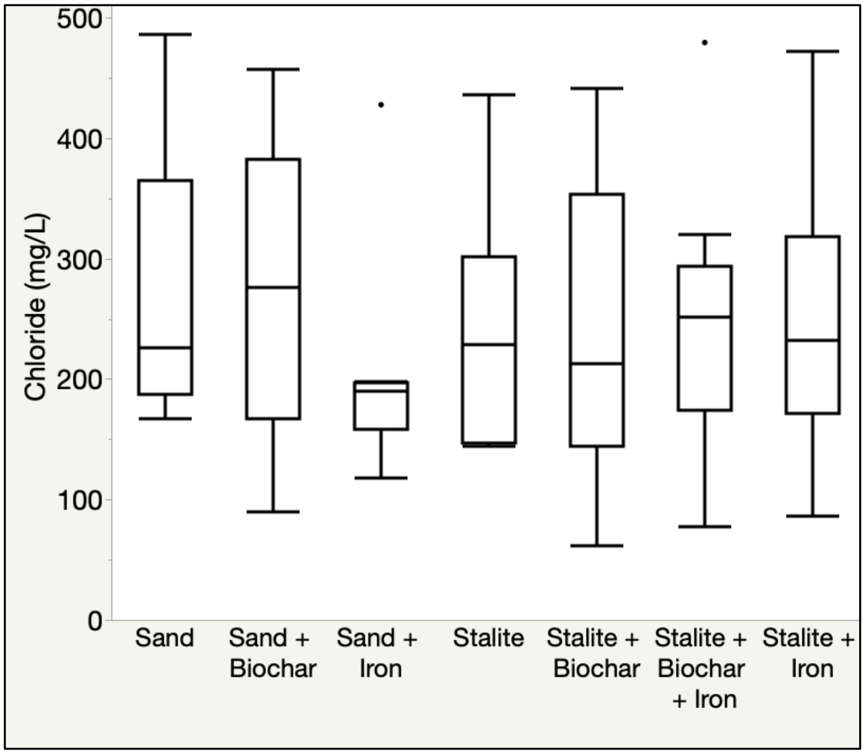

Figure 17. Phase 4.4 spiked stormwater effluent – Chloride.

Table 44. Phase 4.4 spiked stormwater effluent connecting letters report – Chloride.

	Chloride
Influent	A
Sand	A
Sand + biochar	A
Sand + iron	A
Stalite	A
Stalite + biochar	A
Stalite + biochar + iron	A
Stalite + iron	A

*Levels not connected by the same letter are significantly different (p<0.05).

3.5.2.4 Metals

Metal concentrations of aluminum, chromium, copper, manganese, lead, and zinc concentrations were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during an increase in chloride concentrations and cold weather (Figure 18). For aluminum, all stormwater filtration column effluent was significantly different from the influent except for Stalite and Stalite + iron, which were similar to the filtration column influent (Table 45). Sand and sand + iron filtration column effluent displayed significantly greater aluminum concentrations than the filtration column influent, while sand + biochar, Stalite + biochar, and Stalite + biochar + iron filtration column effluent displayed significantly lower aluminum concentrations than the filtration column influent. Between columns, sand and sand + iron displayed the greatest aluminum concentrations and Stalite + biochar + iron displayed the lowest aluminum concentrations.

For chromium, all stormwater filtration column effluent was similar to the influent except for Stalite and Stalite + iron, both displayed significantly lower chromium concentrations than the influent. Between columns, sand and sand + biochar displayed the highest chromium concentrations and Stalite, Stalite + biochar, and Stalite + iron displayed the lowest chromium concentrations.

For copper, all stormwater filtration column effluent was similar to the influent except for sand + iron and Stalite, which were both significantly greater than the influent. Between columns, Stalite displayed the highest copper concentrations while Stalite + biochar and Stalite + biochar + iron displayed the lowest copper concentrations.

For manganese, all stormwater filtration column effluent was similar to the influent, except for sand + iron, which was significantly greater than the filtration column influent. Between columns, sand + iron displayed the greatest manganese concentrations while the remaining filtration columns displayed silmilarly low manganese concentrations.

For lead, all stormwater filtration column effluent was significantly lower than the influent. Between columns, sand displayed the greatest lead concentrations while the remaining columns displayed similarly low lead concentrations.

For zinc, all stormwater filtration column effluent was significantly lower than the influent. Between columns, sand displayed significantly greater zinc concentrations while the remaining columns displayed similarly low zinc concentrations.

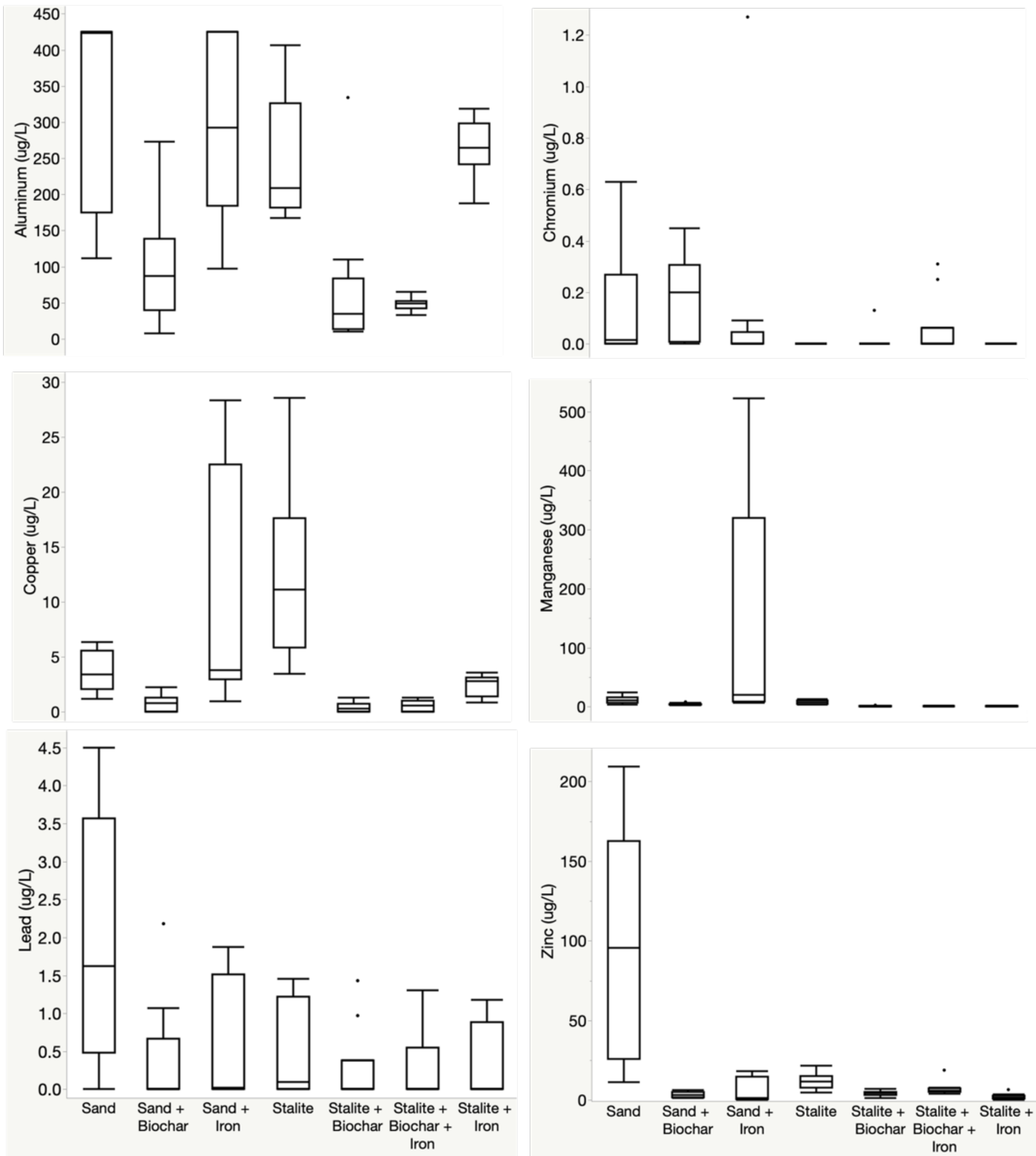

Figure 18. Phase 4.4 spiked stormwater effluent – Aluminum, chromium, copper, manganese, lead, and zinc.

Table 45. Phase 4.4 spiked stormwater effluent connecting letters report – Aluminum, chromium, copper, manganese, lead, and zinc.

	Aluminum			Chromium		Copper		Manganese			Lead			Zinc		
Influent		B		A			B		B		A			A		
Sand	A			A	B		B		B	C		B			B	
Sand + biochar			C	A			B		B	C			C			C
Sand + iron	A			A	B	A		A					C			C
Stalite	A	B			B	A			B	C			C			C
Stalite + biochar			C	A	B		B			C			C			C
Stalite + biochar + iron			C	A	B		B		B	C			C			C
Stalite + iron	A	B			B		B		B	C			C			C

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.6 Spiked Stormwater Column Analyses – Phase 4.5

Phase 4.5 represents the stormwater column filtration media aging phase, in which stormwater was spiked within common stormwater contaminant ranges after the duration of the project. The columns were moved back indoors to the temperature-controlled laboratory. The purpose of this phase was to determine if any contaminant leaching and/or stormwater filtration media clogging occurred on the different stormwater filtrations systems over the duration of the project (8 months), and if the contaminant removal effectiveness deteriorated over time. A total of 7 column volumes were performed through the engineered media filtration column. The sand + biochar + iron column was discontinued due to significant clogging observed. Influent samples were refrigerated at 8°C while the filter effluent was collected over a 15-17 hour period. All spiked stormwater influent samples for phase 4.4 were collected from February 25, 2021 to March 27, 2021.

3.6.1 Influent Analyses

3.6.1.1 pH, ORP, Turbidity, and Total Suspended Solids

Parameters pH, ORP, Turbidity and TSS were analyzed in the spiked stormwater column influent (Table 46). pH ranged from 6.79 to 7.16. ORP ranged from approximately 227 mV to 261 mV. Turbidity ranged from approximately 23.7 to 62.0 NTU. Total suspended solids ranged from 8.33 mg/L to approximately 17.1 mg/L.

Table 46. Phase 4.5 spiked stormwater influent concentrations – pH, ORP, Turbidity and TSS.

	Minimum	Median	Maximum
pH	6.79	7.06	7.16
ORP (mV)	227	238	261
Turbidity (NTU)	23.7	25.6	62.0
TSS (mg/L)	8.33	13.7	17.1

3.6.1.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the spiked stormwater column influent (Table 47). Total phosphorus concentrations ranged higher than phosphate as P at 0.39 to 0.46 mg/L versus 0.15 to 0.21 mg/L, respectively. This indicates that other phosphorus species are present in the spiked stormwater as they were in most of the unspiked stormwater samples. This includes organic phosphorus, which is found from the decomposition of plants/animals.

Table 47. Phase 4.5 spiked stormwater influent concentrations – Total phosphorus and phosphate as P.

	Minimum	Median	Maximum
Phosphate as P (mg/L)	0.152	0.179	0.207
Total Phosphorus (mg/L)	0.390	0.440	0.460

3.6.1.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column influent (Table 48). Influent concentrations ranged from approximately 10 to 16 mg/L.

Table 48. Phase 4.5 spiked stormwater influent concentrations – Chloride.

	Minimum	Median	Maximum
Chloride (mg/L)	10.6	15.5	16.6

3.6.1.4 Metals

Metal concentrations of aluminum, chromium, copper, manganese, lead and zinc were analyzed in the spiked stormwater column influent (Table 49). Influent aluminum concentrations ranged from 123 µg/L to 277 µg/L, influent chromium concentrations ranged from <LOD µg/L to 0.8 µg/L, influent copper concentrations ranged from approximately 1.3 µg/L to 2.4 µg/L, influent manganese concentrations ranged from approximately 50 to 67 µg/L, influent lead concentrations ranged from approximately 1.5 to 6.5 µg/L, and influent zinc concentrations ranged from approximately 205 to 247 µg/L.

Table 49. Phase 4.5 spiked stormwater influent concentrations – Aluminum, copper, manganese, chromium, lead, zinc.

	Minimum	Median	Maximum
Aluminum (µg/L)	123	171	278
Chromium (µg/L)	<LOD	0.205	0.800
Copper (µg/L)	1.32	2.07	2.39
Manganese (µg/L)	49.8	53.1	66.9
Lead (µg/L)	1.51	5.31	6.53
Zinc (µg/L)	205	237	247

3.6.2 Effluent Analyses

3.6.2.1 pH, ORP, Turbidity, and Total Suspended Solids

Parameters pH, ORP, turbidity, total suspended solids were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal over the duration of the project (Figure 19). All stormwater filtration column effluent pH was significantly greater than the influent pH (Table 50). Between filtration columns, sand + iron displayed the greatest pH, while sand and sand + biochar displayed the lowest pH.

For ORP, all stormwater filtration column effluent displayed similar values except for sand + iron, Stalite + biochar + iron, and Stalite +iron effluent, which displayed significantly lower ORP values than the influent. Between columns, sand + iron displayed the lowest ORP values while the remaining columns displayed much higher values.

For turbidity, sand and sand + biochar filtration column effluent was excluded from the statistical analyses as the turbidity for all sand and sand + biochar effluent had a large influence on the statistical analyses. Sand and sand + biochar displayed significantly greater turbidity than the influent and the remaining columns. Sand + iron and Stalite filtration column effluent displayed similar turbidity to the influent while the remaining columns displayed significantly lower turbidity from the influent. Between columns, sand + iron and Stalite filtration column effluent displayed the greatest turbidity values while Stalite + biochar + iron displayed the lowest turbidity values.

For TSS, the sand filtration column effluent was excluded from the statistical analyses as TSS for all sand effluent had a large influence on the statistical analyses. Sand displayed significantly greater TSS than the influent and the remaining columns. Sand + biochar displayed similar TSS to the influent while the remaining stormwater filtration columns displayed significantly lower TSS concentrations. Between columns, sand + biochar filtration column effluent displayed the greatest TSS concentrations while Stalite + biochar + iron and Stalite + iron displayed the lowest TSS concentrations.

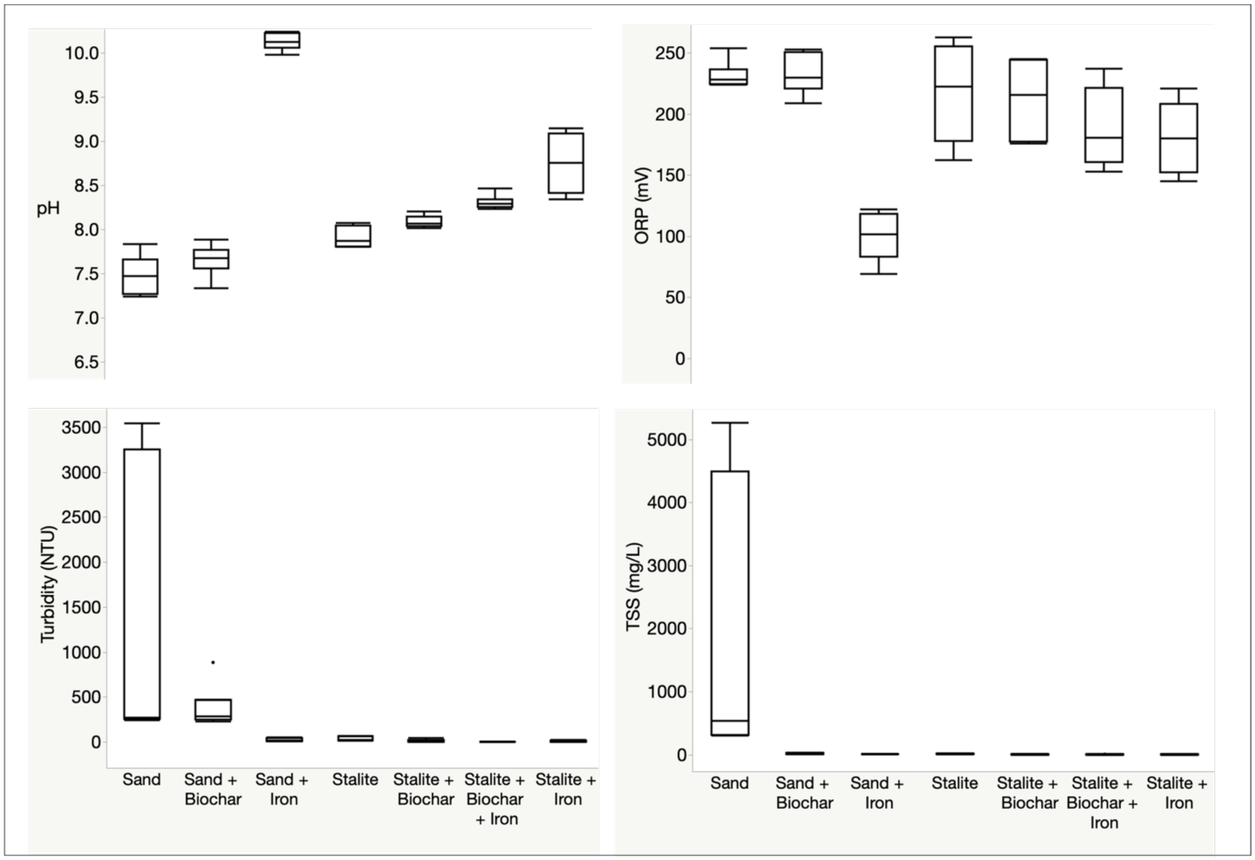

Figure 19. Phase 4.5 spiked stormwater effluent – pH, ORP, turbidity and TSS.

Table 50. Phase 4.5 spiked stormwater effluent connecting letters report – pH, ORP, turbidity, and TSS.

	pH						ORP				Turbidity			TSS		
Influent						F	A				A			A		
Sand**					E		A									
Sand + biochar***					E		A							A		
Sand + iron	A									D	A	B			B	C
Stalite				D			A	B			A				B	
Stalite + biochar				D			A	B				B	C			C
Stalite + biochar + iron			C					B	C				C			C
Stalite + iron		B							C			B	C			C

*Levels not connected by the same letter are significantly different (p<0.05).
**Sand effluent statistical analyses excluded for an accurate analysis of turbidity and TSS.
***Sand + biochar effluent statistical analyses excluded for an accurate analysis of turbidity.

3.6.2.2 Total Phosphorus and Phosphate as P

Total phosphorus and phosphate as P concentrations were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal over the duration of the project (Figure 20). For total phosphorus, Stalite and Stalite + biochar filtration column effluent displayed similar concentrations to filtration column influent (Table 51). Sand and sand + biochar displayed significantly greater total phosphorus concentrations than the influent while sand + iron, Stalite + biochar + iron, and Stalite + iron displayed significantly lower total phosphorous concentrations than the influent. Between columns, sand + biochar displayed the greatest total phosphorus concentrations and Stalite + biochar + iron displayed the lowest total phosphorus concentrations.

For phosphate as P, the sand stormwater filtration column displayed similar concentrations to the influent. Sand + biochar displayed significantly greater phosphate as P concentrations than the influent while the remaining stormwater filtration columns displayed significantly lower phosphate as P concentrations than the influent. Between columns, sand + biochar displayed the greatest phosphate as P concentrations and Stalite + iron displayed the lowest phosphate as P concentrations.

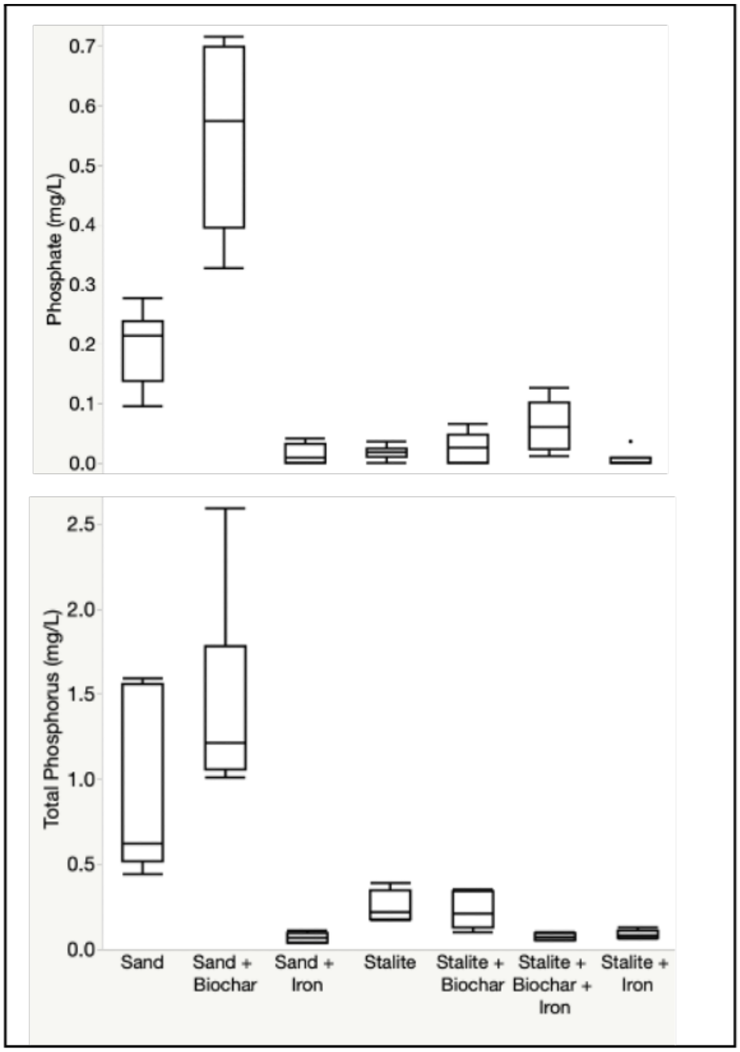

Figure 20. Phase 4.5 spiked stormwater effluent – Total phosphorus and phosphate as P.

Table 51. Phase 4.5 spiked stormwater effluent connecting letters report – Total phosphorus and phosphate as P.

	Total Phosphorus				Phosphate as P		
Influent			C			B	
Sand		B				B	
Sand + biochar	A				A		
Sand + iron				D			C
Stalite			C	D			C
Stalite + biochar			C	D			C
Stalite + biochar + iron				D			C
Stalite + iron				D			C

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.6.2.3 Chloride

Chloride concentrations were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during an increase in chloride concentrations and cold weather (Figure 21). All stormwater filtration column effluent displayed similar chloride concentrations to the influent chloride concentration except for Stalite + iron, which displayed significantly greater chloride concentrations. Between columns, all effluent chloride concentrations were similar (Table 52).

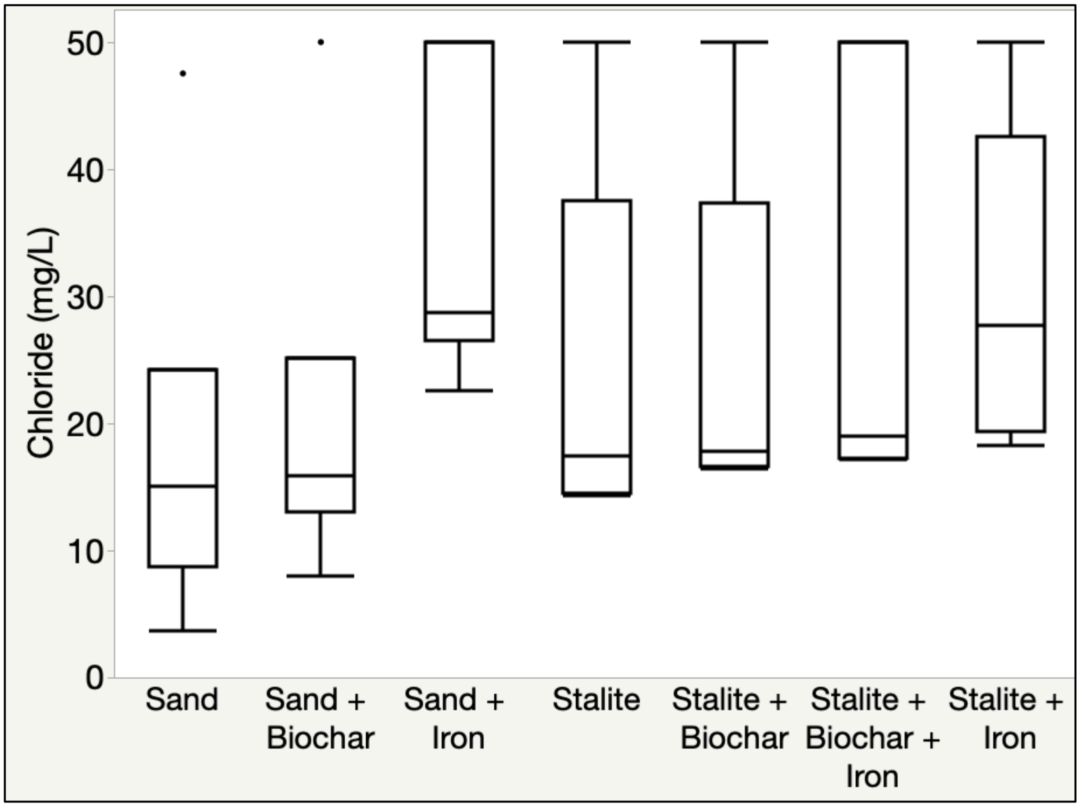

Figure 21. Phase 4.5 spiked stormwater effluent – Chloride.

Table 52. Phase 4.5 spiked stormwater effluent connecting letters report – Chloride.

	Chloride		
Influent			C
Sand		B	C
Sand + biochar	A	B	C
Sand + iron	A		
Stalite	A	B	C
Stalite + biochar	A	B	C
Stalite + biochar + iron	A	B	C
Stalite + iron	A	B	

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.6.2.4 Metals

Metal concentrations of aluminum, chromium, copper, manganese, lead, and zinc were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal over the duration of the project (Figure 22). For aluminum, all stormwater filtration column effluent was similar to the influent except for sand + biochar and Stalite + iron column effluent, which were significantly greater than the column influent (Table 53). Between columns, sand + biochar displayed the greatest aluminum concentrations and Stalite + biochar + iron displayed the lowest aluminum concentrations.

For chromium, all stormwater filtration column effluent was similar to the influent except for sand + biochar and Stalite + biochar + iron, which were both significantly greater than the influent. Between columns, sand + biochar displayed the greatest chromium concentrations and Stalite displayed the lowest chromium concentrations.

For copper, all stormwater filtration column effluent was similar to the influent except for Stalite and Stalite + iron, which were both significantly greater than the influent. Between columns, Stalite + iron displayed the greatest copper concentrations while Stalite + biochar + iron displayed the lowest copper concentrations.

For manganese, all stormwater filtration column effluent displayed significantly lower concentrations than the influent. Between columns, Stalite + biochar displayed the greatest manganese concentrations while Stalite + biochar + iron displayed the lowest manganese concentrations.

For lead, all stormwater filtration column effluent displayed significantly lower concentrations than the influent except for sand, which was similar to the influent lead concentration. Between columns, sand displayed the greatest lead concentrations while the remaining columns displayed similarly low lead concentrations.

For zinc, all stormwater filtration column effluent displayed significantly lower concentrations than the influent. Between columns, sand displayed significantly greatest zinc concentrations while the remaining columns displayed similarly low zinc concentrations.

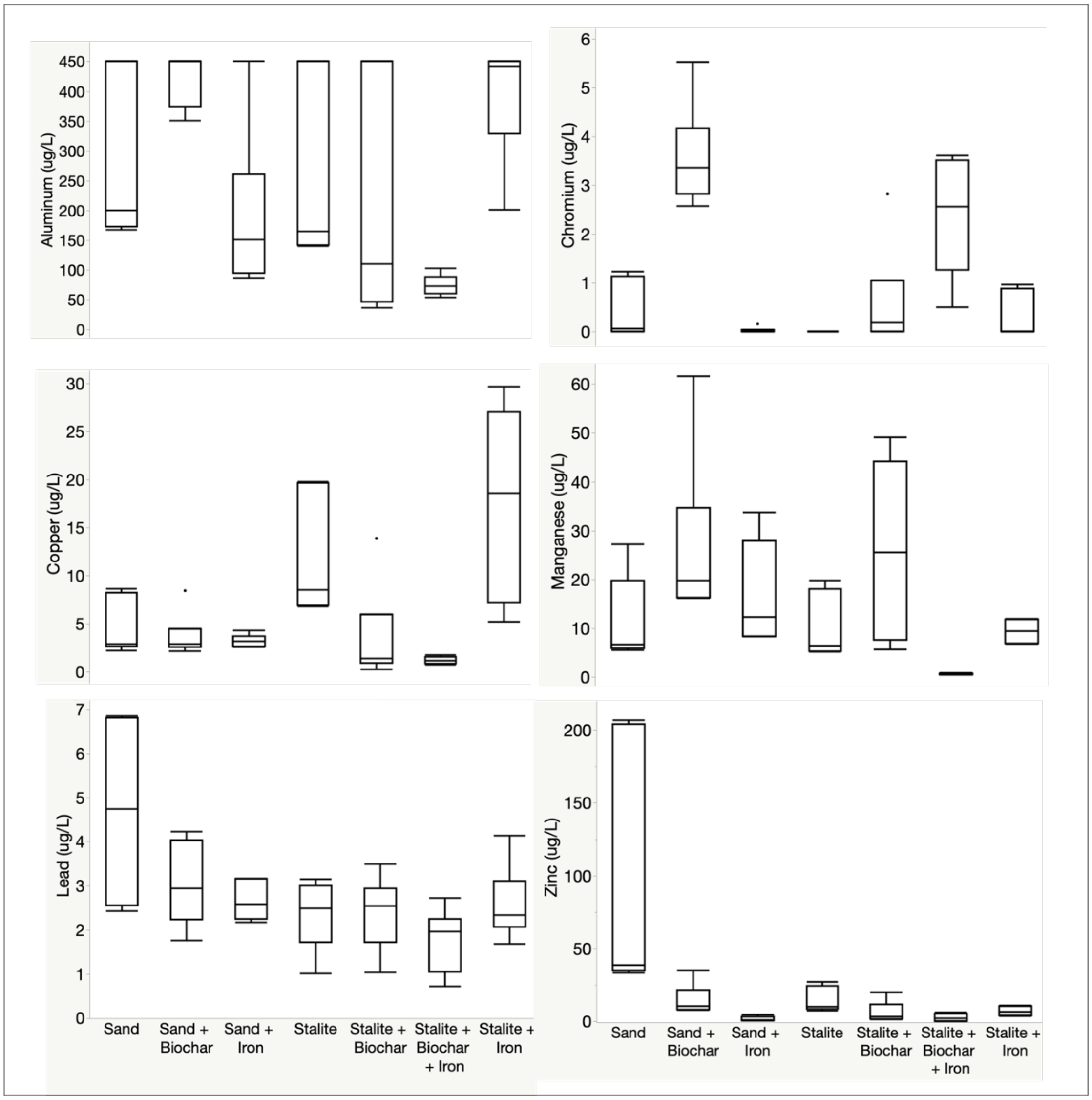

Figure 22. Phase 4.5 spiked stormwater effluent – Aluminum, chromium, copper, manganese, lead, and zinc.

Table 53. Phase 4.5 spiked stormwater effluent connecting letters report – Aluminum, chromium, copper, manganese, lead, and zinc.

	Aluminum				Chromium			Copper			Manganese				Lead		Zinc		
Influent			C	D			C			C	A				A		A		
Sand		B	C				C			C			C	D	A			B	
Sand + biochar	A				A					C		B				B			C
Sand + iron			C	D			C			C		B	C			B			C
Stalite		B	C				C		B				C	D		B			C
Stalite + biochar			C	D			C			C		B				B			C
Stalite + biochar + iron				D		B				C				D		B			C
Stalite + iron	A	B					C	A					C	D		B			C

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.7 Total Recoverable Metals

Some metals may be present in stormwater runoff in the undissolved form, sticking to particulates that are removed upon filtration with the 0.45 µm glass microfiber filter before sample analysis. Therefore, in phases 4.4 and 4.5, additional unfiltered samples were collected from the stormwater column filtration effluent to be digested before analysis to determine concentrations of total recoverable metals (the sum of dissolved and particulate-bound metals). The purpose of analyzing total recoverable metals was to examine stormwater column filtration of particulate-bound metals. These samples were collected on February 2nd through March 27th, 2021. Unfiltered concentrations of aluminum, chromium, copper, manganese, lead and zinc were analyzed in the spiked stormwater column influent for comparison to digested effluent concentrations (Table 54).

Unfiltered influent aluminum concentrations ranged from 88 µg/L to 305 µg/L, influent chromium concentrations ranged from approximately 2.3 µg/L to 4.3 µg/L, influent copper concentrations ranged from approximately 3.3 µg/L to 7.4 µg/L, influent manganese concentrations ranged from approximately 76 to 123 µg/L, influent lead concentrations ranged from approximately 4.2 to 11.63 μg/L, and influent zinc concentration ranged from 236 to 350 μg/L.

Table 54. Total recoverable metals influent concentrations – Aluminum, copper, manganese, chromium, lead, zinc.

	Minimum	Median	Maximum
Aluminum (μg/L)	88.3	212	305
Chromium (μg/L)	2.29	3.49	4.35
Copper (μg/L)	3.34	5.45	7.42
Manganese (μg/L)	76.2	94.5	123
Lead (μg/L)	4.17	8.00	11.6
Zinc (μg/L)	236	307	350

Total recoverable aluminum, chromium, copper, manganese, lead, and zinc were analyzed in the stormwater column effluent to determine the most effective filter media for concurrent contaminant removal over the duration of the project (Figure 23). For aluminum, sand + biochar, sand + iron, and Stalite filtration column effluent displayed similar concentrations to the influent (Table 55). Sand filtration column effluent displayed significantly higher concentrations than the influent, while the remaining filtration columns displayed significantly lower effluent concentrations than the influent. Between columns, sand filtration column effluent displayed the greatest aluminum concentrations while Stalite + biochar + iron displayed the lowest aluminum concentrations.

For chromium, all stormwater filtration column effluent was similar to the influent except for sand, which was significantly greater than the influent. Between columns, sand displayed the greatest chromium concentrations and Stalite + iron displayed the lowest chromium concentrations.

For copper, sand + biochar, Stalite + biochar, and Stalite + biochar + iron filtration column effluent displayed similar concentrations to the influent. The remaining filtration column effluent displayed significantly greater copper concentrations than the influent. Between columns, the Stalite filtration column effluent displayed the greatest copper concentrations and the Stalite + biochar + iron column effluent displayed the lowest copper concentrations.

For manganese, all stormwater filtration column effluent was similar to the influent except for sand + biochar filtration column effluent, which was significantly higher than the influent manganese concentration. Between columns, sand + biochar displayed the highest manganese concentrations while Stalite + biochar + iron displayed the lowest manganese concentrations.

For lead, all stormwater filtration column effluent displayed significantly lower concentrations than the influent except for sand, which was significantly greater than the influent lead concentration. Between columns, sand displayed the greatest lead concentrations while the Stalite + biochar + iron column filtration effluent displayed the lowest lead concentrations.

For zinc, all stormwater filtration column effluent displayed significantly lower concentrations than the influent except for sand, which was similar to the influent zinc concentration. Between columns, sand displayed significantly greater zinc concentrations while the remaining columns displayed similarly low zinc concentrations.

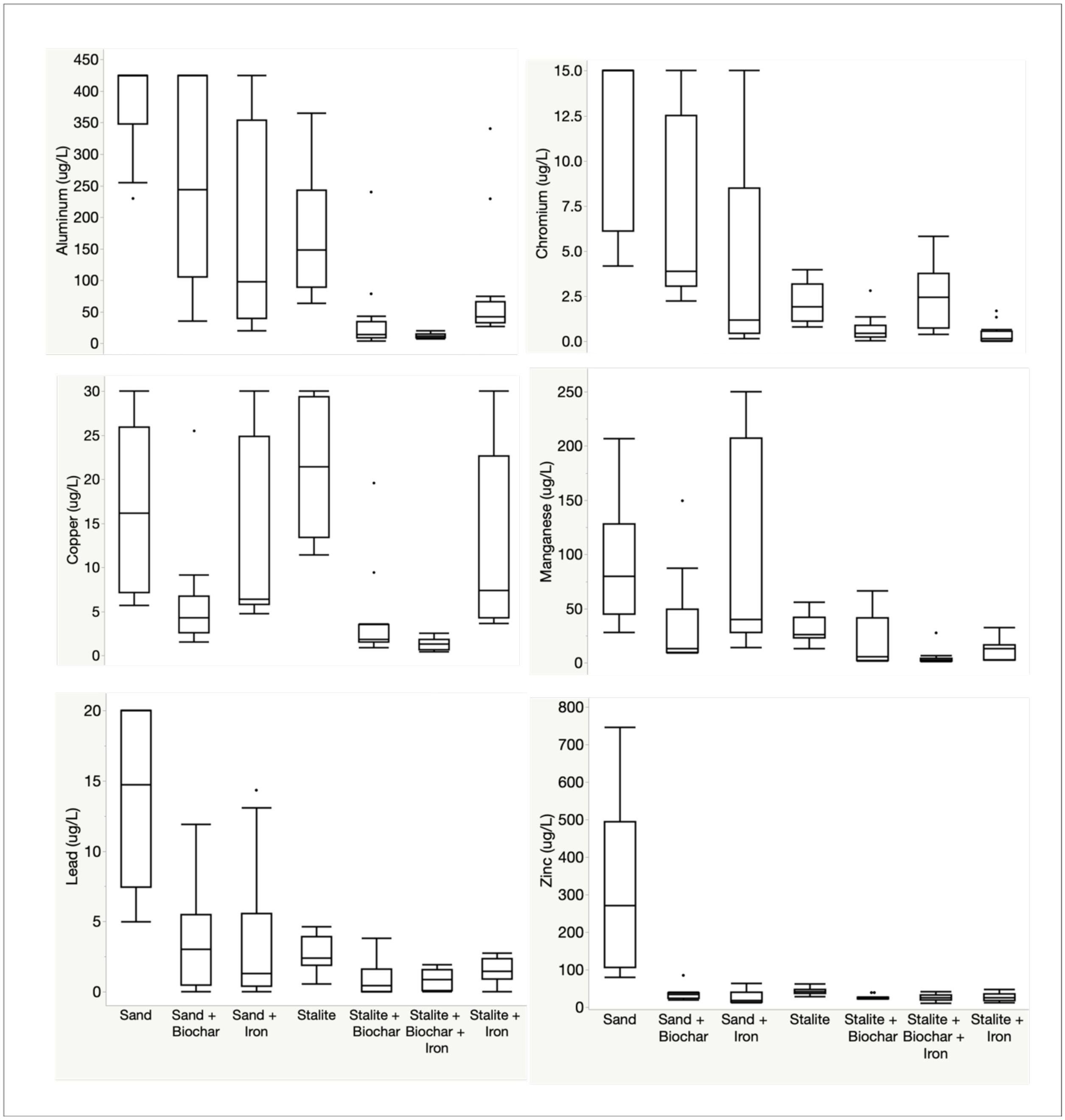

Figure 23. Total recoverable metals effluent – Total aluminum, chromium, copper, manganese, lead, and zinc.

Table 55. Total recoverable metals effluent connecting letters report – Total aluminum, chromium, copper, manganese, lead, and zinc.

	Aluminum				Chromium			Copper			Manganese		Lead			Zinc	
Influent		B	C			B	C			C		B		B		A	
Sand	A				A			A				B	A			A	
Sand + biochar		B				B			B	C		B			C		B
Sand + iron			C			B	C	A			A				C		B
Stalite		B	C				C	A				B			C		B
Stalite + biochar				D			C			C		B			C		B
Stalite + biochar + iron				D		B	C			C		B			C		B
Stalite + iron				D			C	A	B			B			C		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

3.8 Metal Removal Over Time

3.8.1 Aluminum

Over the duration of the project, no significant removal of aluminum was displayed by the sand stormwater filtration column (Table 56). The sand + biochar filtration column displayed significant removal during phases 4.2, 4.3 and 4.4; However, it did not display significant removal during phases 4.1, 4.5, or for total aluminum. No significant removal of aluminum was displayed by the sand + iron filtration column over the duration of the project. The sand + biochar + iron filtration column did display significant aluminum removal; However, the filtration column became clogged and was decommissioned for the rest of the project due to the low hydraulic conductivity. The Stalite filtration column displayed similar aluminum concentrations to the influent in all phases expect for the high spike of phase 4.2. The Stalite + biochar filtration column displayed similar aluminum concentrations as the influent in phase 4.1 and displayed significant removal for the remaining phases. The Stalite + biochar + iron filtration column displayed significantly greater aluminum concentrations than the influent for phases 4.1 and 4.3, similar aluminum concentrations in phases 4.2 and 4.5, and significant removal in phases 4.4 and for total aluminum. The Stalite + iron filtration column displayed significantly greater aluminum concentrations in phases 4.1, 4.3, 4.4, and 4.5, similar aluminum concentrations in phase 4.2, and significant removal for total aluminum. Therefore, Stalite + biochar performed significantly greater for aluminum removal over time (Figure 24).

Studies have shown that sand is not an effective stormwater filter media for metal removal and that non-specific electrostatic adsorption is the most likely removal mechanism (Lenhart et al., 2007; Reddy et al., 2013, 2014). This is likely due to the small amount of negatively charged functional groups located on the sand particles (Reddy et al., 2014). Due to sands weak ability to adsorb positively charged metals, it is recommended that enhanced filtration media be applied for stormwater filtration of metals (Genç-Fuhrman et al., 2008; Haile & Fuerhacker, 2018). Based on the results of this study, biochar and iron enhanced media amendments with sand did display significant removal of aluminum compared to only sand. However, sand, biochar and iron should not be combined as a stormwater filtration system, as significant clogging can rapidly occur as seen in this study. Sand based stormwater filtration systems displayed column leaching of metals over time, as observed for aluminum in phases 4.3, 4.4, 4.5 and for total recoverable aluminum.

Stalite has not yet been studied as a potential stormwater filtration media for metals removal. However, based on its physical properties to sand and the significant removal of other stormwater contaminants (Stalite Environmental, 2014), it was analyzed as a potential stormwater filtration media for metals removal. Stalite alone did not significantly remove aluminum in the simulated field conditions except for the high spike of phase 4.2. Biochar was added to the Stalite media base as a filtration media amendment due to the media’s previous success as an amendment to sand filtration systems (Pawluk & Fronczyk, 2015; Haile &

Fuerhacker, 2018). The abundance of oxygen functional groups on the surface of biochar particles gives the media a high chemical reactivity to positively charged metal species (Reddy et al., 2014). Upon addition of biochar to Stalite, significant aluminum removal occurred over all phases of the project. Therefore, based on previous studies, aluminum removal via biochar media likely occurs through the chemical adsorption of the dissolved aluminum. Iron was also added to Stalite based on the media's previous success as a sand filter media amendment for metal removal (Prabhukumar, 2013; Tiwari & Nayak, 2016). Upon addition of iron to Stalite, significant aluminum leaching occurred throughout all phases of the project. However, total aluminum was successfully removed using a Stalite + iron stormwater filtration system. Therefore, aluminum removal via iron media likely occurs through adsorption, as the removed aluminum is mostly sediment-bound aluminum. Stalite, biochar and iron should not be combined as a stormwater filtration system, as significant aluminum removal is not achieved as well as the Stalite filtration media with the biochar media amendment.

Table 56. All phases - Aluminum connecting letters report.

	Phase 4.1				Phase 4.2 Low Spike			Phase 4.2 High Spike		Phase 4.3					Phase 4.4			Phase 4.5				Total Aluminum			
Influent				D	A	B		A				C	D			B				C	D		B	C	
Sand				D		B		A			B	C	D		A				B	C		A			
Sand + biochar				D			C		B			C	D				C	A					B		
Sand + iron				D	A	B		A			B				A					C	D			C	
Sand + biochar + iron**			C																						
Stalite				D		B			B				D		A	B			B	C			B	C	
Stalite + biochar				D			C		B					E			C			C	D				D
Stalite + biochar + iron	A				A			A			B	C					C				D				D
Stalite + iron		B			A			A		A					A	B		A	B						D

*Levels not connected by the same letter are significantly different (p<0.05).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging.

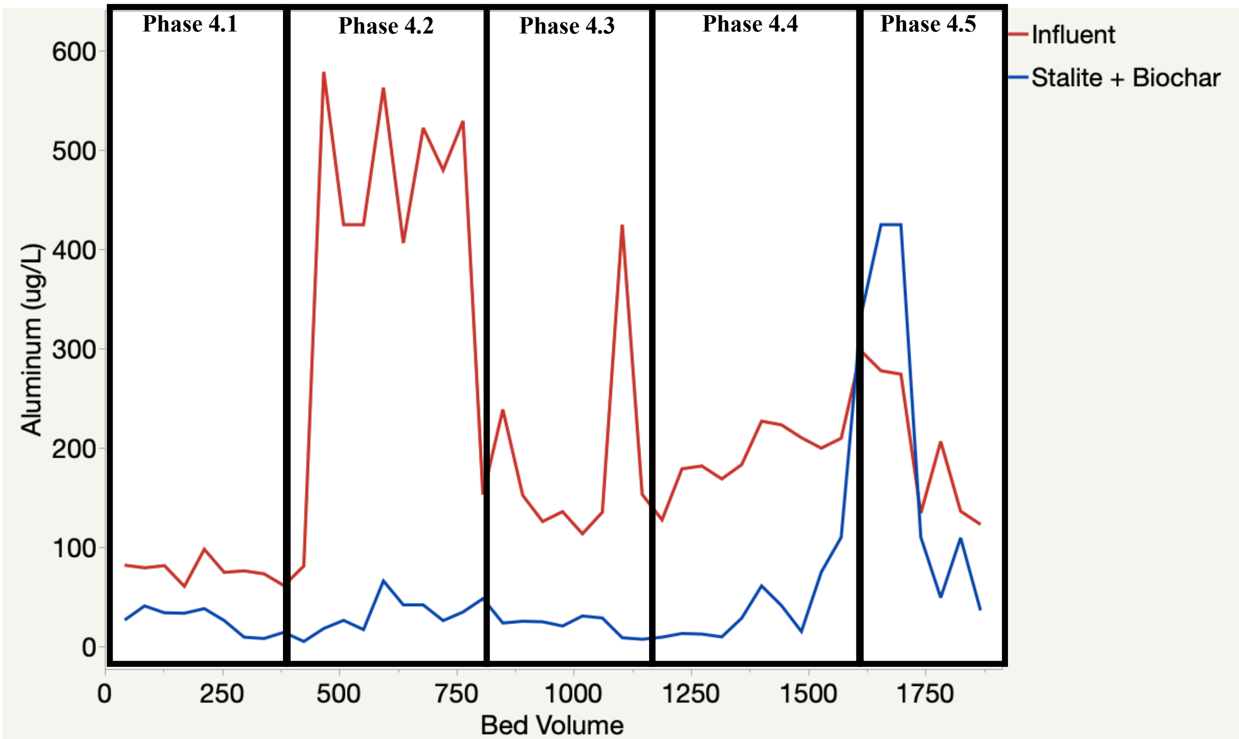

Figure 24. Influent aluminum concentrations and the most effective stormwater filtration system effluent (Stalite + biochar) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.2 Chromium

The sand filtration column displayed significant removal during phases 4.2 (high spike), however it did not display significant removal during phases 4.1, 4.2 (low spike), 4.3, 4.4, 4.5, or for total chromium (Table 57). No significant removal of chromium was displayed by the sand + biochar and the sand + iron filtration column over the duration of the project. The sand + biochar + iron filtration column displayed similar chromium concentrations to the influent during phase 4.1; However, the filtration column became clogged and was decommissioned for the rest of the project due to the slow hydraulic conductivity. The Stalite filtration column displayed similar chromium concentrations as the influent in all phases expect for the phase 4.4, in which the Stalite filtration column displayed significant removal of chromium. The Stalite + biochar filtration column displayed similar chromium concentrations as the influent over the duration of the project. The Stalite + biochar + iron filtration column displayed similar chromium concentrations as the influent for phases 4.1, 4.2, 4.4, and total chromium, however significantly greater chromium concentrations were displayed in phase 4.5 and significant removal was displayed in phase 4.3. The Stalite + iron filtration column displayed significant removal of chromium in phases 4.2 (high spike) and 4.4, and similar chromium concentrations in the remaining phases. Therefore, the Stalite filtration column and the Stalite + iron filtration column performed significantly greater for chromium removal over time (Figure 25).

Chromium removal via sand filtration has been shown to be essentially ineffective (Reddy et al., 2014). In this study, sand displayed significant chromium removal during the high spike of phase 4.2 but did not display significant chromium removal throughout the other phases. While addition of biochar and iron as stormwater filtration media amendments has proven to display significant chromium removal compared to sand alone (Genç-Fuhrman et al., 2008; Reddy et al., 2014; Trenouth & Gharabaghi, 2015) and other metals removal compared to sand alone (Inyang et al., 2012; Reddy et al., 2014), this project did not confirm those findings. The addition of biochar and iron, separately and together, did not aid in chromium removal and did not display significant chromium removal throughout the entire project. Sand based stormwater filtration systems displayed column leaching of chromium over time, as observed in all phases of this project. While adsorption has been the suggested removal method for chromium using biochar and iron (Genç-Fuhrman et al., 2008; Reddy et al., 2014; Tiwari & Nayak, 2016), the small addition of biochar and iron to sand likely allowed other contaminants to be adsorbed to the pore surfaces more often than chromium, that is, other contaminants may have outcompeted chromium for sites.

Effluent through Stalite alone displayed similar chromium concentrations throughout the project, except for phase 4.4 which displayed significantly lower chromium concentrations than the influent. Some studies have observed similar occurrences with different stormwater filtration media, in which high chloride concentrations allowed for successful contaminant removal (Trenouth & Gharabaghi, 2015). It is possible that, as some chloride was retained in the filtration media, chemical adsorption could have occurred between chromium and chloride and aided in the removal of chromium from the Stalite filtration column effluent. The addition of biochar to Stalite did not aid in chromium removal during any of the project phases; however, the addition of iron to Stalite did aid in chromium removal. This has been observed in previous studies (Genç-Fuhrman et al., 2008) and is said to occur based on the high affinity for cationic and anionic species that iron displays.

Table 57. All phases - Chromium connecting letters report.

	Phase 4.1			Phase 4.2 Low Spike		Phase 4.2 High Spike			Phase 4.3			Phase 4.4		Phase 4.5			Total Chromium		
Influent		B	C		B	A	B			B		A				C		B	C
Sand			C		B	A	B	C		B	C	A	B			C	A		
Sand + biochar	A			A		A			A			A		A				B	
Sand + iron		B	C	A		A	B	C		B		A	B			C		B	C
Sand + biochar + iron**		B																	
Stalite			C		B		B	C		B			B			C			C
Stalite + biochar		B	C		B		B	C		B	C	A	B			C			C
Stalite + biochar + iron			C		B		B	C			C	A	B		B			B	C
Stalite + iron			C		B			C		B	C		B			C			C

*Levels not connected by the same letter are significantly different (p<0.05).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging

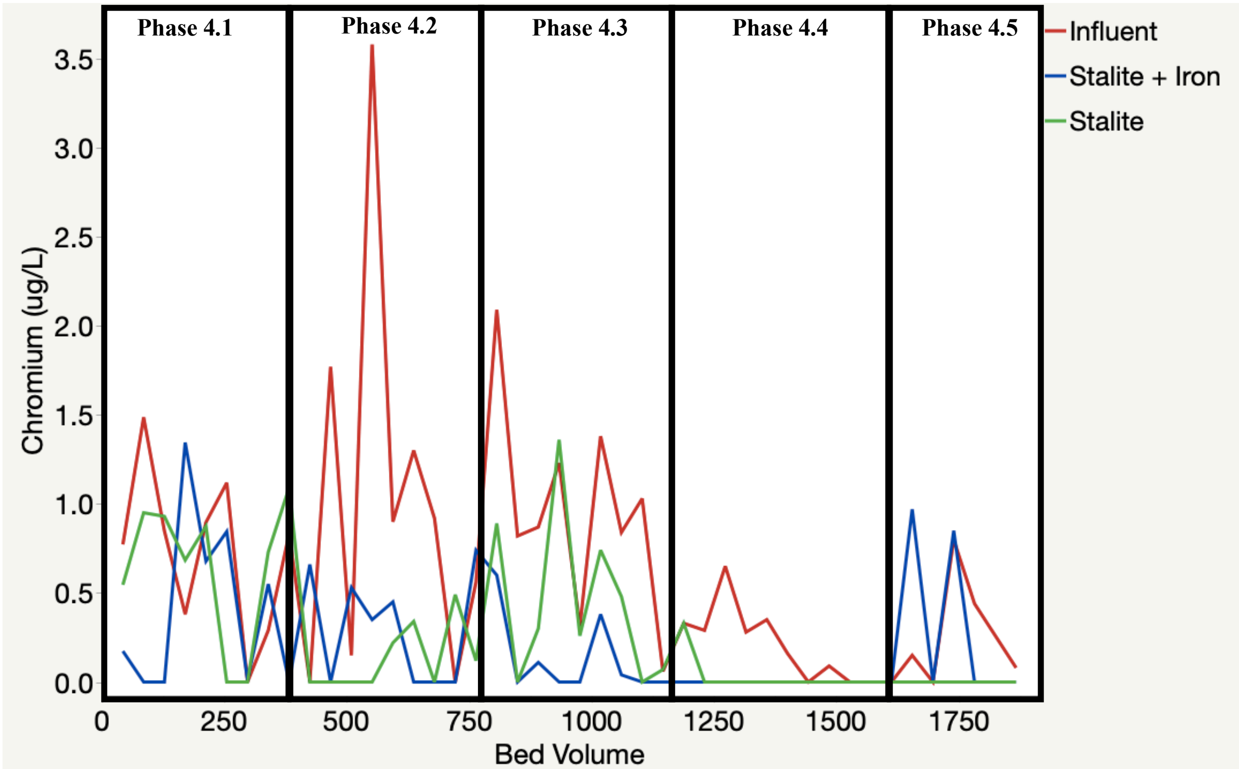

Figure 25. Influent chromium concentrations and the most effective stormwater filtration system effluent (Stalite + iron and Stalite) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.3 Copper

Over the duration of the project, the sand filtration column did not display significant copper removal (Table 58). The sand + biochar filtration column displayed significant copper removal for phase 4.2 and 4.3 and displayed similar copper concentrations to the influent throughout the remaining phases. No significant removal of copper was displayed by the sand + iron filtration column over the duration of the project. The sand + biochar + iron filtration column displayed similar copper concentrations to the influent during phase 4.1; However, the filtration column became clogged and was decommissioned for the rest of the project due to the slow hydraulic conductivity. No significant removal of copper was displayed by the Stalite filtration column over the duration of the project. The Stalite + biochar filtration column displayed similar copper concentrations as the influent for phases 4.1, 4.2 (high spike), 4.4, 4.5, and total copper, and displayed significant removal during phases 4.2 (low spike) and 4.3. The Stalite + biochar + iron filtration column displayed similar copper concentrations as the influent for phases 4.1, 4.2 (high spike), 4.4, 4.5, and total copper, and significant removal during phases 4.2 (low spike) and 4.3. No significant removal of copper was displayed by the Stalite + iron filtration column over the duration of the project. Therefore, the Stalite + biochar filtration column and the Stalite + biochar + iron filtration column performed significantly greater for chromium removal over time (Figure 26).

In previous studies, sand stormwater filtration systems have been shown to have low removal efficiency of copper (Reddy et al., 2014). Sand was also determined to be an ineffective filter for copper removal throughout this project, as it did not display dissolved copper removal and displayed copper leaching when analyzing total copper. The addition of biochar to the sand stormwater filtration system displayed significant copper removal in phase 4.2 and 4.3, but not throughout the remainder of the project. While biochar has been displayed as an effective stormwater filtration media for the removal of copper through chemical adsorption with the oxygen-containing functional groups present on biochar (Inyang et al., 2012), it is likely that there was not enough biochar in the stormwater filtration system to effectively remove copper by chemical adsorption over a long period of time. Also, one study showed that the biochar content was composed mainly of carboxyl groups that can mobilize copper due to competition with negatively charged compounds at adsorption sites, which may have occurred in this project as well (Uchimiya et al., 2010). Iron has also been shown as an effective stormwater filtration media amendment for copper removal due to iron’s high affinity for dissolved metals (Genç-

Fuhrman et al., 2008). In this study, the iron amended stormwater filtration system with sand displayed significant dissolved copper leaching in most project phases and displayed similar copper concentrations through the remaining phases. This could be because not enough iron is present in the amended filtration column for significant copper adsorption and removal. Sand based stormwater filtration systems displayed column leaching of copper over time, as observed in all phases for sand + iron chromium concentrations and in the total recoverable copper phase for all sand filtration systems.

Stalite alone as a stormwater filtration system did not significantly remove copper throughout the duration of the project and significant leaching of copper was observed. Upon the addition of biochar to Stalite, similar copper concentrations in the influent and effluent were displayed for phases 4.1, 4.2 (high spike), 4.4, 4.5, and total copper, and displayed significant copper removal during phases 4.2 (low spike) and 4.3. This is likely due to the chemical adsorption of copper by the reactive oxygen-containing functional groups present on the surface of the biochar media. No significant removal of copper was observed for the Stalite + iron filtration system, however the Stalite + biochar + iron filtration column displayed similar copper concentrations as the influent for phases 4.1, 4.2 (high spike), 4.4, 4.5, and total copper, and significant copper removal during phases 4.2 (low spike) and 4.3. This is likely due to the high chemical affinity that iron displays to form complexes with charged copper species; however, there is likely competition between copper and other chemical species that could react with iron.

Table 58. All phases - Copper connecting letters report.

	Phase 4.1				Phase 4.2 Low Spike			Phase 4.2 High Spike				Phase 4.3			Phase 4.4		Phase 4.5			Total Copper		
Influent			C	D		B			B	C	D		B			B			C			C
Sand			C	D		B	C		B	C			B			B			C	A		
Sand + biochar				D			C				D			C		B			C		B	C
Sand + iron	A				A				B				B		A				C	A		
Sand + biochar + iron**		B	C	D																		
Stalite		B			A			A				A			A			B		A		
Stalite + biochar			C	D			C			C	D			C		B			C			C
Stalite + biochar + iron				D			C			C	D			C		B			C			C
Stalite + iron		B	C		A				B	C	D		B			B	A			A	B	

*Levels not connected by the same letter are significantly different (p<0.05).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging.

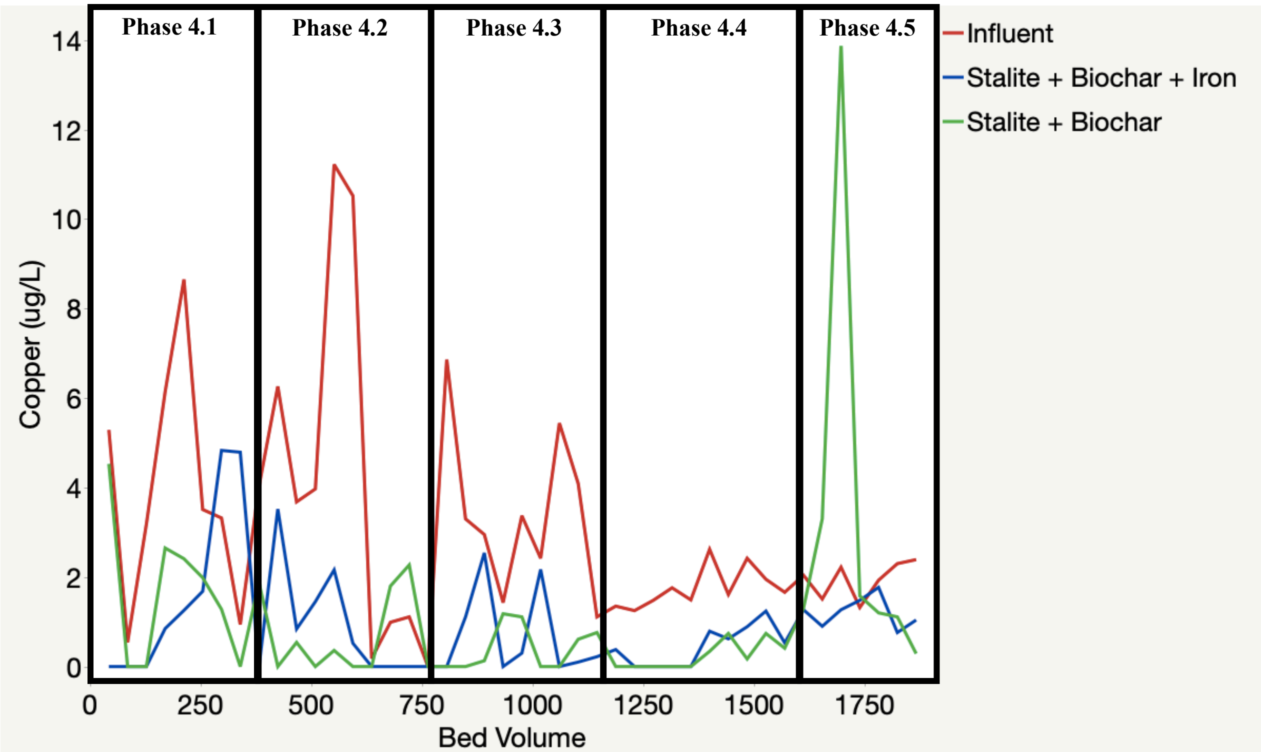

Figure 26. Influent copper concentrations and the most effective stormwater filtration system effluent (Stalite + biochar and Stalite + biochar + iron) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.4 Manganese

The sand filtration column displayed significant removal of manganese from the influent for phases 4.1, 4.2 (high spike), 4.3, and 4.5, and displayed similar manganese concentrations to the influent throughout the remaining phases (Table 59). The sand + biochar filtration column displayed significant manganese removal for phase 4.1, 4.2 (high spike), 4.3 and 4.5, and displayed similar manganese concentrations to the influent throughout the remaining phases. The sand + iron filtration column displayed significantly greater manganese concentrations than the influent for phases 4.2 (low spike), 4.4, and total manganese, and similar manganese concentrations throughout the remainder of the phases. The sand + biochar + iron filtration column displayed significant removal of manganese from the influent during phase 4.1; However, the filtration column became clogged and was decommissioned for the rest of the project due to the slow hydraulic conductivity. The Stalite filtration column displayed significant removal of manganese from the influent for phases 4.1, 4.3, and 4.5, significantly greater manganese concentrations in phase 4.2 (low spike), and similar manganese concentrations in phases 4.2 (high spike) 4.4, and total manganese. The Stalite + biochar filtration column displayed significant removal of manganese from the influent in phases 4.1, 4.2 (high spike), 4.3, and 4.4, and displayed similar manganese concentrations throughout the remaining phases. The Stalite + biochar + iron filtration column displayed significant removal of manganese from the influent for phases 4.1, 4.2 (high spike), 4.3, and 4.5, and similar manganese concentrations throughout the remaining phases. The Stalite + iron filtration column displayed significant removal of manganese from the influent for phase 4.1, 4.2 (high spike), and 4.3, and displayed similar manganese concentrations throughout the remaining phases. Therefore, the Stalite + iron filtration column and the Stalite + biochar + iron filtration column performed significantly greater for manganese removal over time (Figure 27).

Sand stormwater filtration media displayed significant manganese removal throughout phases 4.1, 4.2 (high spike), 4.3, and 4.5, and displayed similar manganese concentrations to the influent throughout the remaining phases. This is likely due to the high reactivity of manganese in most oxidation states. In this project, it likely that manganese oxidation commonly occurred through microbial mediated pathways (Remucal & Ginder-Vogel, 2014). Upon oxidation, manganese oxides could be formed, which are powerful oxidants themselves that may be involved in chemical reactions within the filtration media pore space. Manganese oxide formation could essentially immobilize manganese within the filter media, as the manganese is aiding in redox reactions with additional contaminants. The addition of biochar and iron to sand has been shown to be successful for metals removal (Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008; Pawluk & Fronczyk, 2015; Haile & Fuerhacker, 2018) but has not be studied for manganese. Sand with biochar as a media amendment displayed significant manganese removal for phase 4.1, 4.2 (high spike), 4.3 and 4.5, and displayed similar manganese concentrations to the influent throughout the remaining phases. The sand + iron filtration column displayed significant leaching for phases 4.2 (low spike), 4.4, and total manganese, and similar manganese concentrations to the influent for the remainder of the phases. Therefore, biochar amended sand filtration did remove more manganese than sand alone, which is likely due the reactivity of both the biochar media oxygen-containing surface ligands and the reactivity of present manganese species (Remucal & Ginder-Vogel, 2014). Iron amended sand filtration did not remove more manganese than sand alone. Zero-valent iron is a strong reductant; however, due to the small amount of removal of manganese from the iron amended Stalite column, there likely wasn't enough iron media present for chemical adsorption of all manganese species. Also, there was likely competition between different reactive metals for the complexation with the iron media.

The Stalite filtration column displayed significant removal of manganese from the influent for phases 4.1, 4.3, and 4.5, significantly greater manganese concentrations in phase 4.2 (low spike), and similar manganese concentrations in phases 4.2 (high spike) 4.4, and total manganese. The greater concentration of manganese (and other contaminants) in phase 4.2 effluent likely overloaded all adsorption sites present in the Stalite media. Significant removal of manganese over different periods of time in the Stalite filtration system could mean that surrounding field conditions such as higher contaminant loading, drought periods, and temperature, have a large impact on manganese removal. Stalite with biochar amended media displayed significant manganese removal in most phases, making the biochar amended media a more successful stormwater filtration system than Stalite alone. This is likely due to the reactive oxygen-containing functional groups on the surface of the biochar. Stalite as an iron amended media also displayed more significant removal than the biochar media amendment. This is likely due to the adsorption of manganese with Stalite and the additional chemical adsorption of manganese with iron, which has a high chemical affinity for charged metal species (Genç-Fuhrman et al., 2008). The Stalite filtration system amended with biochar and iron also significantly removed manganese in most phases, which is likely due to the additional adsorption reaction sites offered by the biochar and iron media surfaces which was previously discussed.

Table 59. All phases - Manganese connecting letters report.

	Phase 4.1			Phase 4.2 Low Spike		Phase 4.2 High Spike		Phase 4.3			Phase 4.4			Phase 4.5				Total Manganese	
Influent	A				B	A		A				B		A					B
Sand			C		B		B			C		B	C			C	D		B
Sand + biochar			C		B		B			C		B	C		B				B
Sand + iron		B		A			B		B		A				B	C		A	
Sand + biochar + iron**		B																	
Stalite			C	A			B			C		B	C			C	D		B
Stalite + biochar			C		B		B			C			C		B				B
Stalite + biochar + iron			C		B		B			C		B	C				D		B
Stalite + iron			C		B		B			C		B	C			C	D		B

*Levels not connected by the same letter are significantly different ($p<0.05$).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging

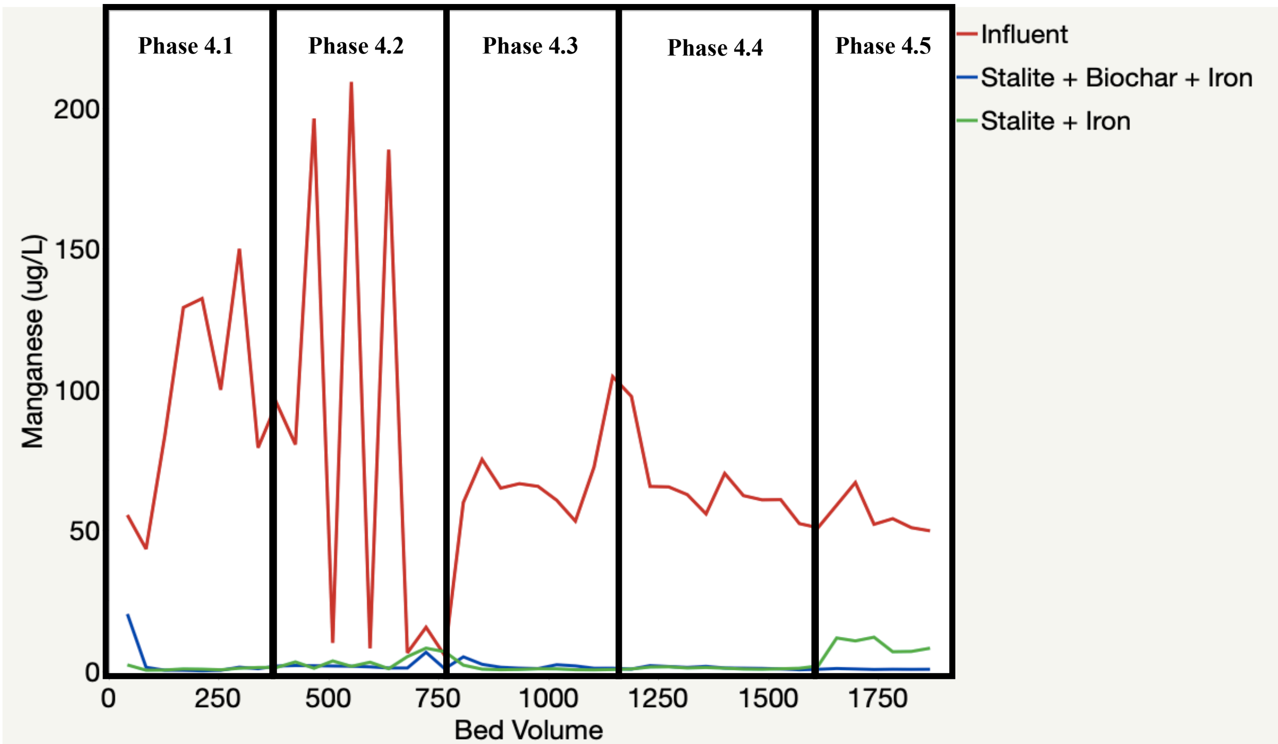

Figure 27. Influent manganese concentrations and the most effective stormwater filtration system effluent (Stalite + iron and Stalite + biochar + iron) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.5 Lead

The sand filtration column displayed significant removal of lead from the influent for phases 4.2 (high spike), and 4.4, displayed similar lead concentrations to the influent in phases 4.2 (low spike), 4.3, and 4.5, and displayed significantly greater lead concentrations than influent during phase 4.1 and the total lead phase (Table 60). The sand + biochar filtration column displayed significant lead removal for phase 4.2 (high spike), 4.4, 4.5, and total lead, and displayed similar lead concentrations to the influent throughout the remaining phases. The sand + iron filtration column displayed significantly greater lead concentrations than the influent for phase 4.1, displayed similar lead concentrations to the influent in phases 4.2 and 4.3, and displayed significant removal from the influent during phases 4.4, 4.5, and total lead. The sand +

biochar + iron filtration column did not display significant removal of lead from the influent during phase 4.1; However, the filtration column became clogged and was decommissioned for the rest of the project due to the slow hydraulic conductivity. The Stalite filtration column displayed significant removal of lead from the influent for phases 4.4, 4.5, and total lead, and displayed similar lead concentrations throughout the remaining phases. The Stalite + biochar filtration column displayed significant removal of lead from the influent in phases 4.2 (high spike), 4.4, 4.5, and total lead, and displayed similar lead concentrations throughout the remaining phases. The Stalite + biochar + iron filtration column displayed significant removal of lead from the influent for phases 4.2 (high spike), 4.4, 4.5, and total lead, and displayed similar lead concentrations throughout the remaining phases. The Stalite + iron filtration column displayed significant removal of lead from the influent for phases, 4.4, 4.5, and total lead, and displayed similar lead concentrations throughout the remaining phases. Therefore, the Stalite + biochar filtration column and the Stalite + biochar + iron filtration column performed significantly greater for lead removal over time (Figure 28).

Ineffective lead removal with sand filtration has been observed in previous studies (Lenhart et al., 2007; Reddy et al., 2014; Haile & Fuerhacker, 2018). For this project, the sand filtration system was not effective as a stormwater filtration media for lead removal throughout most phases. Sand with biochar as a filtration media amendment displayed significantly more effective lead removal than sand alone, which is likely due to adsorption via non-electrostatic mechanisms, as lead likely forms surface complexes with functional groups present on the biochar (Inyang et al., 2013; Reddy et al., 2014). Sand with iron as a filtration media amendment has been shown to effectively remove lead from stormwater via adsorption and precipitation processes (Reddy et al., 2014; Trenouth & Gharabaghi, 2015). However, sand with iron as a filtration media amendment displayed ineffective lead removal throughout most of the project, which could be due to the small amount of iron that was mixed in as a media amendment.

The Stalite stormwater filtration system displayed significant removal of lead from the influent for phases 4.4, 4.5, and total lead, and displayed similar lead concentrations throughout the remaining phases. Therefore, the Stalite stormwater filtration system alone may need to go through several bed volumes before successful lead removal can occur. The addition of the biochar filter media to Stalite displays a similar relationship in which a number of bed volumes must occur before successful lead removal. Successful lead removal from the Stalite + biochar amended filtration media is likely due to the formation complexes with the biochar, which has been shown to aid in the adsorption of lead (Inyang et al., 2013; Reddy et al., 2014). The addition of the iron filter media to Stalite also displayed a similar relationship to Stalite and Stalite + biochar stormwater filtration columns, in which a number of bed volumes must occur before successful lead removal. Successful lead removal from the Stalite + iron amended filtration media is likely due to the chemical adsorption by the reactive iron media as seen with other metal species such as copper and zinc (Rangsivek & Jekel, 2005; Genç-Fuhrman et al., 2008) The Stalite filtration system with biochar and iron media amendments is as effective as the biochar amended Stalite filtration system without the addition of iron, and therefore is not necessary since it would be more expensive to obtain.

Table 60. All phases - Lead connecting letters report.

	Phase 4.1		Phase 4.2 Low Spike		Phase 4.2 High Spike		Phase 4.3		Phase 4.4			Phase 4.5		Total Lead		
Influent		B	A	B	A		A	B	A			A			B	
Sand	A	B	A	B		B	A			B		A		A		
Sand + biochar		B	A	B		B	A	B			C		B			C
Sand + iron	A		A		A	B	A	B			C		B			C
Sand + biochar + iron**		B														
Stalite		B	A	B	A	B		B			C		B			C
Stalite + biochar		B		B		B	A	B			C		B			C
Stalite + biochar + iron		B	A	B		B		B			C		B			C
Stalite + iron		B	A	B	A	B		B			C		B			C

*Levels not connected by the same letter are significantly different ($p<0.05$).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging

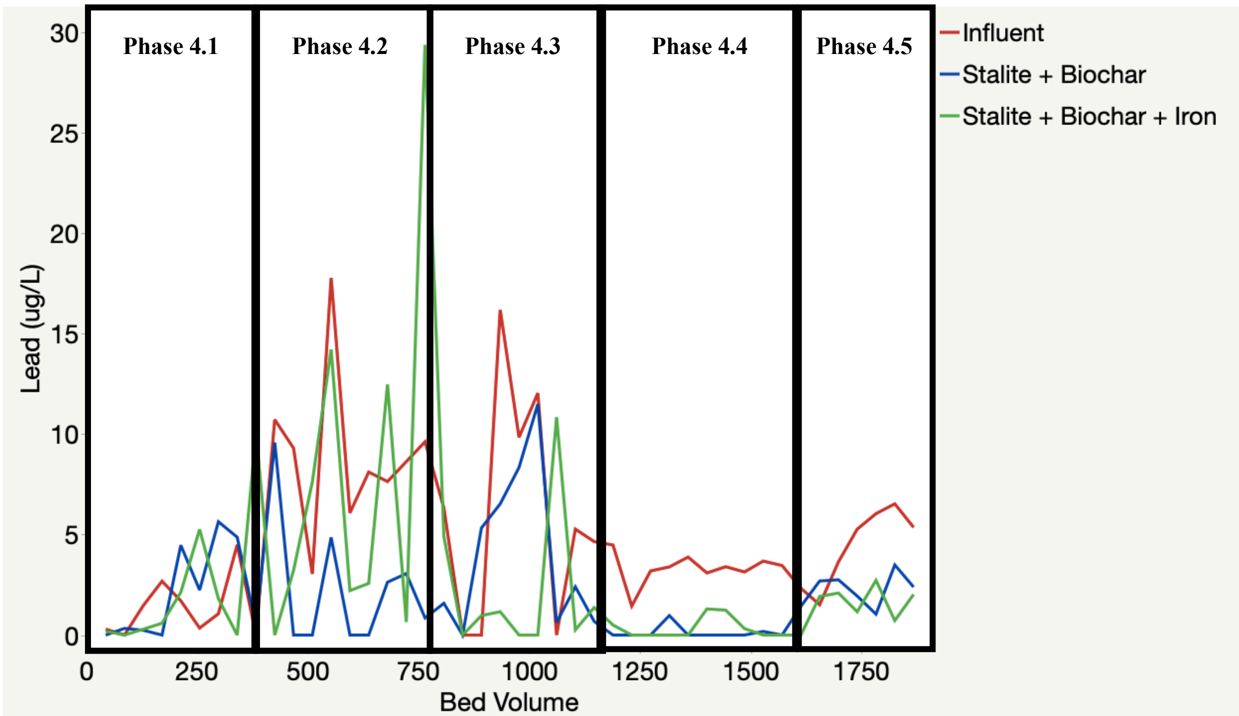

Figure 28. Influent lead concentrations and the most effective stormwater filtration system effluent (Stalite + biochar and Stalite + biochar + iron) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.6 Zinc

The sand filtration column displayed significant removal of zinc from the influent for phases 4.1, 4.2 (high spike), 4.3, 4,4, and 4.5, and displayed similar zinc concentrations to the influent in phases 4.2 (low spike), and total metals (Table 61). The sand + biochar, sand + iron, Stalite, Stalite + biochar, Stalite + biochar + iron, and Stalite + iron filtration columns displayed significant zinc removal throughout all phases of the project. The sand + biochar + iron filtration column displayed significant removal of zinc from the influent during phase 4.1; However, the filtration column became clogged and was decommissioned for the rest of the project due to the slow hydraulic conductivity. Therefore, sand + biochar, sand + iron, Stalite, Stalite + biochar, Stalite + biochar + iron, and Stalite + iron filtration columns performed similar zinc removal over time (Figure 29).

Zinc removal in stormwater filtration systems has been shown to be moderately successful with sand filtration media as well as filtration systems with filter media amendments (Hatt et al., 2011; Reddy et al., 2014; Haile & Fuerhacker, 2018). In this project, zinc displayed significant removal from the sand filtration system over most phases. The addition of biochar to the sand filtration system displayed significantly greater zinc removal than the sand filtration system alone, which is likely due to the formation of surface complexes with functional groups present on the biochar (Inyang et al., 2013; Reddy et al., 2014). The addition of iron to the sand filtration system also displayed significantly greater zinc removal than the sand filtration system alone, which is likely due to the adsorption and precipitation processes that iron exhibits towards metals (Reddy et al., 2014; Trenouth & Gharabaghi, 2015).

The Stalite stormwater filtration system significantly removed zinc during all phases of the project. The addition of biochar and iron, separately and together, to the Stalite filtration system also significantly removed zinc during all phases of the project. This is likely due to the adsorption properties that Stalite exhibits and the high reactivity of zinc that allows the metal to be significantly removed from non-amended filtration systems such as sand (Reddy et al., 2014).

Table 61. All phases - Zinc connecting letters report.

	Phase 4.1		Phase 4.2 Low Spike		Phase 4.2 High Spike		Phase 4.3		Phase 4.4			Phase 4.5			Total Zinc	
Influent	A		A		A		A		A			A			A	
Sand		B	A	B		B		B		B			B		A	
Sand + biochar		B		B		B		B			C			C		B
Sand + iron		B		B		B		B			C			C		B
Sand + biochar + iron**		B														
Stalite		B		B		B		B			C			C		B
Stalite + biochar		B		B		B		B			C			C		B
Stalite + biochar + iron		B		B		B		B			C			C		B
Stalite + iron		B		B		B		B			C			C		B

*Levels not connected by the same letter are significantly different (p<0.05).
**Sand + biochar column decommissioned after phase 4.1 due to media clogging

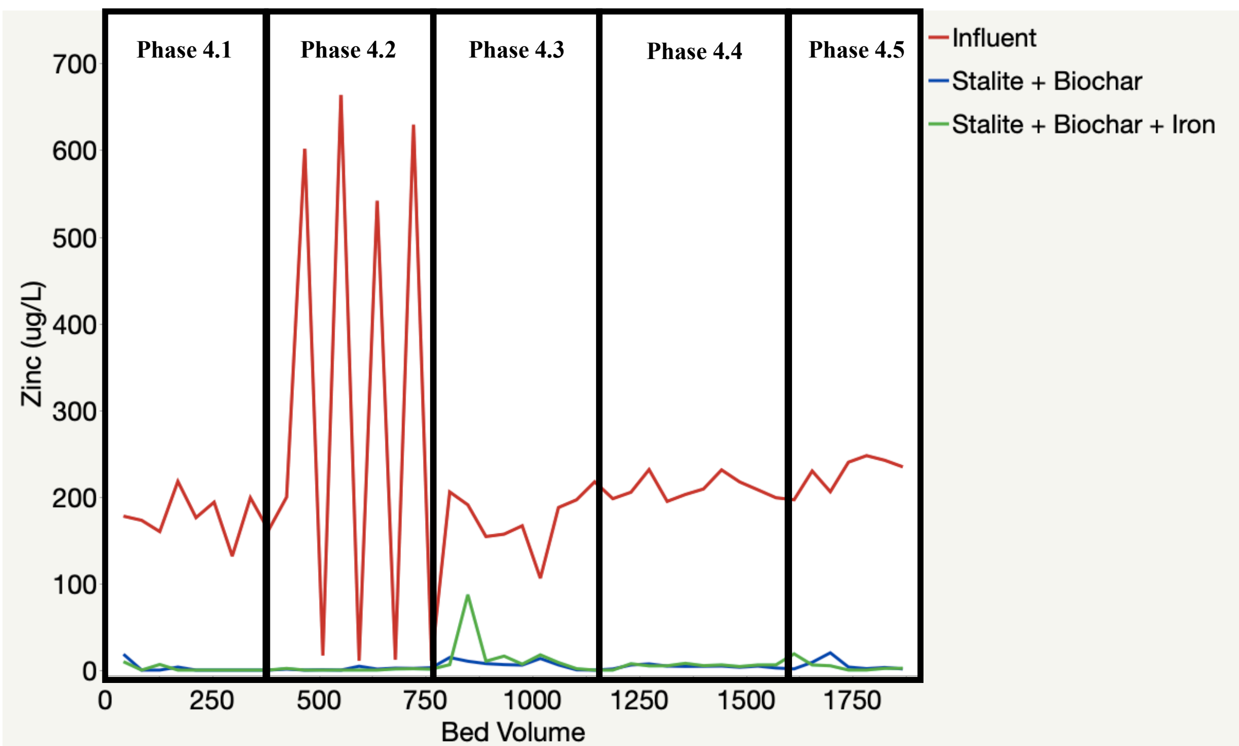

Figure 29. Influent zinc concentrations and the most effective stormwater filtration system effluent (Stalite + biochar and Stalite + biochar + iron) through all phases. Phases are outlined by bed volumes experienced in each phase (outline is approximate).

3.8.8 pH, ORP, Turbidity, and TSS Effect on Metals

pH has a strong influence on filtration media system chemistry and metal mobility (Reddy et al., 2014; Haile & Fuerhacker, 2018). At low pH, the solubility and mobility of metals generally increases, and more dissolved metals are released to the aqueous phase. At high pH, the solubility of metals generally decreases, and metals are more likely to adsorb to media and sediment particles to form minerals. Throughout this project, the influent pH remained between 6 and 8, which is considered the chemically neutral range. In this range, some metals including aluminum, chromium, copper, manganese, lead, and zinc were likely present as metal hydroxide species and some dissolved metal present, based on previous literature of metal speciation (Santos, et al., 2012; Pitre et al., 2014; Remucal & Ginder-Vogel, 2014; Smith et al., 2015; Xie et al., 2017). Throughout this project, the pH for the filtration column effluent appeared to depend on the presence of biochar and/or iron. For biochar amended sand and Stalite effluent, the pH ranged from 7 to 9. In this range, metals are more likely to react and become oxidized to form the hydroxide species with the oxygen-containing functional groups on the biochar media surface, which this pH range is suitable for. For iron amended sand and Stalite effluent, the pH ranged from 7 to 11. In this range, metals are more likely to form complexes with the iron media and be removed from the stormwater; however, that was not the case for this project. It is possible that additional chemical reactions occurred that prevented some metals, including aluminum and copper, from being adsorbed by iron amended media.

ORP can also have a strong influence on the filtration media system chemistry and metal mobility, as a low ORP can be indicative of a reducing environment and a high ORP can be indicative of an oxidizing environment (Reddy et al., 2014). In a reducing environment, more metals can be released from their mineral and/or sediment bound form. Throughout this project, the influent ORP ranged from approximately 100 to 300 mV. In this range, it is possible that some metals were present in the dissolved form and some in the particulate form, as the ORP was not very low and also not very high. Like pH, the ORP for the filtration column effluent generally depended on the presence of biochar and/or iron. For biochar amended sand and Stalite effluent, the ORP ranged from approximately 100 to 250 mV. In this range, metals are more likely to be prevalent in both the dissolved form and the particulate bound form, in which they could chemically react with biochar's oxygen-containing functional groups or be physically adsorbed as a precipitated particulate. However, it is difficult to determine this based on ORP alone, as common standard potentials for metal redox reactions are lower for magnesium, aluminum, zinc, and lead (-2.38 volts through -0.13 volts, respectively), and higher for copper (0.34 volts) than what was observed for this project (Younis, 2012). For iron amended sand and Stalite effluent, the ORP ranged from approximately 10 to 225 mV. In this range, metals are more likely to be in the dissolved form with lower ORP and react with the iron media through chemical adsorption; however, that was not the case for all filtration column effluent in this project as some dissolved metals such as aluminum and copper were significantly leached from iron amended media. It is possible that additional chemical reactions occurred that prevented these metals from being removed by iron amended media.

In previous studies it has been found that there is a generally linear relationship between TSS/turbidity and total metals, as metals can be bound to suspended solids in a turbid environment (Reddy et al., 2014; Nasrabadi et al., 2018). This means that when TSS/turbidity increases, total metal concentrations also increase and vice versa. This statement is true for all metals analyzed in this project. The highest concentrations of total metals and TSS were seen in the sand filtration column for all metals analyzed in this project, except manganese, at TSS concentrations up to approximately 6,000 mg/L, while the influent concentrations were generally between 100 and 300 mg/L TSS. Also, the lowest concentrations of total metals and TSS were seen in the Stalite + biochar column effluent for aluminum, copper, and zinc; Stalite + iron column effluent for chromium, and Stalite + biochar + iron, of which all filtration column effluent displayed TSS concentrations around 0 mg/L. The removal of suspended solids by stormwater filtration media in general is likely due to chemical and physical adsorption of the reactive dissolved and solid particulates. Over time, aqueous metal species likely reacted with the filtration medias to form precipitated particulates within the sand, sand + biochar, and sand + iron filtration columns when conditions allowed, causing significant TSS leaching and subsequent metal leaching.

3.8.9 Chloride and Phosphate Effect on Metals

Chloride has been shown to have a significant impact on metal mobilization/transformation in urban stormwater runoff (Corsi et al., 2015; Haile & Fuerhacker, 2018; Schuler & Relyea, 2018). This is hypothesized to be due to complexation of metals and chloride, in which positively charged metal cations are chemically attracted to negatively charged chloride anions. Since chloride is generally conservative, metal complexation (and therefore mobilization) can transport dissolved metal contaminants from soils or stormwater filtration media to receiving bodies of water. During phase 4.4 of this project, simulated de-icing salt (sodium chloride) was added to the spiked stormwater influent in significantly greater concentrations than the remaining phases to test its effects on the remaining stormwater contaminants. In response to an increase in chloride, concentrations of aluminum, chromium, copper, manganese, lead, and zinc did not appear to be notably different in the stormwater influent or the stormwater filtration column effluent over the duration of this project. This could be because chloride concentrations were not high enough to successfully form metal-chloride complexes that can promote metal mobilization, as previous literature has shown that significantly greater chloride concentrations can cause increased mobilization of copper, lead and zinc (Haile & Fuerhacker, 2018). In this study, phase 4.4 influent chloride concentrations remained between 100 mg/L to 500 mg/L, where metal mobilization from high chloride concentrations have been shown at influent chloride concentrations of 5 g/L (5,000 mg/L), which is one order of magnitude greater than what was used in this project. The insignificant effluent metal concentrations could also be due to high chloride concentrations throughout all phases of the project. Therefore, most metals could be in the complexed form, leaving little metal concentrations to further complex during the de-icing agent phase.

Phosphate-containing materials have been shown to effectively immobilize metals including aluminum, lead, copper and zinc (Erickson et al., 2007; Nzihou & Sharrock, 2010). This is likely due to the adsorption of metals onto a phosphate-containing surface, such as minerals, organic soils, and/or stormwater filtration media. One previous study discussed the mechanism of metal immobilization by phosphate materials adsorption mechanisms of ion exchange reactions and precipitation reactions (Nzihou & Sharrock, 2010). For this project, phosphate was significantly removed from most stormwater filtration columns in phases 4.1, 4.2 (high spike), 4.4 and 4.5., notably in the Stalite-based filtration columns. This was likely due to the adsorption of phosphate by the stormwater filtration media and precipitation as insoluble phosphates, including iron phosphates and metal phosphates (Erickson et al., 2007). Upon dissolved phosphate adsorption onto stormwater filtration media, it is possible that metal cations participated in ion exchange reactions with negatively charged phosphate since metal concentrations were significantly removed during the same phases by the Stalite-based filtration columns as well.

4. Conclusions

Increasing urbanization can introduce heavy metals to highway stormwater runoff. The objective of this project was to quantify the removal of the metals aluminum, chromium, copper, manganese, lead and zinc over time and over different simulated field conditions for the media amendments biochar and zero-valent iron to sand and Stalite over different simulated field conditions. Different stormwater filtration systems with sand and Stalite as filtration media bases and biochar and iron as filtration media amendments were analyzed to for metals aluminum, chromium, copper, manganese, lead and zinc removal. The stormwater filtration systems were also analyzed in various simulated field conditions to determine how the field conditions will impact contaminant removal.

Throughout this project, stormwater filtration media successfully removed metals from stormwater over different field conditions. While field conditions seemed to have less of an impact, metal type and stormwater filtration media were very important in observing effective metal removal. It appeared that pH, ORP, and TSS/turbidity had important impacts on metal speciation and adsorption by the different stormwater filtration media. Generally, a higher effluent pH and ORP, and a lower effluent turbidity/TSS concentration, appeared to display greater metal removal within the filtration columns. Overall, the Stalite base displayed the most effective overall for metals removal as opposed to sand. Statistical analyses showed that Stalite + biochar stormwater filtration amended system displayed the most effective overall metals removal, except for chromium.

For all metals in all stormwater filtration systems, the suspected removal method is adsorption over the surface of the filtration media based on the known chemical reactions of metals with biochar and iron filtration media. Stalite showed significantly greater removal for all metals, which likely occurs through adsorption of the reactive metal species. Biochar and iron aid in metal adsorption due to their chemically reactive surfaces that are attracted to the charged metal species. While the media amendments were added to the stormwater filtration media in low amounts due to cost, biochar proved to be an effencient stormwater filtration media amendment for the studied metals by being mixed with 95% Stalite by weight and 5% biochar stormwater filtration media.

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6. APPENDIX – SUPPLEMENTARY INFORMATION

A1. Unspiked Stormwater Influent - Pathogen Indicators

Total coliform (TC), fecal coliform (FC), enterococci (Ent) and *E. coli* were analyzed in stormwater to determine the background concentration of pathogen indicators (Table A1). Units for pathogen indicators are depicted as the most probable number (MPN) per 100 mL of sample. Analyses were conducted immediately after stormwater collection on August 31, 2020, November 30, 2020 and February 1, 2021. Pathogen indicators stayed high in stormwater for warmer months and showed a significant decrease during colder months, particularly *E. coli*.

Table A1. Unspiked stormwater influent – Total Coliform, fecal coliform, enterococci, and E. coli.

Date	**MPN TC/100 mL**	**MPN FC/100 mL**	**MPN Ent/100 mL**	**MPN E. coli/100 mL**
August 31, 2020	2419.6	2419.6	2419.6	2419.6
November 30, 2020	2419.6	2419.6	2419.6	2419.6
February 1, 2021	2419.6	1	727	107.6

A2. Unspiked Stormwater Influent - UVA and SUVA

UV-254 units are depicted as ultraviolet absorbance (UVA) cm^{-1}, SUVA units are depicted as L/mg-M. Analyses were conducted immediately or soon after stormwater collection on August 31, 2020, September 29, 2020, November 30, 2020, January 5, 2021, and February 1, 2021 (Table A2).

Table A2. Unspiked stormwater influent – UVA and SUVA.

Date	UV-254 (cm-1)	SUVA (L/mg-M)
August 31, 2020	NA	NA
September 29, 2020	0.3480	0.0349
November 30, 2020	0.3500	0.0574
January 5, 2021	0.497	0.155
February 1, 2021	0.657	0.187

*NA – Results are not available.

A3. Unspiked Stormwater Influent- Dissolved Organic Carbon

Background concentrations of dissolved organic carbon (DOC) were measured in stormwater (Table A3). Parameter units are depicted as mg/L. Analyses were conducted soon after stormwater collection on August 31, 2020, September 29, 2020, November 30, 2020, January 5, 2021, and February 1, 2021.

Table A3. Unspiked Stormwater – DOC.

Date	DOC (mg/L)
August 31, 2020	7.65
September 29, 2020	9.95
November 30, 2020	6.10
January 5, 2021	3.21
February 1, 2021	3.51

A4. Phase 4.1 – Pathogen Indicators Influent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent (Table x). Influent concentrations displayed high TC, however FC, Ent and E. Coli concentrations ranged from 0, 250 and 275 MPN/100mL, respectively. Pathogen indicator influent samples for Phase 4.1 were analyzed approximately 2 hours after being removed from the refrigerator.

Table A4. Phase 4.1 spiked stormwater influent data – Total coliform, fecal coliform, enterococci and E. coli.

	Influent		
	Minimum	Median	Maximum
MPN TC/100 mL	2419.6	2419.6	2419.6
MPN FC/100mL	1	26.95	1119.9
MPN Ent/100 ml	1	30.55	120.1
MPN E. coli/100 mL	1	13.6	2419.6

A5. Phase 4.1 - Pathogen Indicators Effluent

Pathogen indicators were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure A1). All columns displayed significant total coliform, fecal coliform and E. coli removal from the influent in phase 4.1. Most columns displayed significant enterococci removal from the influent other than Stalite and sand + iron. Stalite + iron, Sand + biochar and Stalite + biochar + iron displayed the most significant total coliform removal from the other columns (Table x). No columns displayed significant fecal coliform removal or E. coli removal from the other columns. All columns displayed significant enterococci removal compared to the Stalite and sand + iron column.

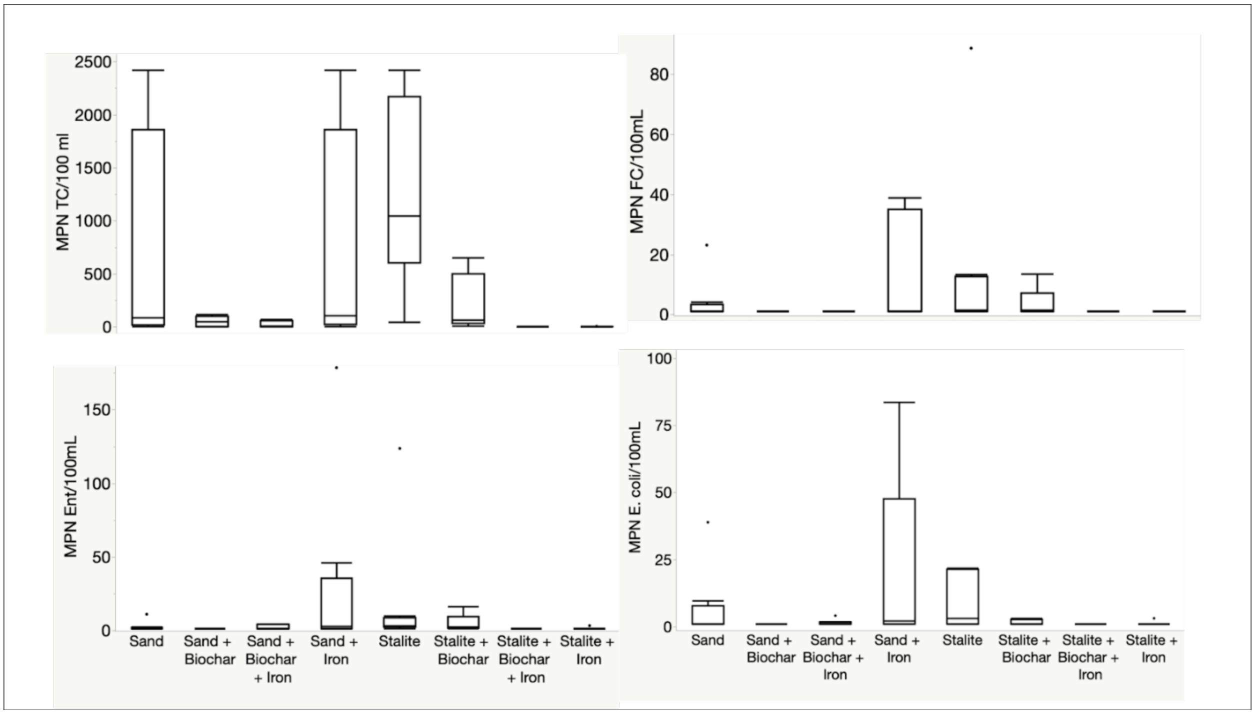

Figure A1. Phase 4.1 spiked stormwater effluent – Total coliform, fecal coliform, E. coli, and enterococci.

Table A5. Phase 4.1 spiked stormwater effluent connecting letters report - Total coliform, fecal coliform, E. coli, and enterococci.

	Total Coliform (MPN/100mL)				Fecal Coliform (MPN/100mL)		Enterococci (MPN/100mL)		E. coli (MPN/100mL)	
Influent	A				A		A		A	
Stalite		B				B	A	B		B
Sand + iron		B	C			B	A	B		B
Sand		B	C			B		B		B
Stalite + biochar			C	D		B		B		B
Sand + biochar + iron			C	D		B		B		B
Stalite + iron				D		B		B		B
Sand + biochar				D		B		B		B
Stalite + biochar + iron				D		B		B		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

A6. Phase 4.1 - UVA and SUVA Influent

UV-254 and SUVA are both low, ranging from 0.35 to 0.50 cm^{-1} and 0.04 to 0.14 L/mg-M, respectively. These values were similar to unspiked stormwater UV-254 and SUVA (Table A6).

Table A6. Phase 4.1 spiked stormwater influent data – UVA and SUVA.

	Influent		
	Minimum	Median	Maximum
UV-254 (cm-1)	0.350	0.412	3.42
SUVA (L/mg-M)	0.0315	0.0934	0.135

A7. Phase 4.1 - UVA and SUVA Effluent

Chemical parameters UVA and SUVA were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure A2). All columns displayed a significantly greater UV-254 from the influent other than sand + biochar + iron, sand + iron, and Stalite. However, no columns displayed a significantly different SUVA from the influent other than sand + biochar + iron and sand + iron, all of which were significantly greater than influent concentrations. This indicates that leaching of suspended solids occurred in these columns.

A significant difference was observed between the filtration columns for UVA and SUVA. For UVA, sand + biochar + iron, sand + iron, and Stalite + biochar displayed similar values to the influent while the remaining columns displayed significantly lower values. For SUVA, sand + biochar + iron displayed significantly greater values than the influent while the remaining columns displayed similar values.

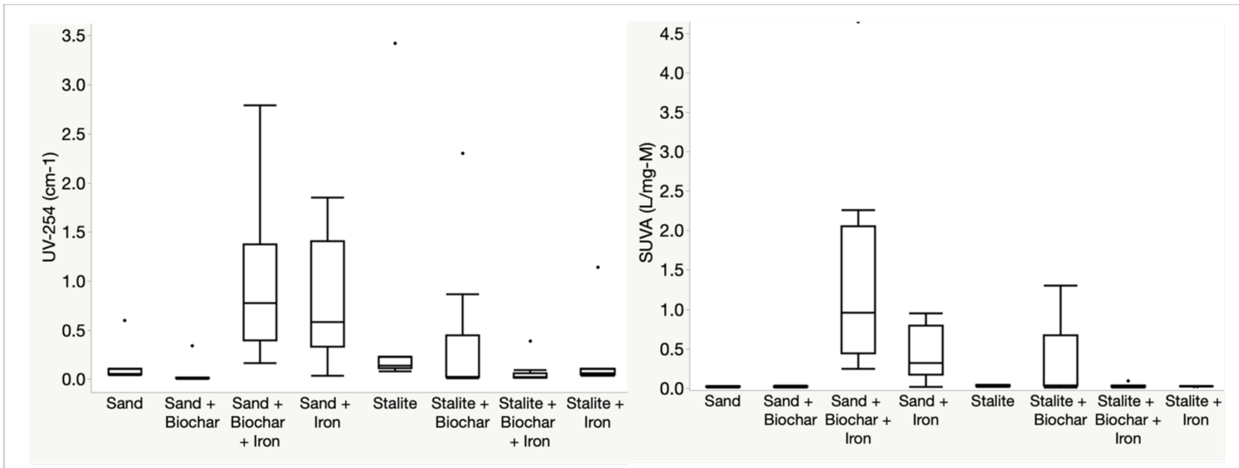

Figure A2. Phase 4.1 spiked stormwater effluent – UV-254 and SUVA.

Table A7. Phase 4.1 spiked stormwater effluent connecting letters report – UV-254 and SUVA.

	UV-254 (cm-1)		SUVA (L/mg-M)	
Influent	A			B
Sand		B		B
Sand + biochar		B		B
Sand + biochar + iron	A	B	A	
Sand + iron	A	B		B
Stalite		B		B
Stalite+ biochar	A	B		B
Stalite + biochar + iron		B		B
Stalite + iron		B		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

A8. Phase 4.1 - Dissolved Organic Carbon Influent

Dissolved organic carbon was analyzed in the spiked stormwater column influent (Table A8). Concentrations ranged from approximately 3 to 13 mg/L. This is slightly higher than what was measured in unspiked stormwater due to the added dissolved organic carbon spike.

Table A8. Phase 4.1 spiked stormwater influent data – Dissolved organic carbon.

	Minimum	Median	Maximum
DOC (mg/L)	2.80	5.16	12.9

A9. Phase 4.1 - Dissolved Organic Carbon Effluent

Dissolved organic carbon was analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal (Figure A3). For phase 4.1, all stormwater filtration columns significantly removed dissolved organic carbon from the spiked influent other than the Stalite filtration column (Table A9).

Significantly different removal rates were observed in the stormwater filtration columns for dissolved organic carbon (Table A3). The most significant removal rates of dissolved organic carbon from the spiked stormwater influent are observed for the sand + biochar, sand + biochar + iron, Stalite + biochar and Stalite + biochar + iron columns. For phase 4.1 here was no significant difference between the previously mentioned columns and they all removed dissolved organic carbon similarly.

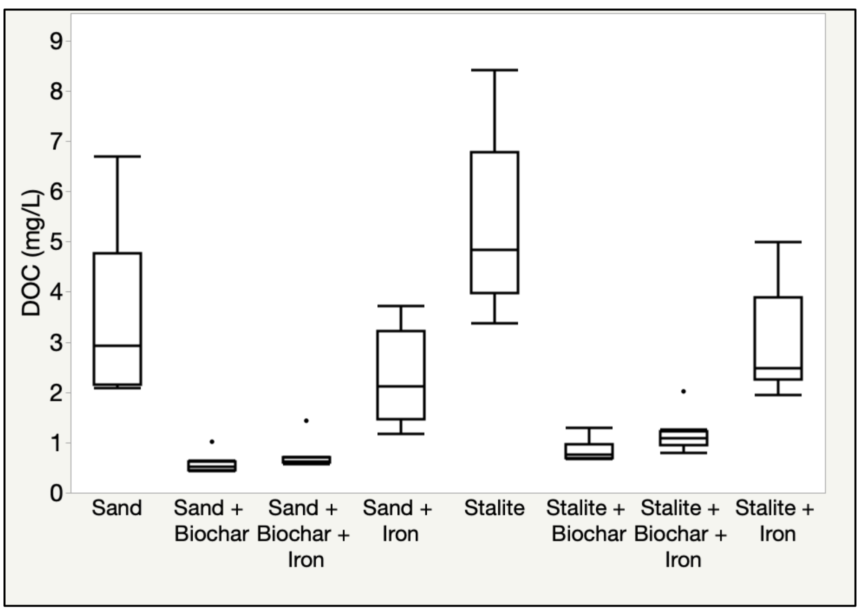

Figure A3. Phase 4.1 spiked stormwater effluent - Dissolved organic carbon.

Table A9. Phase 4.1 spiked stormwater effluent connecting letters report – Dissolved organic carbon.

	Dissolved Organic Carbon (mg/L)			
Influent	A			
Sand		B		
Sand + biochar				D
Sand + biochar + iron				D
Sand + iron		B	C	
Stalite	A			
Stalite + biochar				D
Stalite + biochar + iron			C	D
Stalite + iron		B		

*Levels not connected by the same letter are significantly different ($p<0.05$).

A10. Phase 4.2 - UVA and SUVA Influent

Parameters UVA and SUVA were analyzed in the spiked stormwater column influent (Table A10).

Table A10. Phase 4.2 spiked stormwater influent data - UV-254 and SUVA.

	Minimum	Median	Maximum
UVA Low Spike	0.318	0.333	0.558
UVA High Spike	2.51	2.86	3.03
SUVA Low Spike	0.0302	0.0416	0.195
SUVA High Spike	0.0737	0.388	0.443

A11. Phase 4.2 - UVA and SUVA Effluent

Parameters UVA and SUVA were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during high and low contaminant concentration periods (Figure A4). For phase 4.2, stormwater contaminant concentrations were alternated between low and high concentrations, as described in the methods section.

When stormwater influent had low contaminant concentrations, UV-254 was significantly different for sand and sand + iron, which were significantly greater than the influent

(Table A11). When stormwater influent had high contaminant concentrations, UV-254 was significantly greater than all stormwater filtration column effluent. With low contaminant concentrations, UV-254 for sand and sand + iron was significantly greater than all other filtration columns, and all other filtration columns were not significantly different from each other. With high contaminant concentrations, UV-254 for sand was significantly greater than all other filtration columns (Table A12).

When stormwater influent had low contaminant concentrations, SUVA for sand and sand + iron were significantly greater than the influent. When stormwater influent had high contaminant concentrations, SUVA was significantly greater than all stormwater filtration column effluent except for sand. With low contaminant concentrations, SUVA for sand + iron was significantly greater than all other filtration columns, and all other filtration columns were not significantly different from each other, other than sand, which was significantly greater than the remaining stormwater filtration columns. With high contaminant concentrations, SUVA for sand was significantly greater than all other filtration columns.

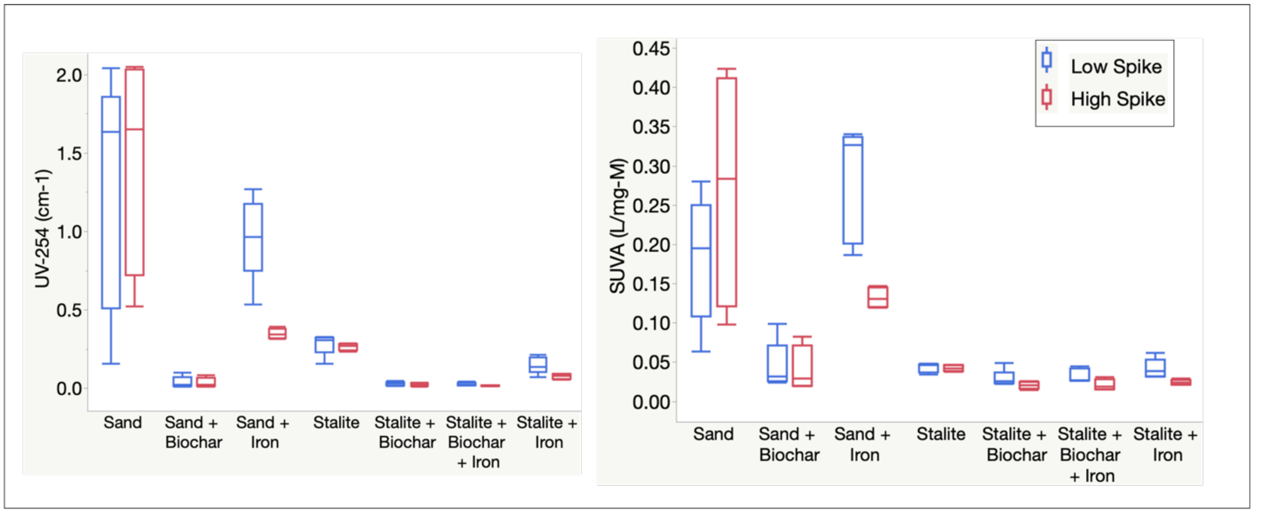

Figure A4. Phase 4.2 spiked stormwater effluent – UV-254 and SUVA.

Table A11. Phase 4.2 low-spiked stormwater effluent connecting letters report – UV-254 and SUVA.

	UV-254		SUVA		
Influent		B			C
Sand	A			B	
Sand + biochar		B			C
Sand + iron	A		A		
Stalite		B			C
Stalite+ biochar		B			C
Stalite + biochar + iron		B			C
Stalite + iron		B			C

Levels not connected by the same letter are significantly different ($p<0.05$).

Table A12. Phase 4.2 high-spiked stormwater effluent connecting letters report – UV-254 and SUVA.

	UV-254			SUVA	
Influent	A			A	
Sand		B		A	
Sand + biochar			C		B
Sand + iron			C		B
Stalite			C		B
Stalite+ biochar			C		B
Stalite + biochar + iron			C		B
Stalite + iron			C		B

Levels not connected by the same letter are significantly different ($p<0.05$).

A12. Phase 4.2 - DOC Influent

Dissolved organic carbon was analyzed in the spiked stormwater column influent (Table x).

Table A13. Phase 4.2 spiked stormwater influent concentrations – DOC.

	Minimum	Median	Maximum
DOC Low Spike	2.85	8.88	10.5
DOC High Spike	6.31	6.98	41.1

A13. Phase 4.2 – DOC Effluent

Dissolved organic carbon was analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal during high and low contaminant concentration periods (Figure A5).

When stormwater influent had low contaminant concentrations, sand and Stalite stormwater filtration column effluent displayed similar DOC concentrations (Table A14). The remaining filtration columns displayed significantly lower DOC concentrations than the influent. With low contaminant concentrations, sand and Stalite displayed similar DOC concentrations, sand + iron and Stalite + iron displayed similar DOC concentrations and sand + biochar, Stalite + biochar, and Stalite + biochar + iron displayed similar DOC concentrations. With high contaminant concentrations, all stormwater filtration column effluent DOC concentrations were significantly different from influent DOC concentrations (Table A15). With high contaminant concentrations, stormwater filtration column effluent were not significantly different between filtration columns.

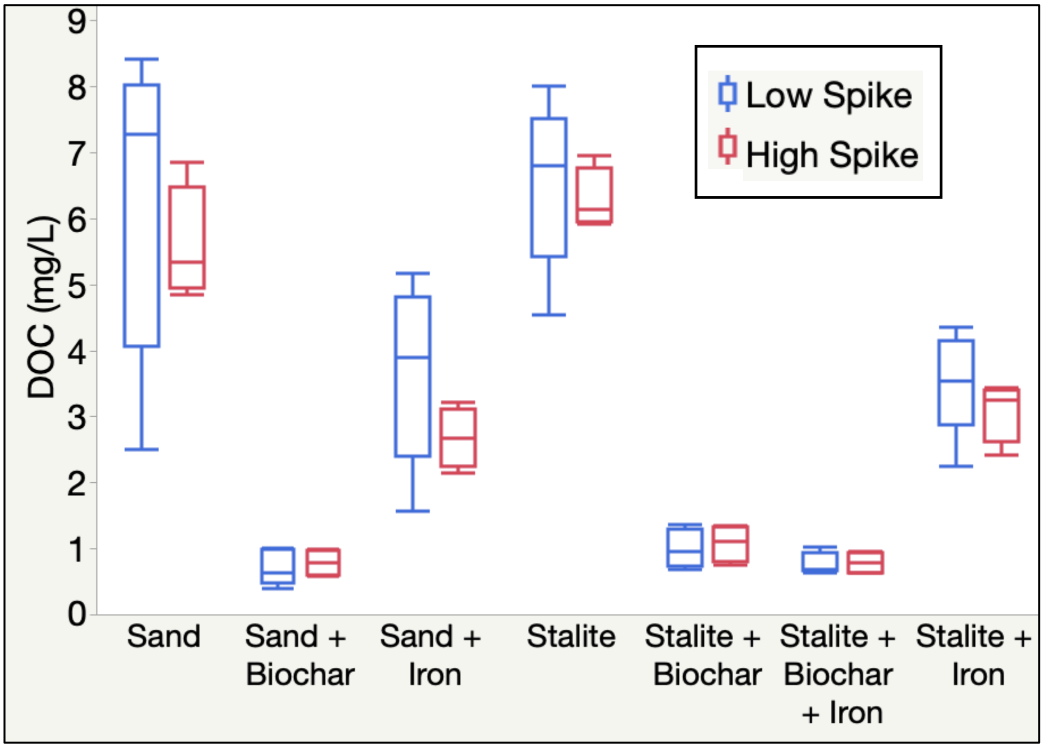

Figure A5. Phase 4.2 spiked stormwater effluent – DOC.

Table A14. Phase 4.2 low-spiked stormwater effluent connecting letters report – DOC.

	Dissolved Organic Carbon		
Influent	A		
Sand	A		
Sand + biochar			C
Sand + iron		B	
Stalite	A		
Stalite+ biochar			C
Stalite + biochar + iron			C
Stalite + iron		B	

Levels not connected by the same letter are significantly different ($p<0.05$).

Table A15. Phase 4.2 high-spiked stormwater effluent connecting letters report – DOC.

	Dissolved Organic Carbon	
Influent	A	
Sand		B
Sand + biochar		B
Sand + iron		B
Stalite		B
Stalite+ biochar		B
Stalite + biochar + iron		B
Stalite + iron		B

Levels not connected by the same letter are significantly different ($p<0.05$).

A14. Phase 4.3 – Pathogenic Indicator Influent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent (Table A16). Total coliform and fecal coliform displayed high influent concentrations; however, E. coli and enterococci ranged much lower for phase 4.3 influent. Pathogen indicator influent samples for Phase 4.3 were analyzed approximately 2 hours after column filtration.

Table A16. Phase 4.3 spiked stormwater influent data – Total coliform, fecal coliform, enterococci and E. coli.

	Minimum	Median	Maximum
MPN TC/100 mL	198.9	298.7	2419.6
MPN FC/100mL	1	456.45	2419.6
MPN Ent/100 ml	2	100.75	344.8
MPN E. coli/100 mL	17.3	140.2	344.8

A15. Phase 4.3 - Pathogen Indicator Effluent

Pathogen indicators were analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal after an antecedent drought (Figure A6). No significant total coliform removal was displayed from the influent (Table A17). Sand displayed the lowest removal of total coliform between the stormwater filtration columns while Stalite + biochar + iron and Stalite + iron displayed the greatest removal of total coliform.

No significant fecal coliform removal was displayed from the influent. Sand displayed the lowest removal of fecal coliform between the stormwater filtration columns while the remaining column displayed significantly greater fecal coliform removal.

All columns displayed significant E. coli and Enterococci removal from the influent except for sand. All stormwater filtration columns displayed similar E. coli and Enterococci removal except for sand, which displayed significantly lower removal for the two pathogen indicators.

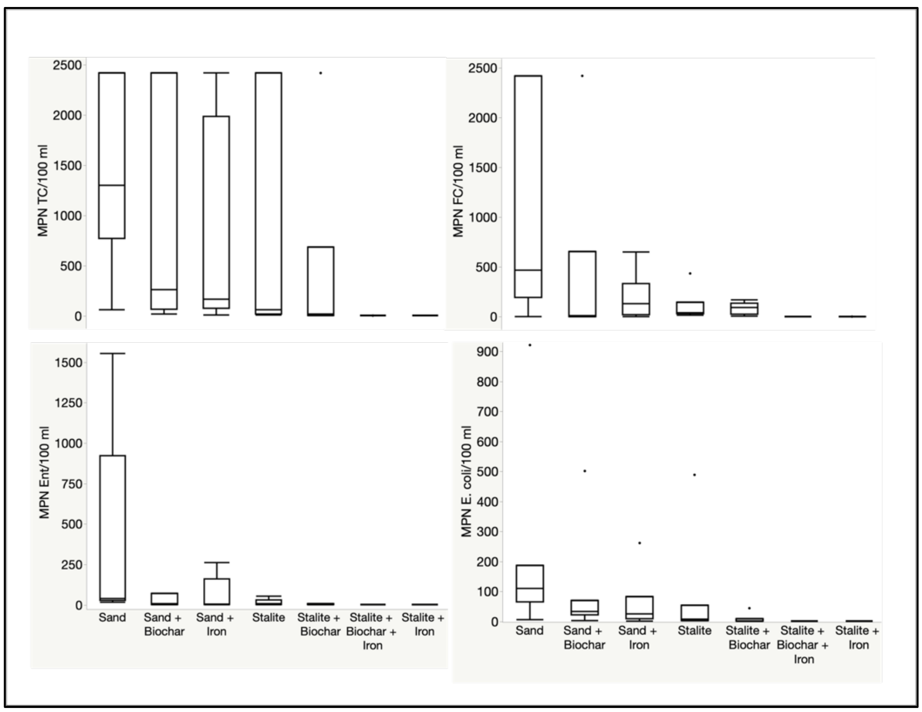

Figure A6. Phase 4.3 spiked stormwater effluent - Total coliform, fecal coliform, E. coli, and enterococci.

Table A17. Phase 4.3 spiked stormwater effluent connecting letters report - Total coliform, fecal coliform, E. coli, and enterococci.

	Total Coliform			Fecal Coliform		E. coli		Enterococci	
Influent	A	B	C	A	B	A		A	
Sand	A			A		A	B	A	B
Sand + biochar	A	B		A	B		B		B
Sand + iron	A	B	C		B		B		B
Stalite	A	B	C		B		B		B
Stalite + biochar		B	C		B		B		B
Stalite + biochar + iron			C		B		B		B
Stalite + iron			C		B		B		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

A16. Phase 4.3 - UVA and SUVA Influent

UV-254 and SUVA are both low, ranging from 0.603 to 0.9 cm-1 and 0.114 to 0.291 L/mg-M, respectively (Table A18).

Table A18. Phase 4.3 spiked stormwater influent data – SUVA and UV-254.

	Minimum	Median	Maximum
UV-254 (cm-1)	0.603	0.716	0.900
SUVA (L/mg-M)	0.114	0.131	0.291

A17. Phase 4.3 – UVA and SUVA Effluent

All stormwater filtration columns displayed significantly different UV-254 from the influent (Figure A7). Sand displayed significantly greater UV-254 while the remaining filtration columns displayed significantly lower UV-254 (Table A19). All filtration columns displayed significantly different SUVA from the influent. Sand, sand + biochar, and sand + iron displayed significantly greater SUVA while the remaining columns displayed significantly lower SUVA.

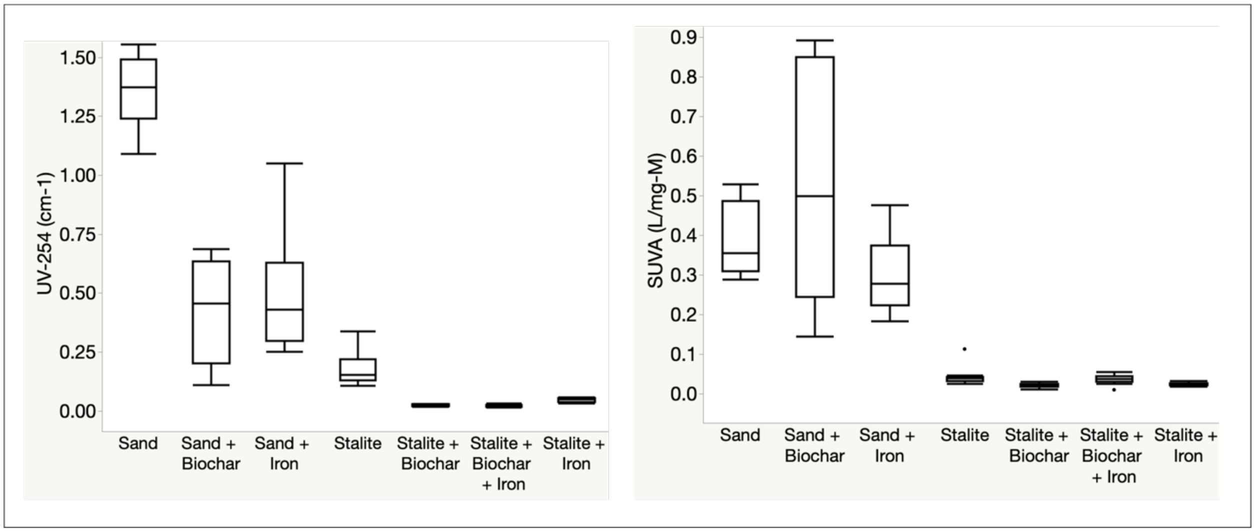

Figure A7. Phase 4.3 spiked stormwater effluent – UV-254 and SUVA.

Table A19. Phase 4.3 stormwater effluent connecting letters report –UV-254 and SUVA.

	UV-254					SUVA			
Influent		B						C	
Sand	A						B		
Sand + biochar			C			A			
Sand + iron			C				B		
Stalite				D					D
Stalite+ biochar					E				D
Stalite + biochar + iron					E				D
Stalite + iron					E				D

Levels not connected by the same letter are significantly different ($p<0.05$).

A18. Phase 4.3 – DOC Influent

Dissolved organic carbon was analyzed in the spiked stormwater column influent (Table A20). Influent DOC concentrations ranged from approximately 2.9 to 6.3 mg/L.

Table A20. Phase 4.3 spiked stormwater influent data – DOC.

	Minimum	Median	Maximum
DOC (mg/L)	2.87	5.08	6.29

A19. Phase 4.3 – DOC Effluent

Dissolved organic carbon was analyzed in the spiked stormwater column effluent to determine the most effective filter media for concurrent contaminant removal after an antecedent drought (Figure A8). All stormwater filtration columns displayed significantly lower DOC concentrations than the influent except for the Stalite filtration column (Table A21). Between filtration columns, Stalite + biochar + iron had the lowest DOC concentrations while Stalite had the greatest DOC concentrations.

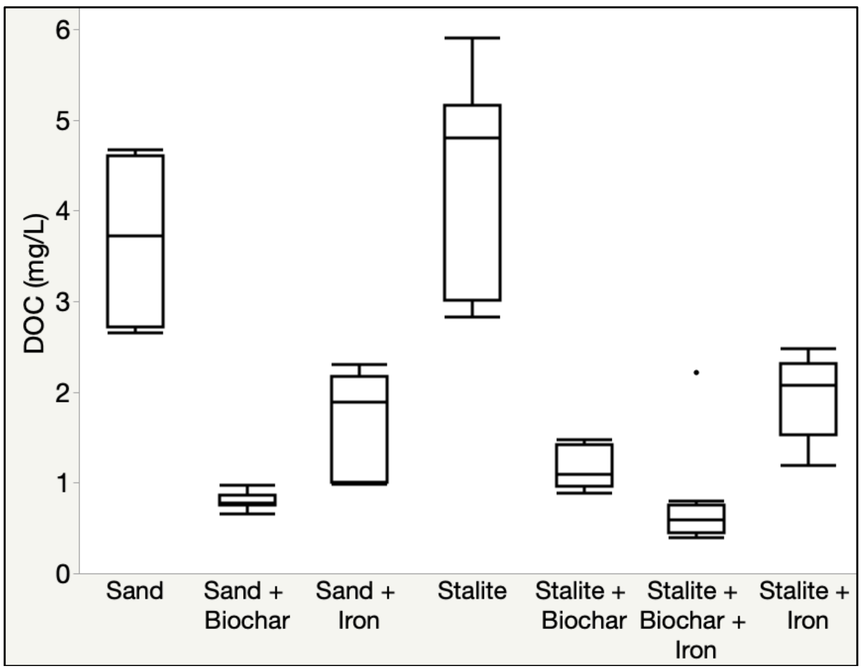

Figure A8. Phase 4.3 spiked stormwater effluent – DOC.

Table A21. Phase 4.3 spiked stormwater effluent connecting letters report – DOC.

	Dissolved Organic Carbon				
Influent	A				
Sand		B			
Sand + biochar					E
Sand + iron			C	D	
Stalite	A	B			
Stalite + biochar				D	E
Stalite + biochar + iron					E
Stalite + iron			C		

*Levels not connected by the same letter are significantly different ($p<0.05$).

A20. Phase 4.4 – Pathogen Indicator Influent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent (Table A22). Average influent concentrations were lower in Phase 4.4 than in earlier phases. Pathogen indicator influent samples for Phase 4.4 were analyzed approximately 2 hours after being removed from the refrigerator.

Table A22. Phase 4.4 spiked stormwater influent data – Total coliform, fecal coliform, enterococci and E. coli.

	Minimum	Median	Maximum
MPN TC/100 mL	29.2	303.75	2419.6
MPN FC/100mL	1	1	3.1
MPN Ent/100 ml	6.3	23.75	95.9
MPN E. coli/100 mL	1	4.25	30.1

A21. Phase 4.4 - Pathogen Indicator Effluent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent for comparison to effluent pathogen indicator concentrations (Figure A9). For total coliform, all stormwater filtration columns displayed significantly lower concentrations, except for sand which was similar to the influent (Table A23). Between columns, sand, sand + biochar and Stalite displayed significantly greater total coliform concentrations than the remaining stormwater filtration columns.

For fecal coliform, all stormwater filtration columns displayed similar concentrations to the influent except for Stalite + biochar, which displayed significantly greater concentrations. Between filtration columns, Stalite + biochar displayed significantly greater fecal coliform concentrations than the remaining filtration columns.

For E. coli, sand, sand + biochar, and Stalite stormwater filtration columns displayed similar concentrations to the influent while the remaining filtration columns displayed significantly lower concentrations. Between filtration columns, sand, sand + biochar, and Stalite displayed significantly greater E. coli concentrations than the remaining filtration columns.

For Enterococci, the Stalite stormwater filtration column displayed a similar concentration to the influent while the remaining filtration columns displayed significantly different concentrations. Between columns, the sand filtration column displayed the greatest enterococci concentrations while Stalite + iron filtration column displayed the lowest enterococci concentrations.

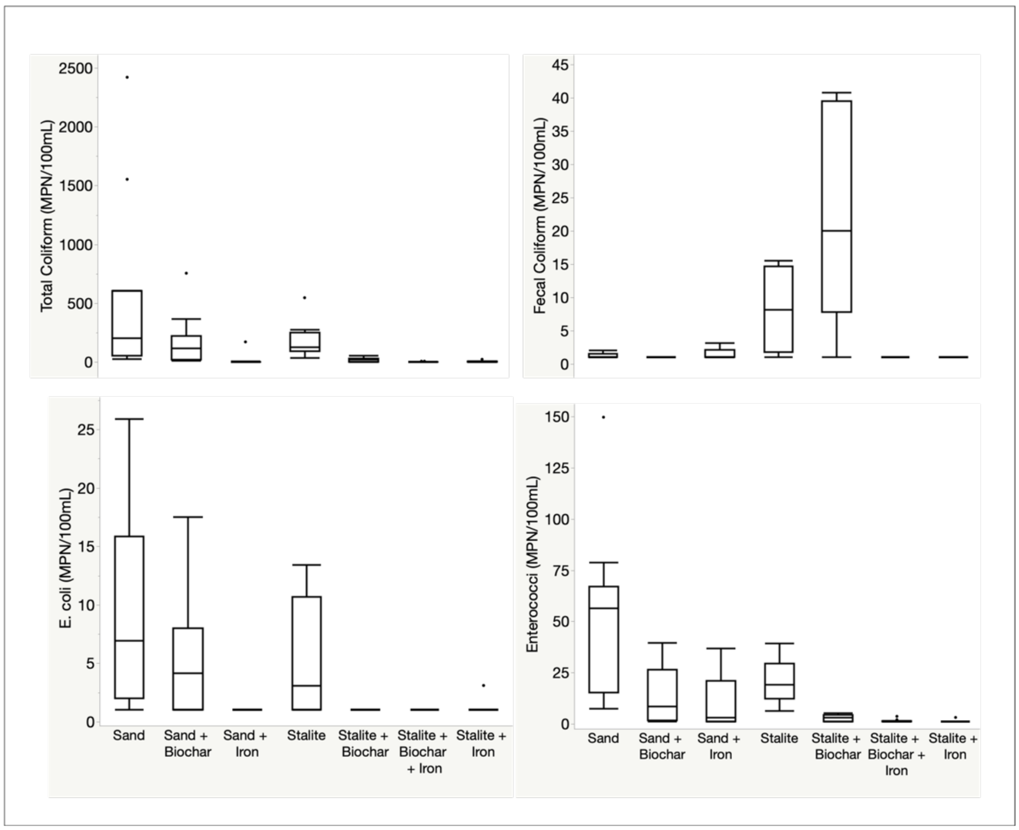

Figure A9. Phase 4.4 spiked stormwater effluent – Total coliform, fecal coliform, E. coli, and enterococci.

Table A23. Phase 4.4 spiked stormwater effluent connecting letters report – Total coliform, fecal coliform, E. coli, and enterococci.

	Total Coliform			Fecal Coliform		E. coli		Enterococci			
Influent	A				B	A			B		
Sand	A	B			B	A		A			
Sand + biochar		B	C		B	A	B			C	D
Sand + iron			C		B		B			C	D
Stalite		B	C		B	A	B		B	C	
Stalite + biochar			C	A			B			C	D
Stalite + biochar + iron			C		B		B			C	D
Stalite + iron			C		B		B				D

*Levels not connected by the same letter are significantly different ($p<0.05$).

A22. Phase 4.4 – UVA and SUVA

Parameters UVA and SUVA were analyzed in the spiked stormwater column influent (Table A24). UV-254 and SUVA are both low, ranging from 0.941 to 1.105 cm-1 and 0.244 to 0.332 L/mg-M, respectively.

Table A24. Phase 4.4 spiked stormwater influent data – UV-254 and SUVA.

	Minimum	Median	Maximum
UV-254 (cm-1)	0.941	1.06	1.10
SUVA (L/mg-M)	0.244	0.293	0.333

A23. Phase 4.4 - UVA and SUVA Effluent

For UVA, all stormwater filtration column effluent displayed significantly different values except for sand + biochar, sand + iron and Stalite column effluent, which was similar to the influent UVA value (A10). Sand column effluent displayed significantly greater values than the influent. Between columns, sand filtration column effluent displayed significantly greater UVA values than the remaining filtration columns, while Stalite + biochar, Stalite + biochar + iron, and Stalite + iron column effluent displayed the lowest UVA values.

For SUVA, all stormwater filtration column effluent displayed significantly different values from the influent except for sand + biochar, Stalite, and Stalite + biochar + iron column effluent, which was similar to the influent. Sand and sand + iron column effluent displayed significantly greater values than the influent. Between columns, sand and sand + iron displayed significantly greater SUVA values while Stalite + biochar and Stalite + iron column effluent displayed the lowest SUVA values.

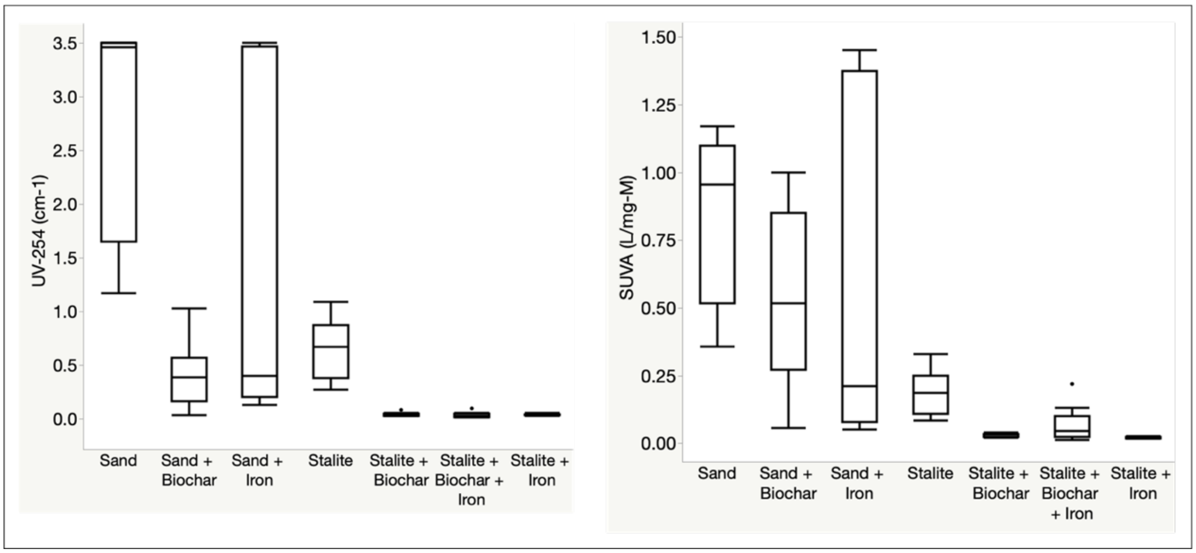

Figure A10. Phase 4.4 spiked stormwater effluent – UV-254 and SUVA.

Table A25. Phase 4.4 spiked stormwater effluent connecting letters report – UV-254 and SUVA.

	UV-254				SUVA				
Influent		B	C				C	D	
Sand	A				A				
Sand + biochar			C	D		B	C		
Sand + iron		B			A	B			
Stalite			C	D				D	E
Stalite + biochar				D					E
Stalite + biochar + iron				D				D	E
Stalite + iron				D					E

A24. Phase 4.4 - DOC Influent

Dissolved organic carbon was analyzed in the spiked stormwater column influent (Table A26). Influent concentrations ranged from approximately 3.2 to 4 mg/L.

Table A26. Phase 4.4 spiked stormwater influent data – DOC.

	Influent		
	Minimum	Median	Maximum
DOC (mg/L)	3.26	3.49	3.92

A25. Phase 4.4 - DOC Effluent

Dissolved organic carbon was analyzed in the spiked stormwater column influent for comparison to effluent concentrations (Figure A11). All stormwater filtration columns except for sand and Stalite displayed significantly lower DOC concentrations than the influent (Table A27). Between columns, sand filtration column effluent displayed similar concentrations to Stalite column effluent, which both displayed the highest DOC concentrations. Sand + biochar and Stalite + biochar + iron displayed the lowest DOC concentrations.

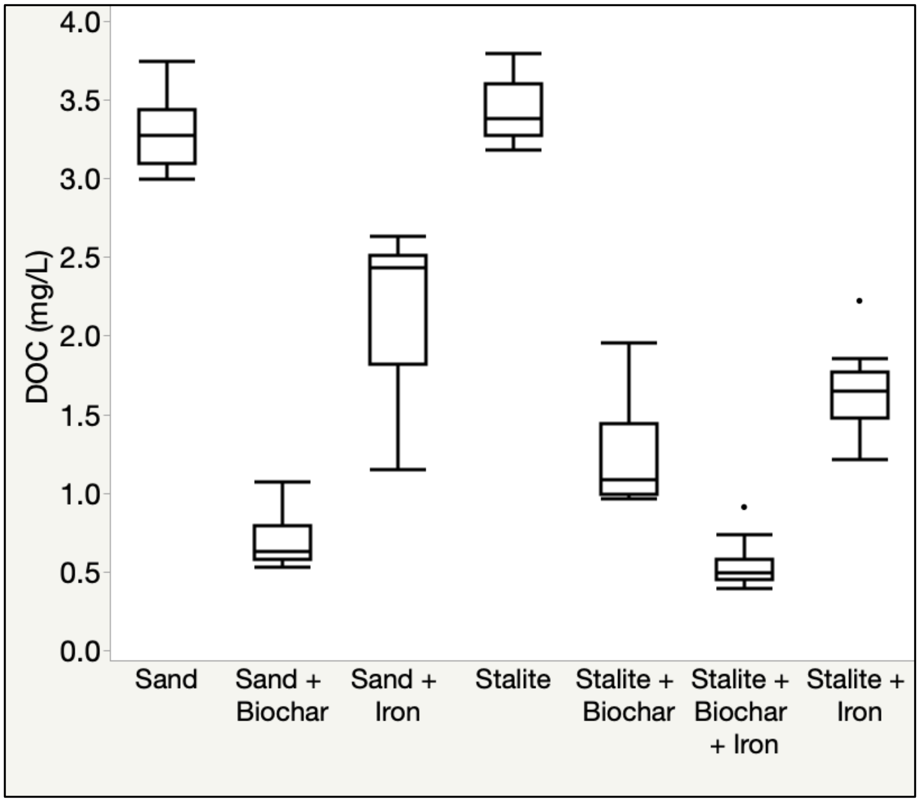

Figure A11. Phase 4.4 spiked stormwater effluent – DOC.

Table A27. Phase 4.4 spiked stormwater effluent connecting letters report – DOC.

	DOC					
Influent	A					
Sand		B				
Sand + biochar						F
Sand + iron			C			
Stalite	A	B				
Stalite + biochar					E	
Stalite + biochar + iron						F
Stalite + iron				D		

*Levels not connected by the same letter are significantly different ($p<0.05$).

A26. Phase 4.5 – Pathogen Indicator Influent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent (Table A28). Average influent concentrations were lower in Phase 4.5 than in earlier phases. Pathogen indicator influent samples for Phase 4.5 were analyzed approximately 2 hours after being removed from the refrigerator.

Table A28. Phase 4.5 spiked stormwater influent data – Total coliform, fecal coliform, enterococci and E. coli.

	Minimum	Median	Maximum
MPN TC/100 mL	9.8	80.55	461.1
MPN FC/100mL	1	1	1
MPN Ent/100 ml	1	1	5.2
MPN E. coli/100 mL	1	5.2	16

A27. Phase 4.5 – Pathogen Indicator Effluent

TC, FC, Ent, and E. coli were analyzed in the spiked stormwater column influent for comparison to effluent pathogen indicator concentrations (Figure A12). For total coliform, sand, sand + biochar, sand + iron, and Stalite displayed similar concentrations to the influent while the remaining filtration columns displayed significantly lower concentrations to the influent (Table A29). Between columns, Stalite + biochar + iron displayed the lowest total coliform concentrations.

For fecal coliform, all columns displayed similar concentrations to the influent except for the Stalite + biochar column, which displayed significantly greater fecal coliform concentrations. Between columns, Stalite + biochar displayed the greatest fecal coliform concentrations while sand and sand + iron displayed the lowest concentrations.

For E. coli, all columns were similar to the influent E. coli concentration and each other, with E. coli concentrations close to zero for the influent and all columns.

For Enterococci, all columns were similar to the influent Enterococci concentration except for sand, which displayed significantly higher concentrations than the influent. Sand displayed significantly greater Enterococci concentrations than the remaining stormwater filtration columns as well.

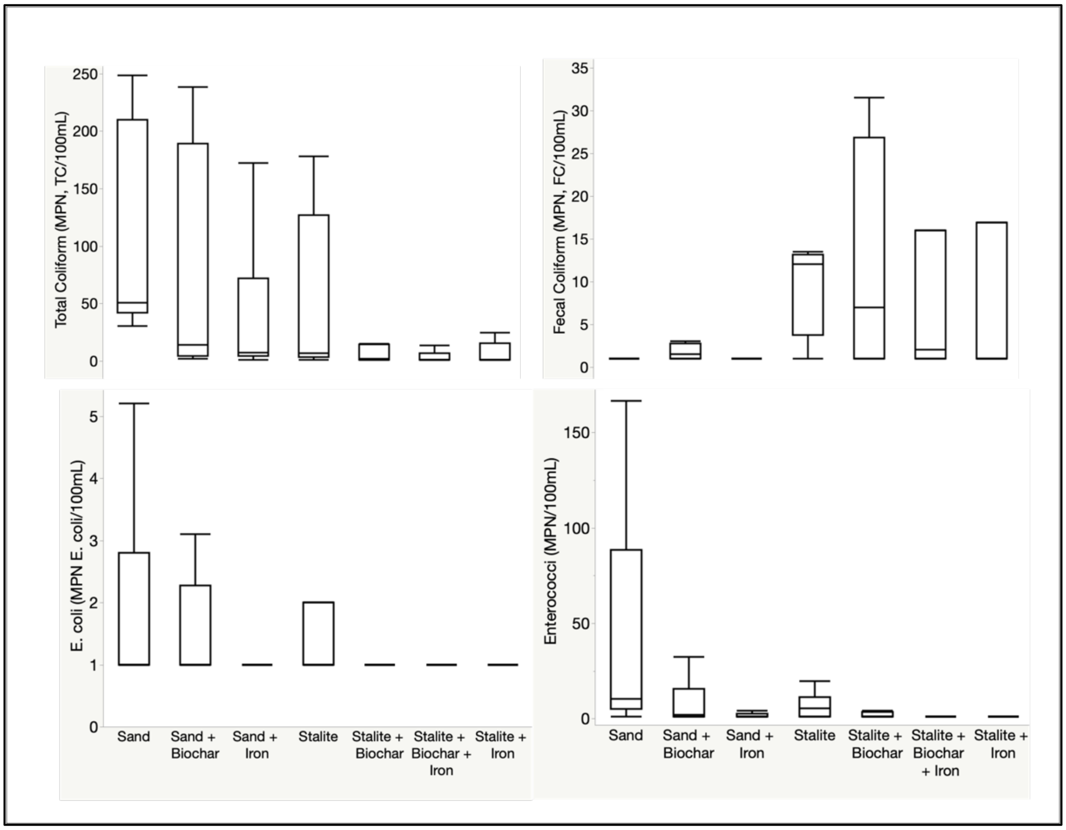

Figure A12. Phase 4.5 spiked stormwater effluent – Total coliform, fecal coliform, E. coli, and enterococci.

Table A29. Phase 4.5 spiked stormwater effluent connecting letters report - Total coliform, fecal coliform, E. coli, and enterococci.

	Total Coliform			Fecal Coliform		E. coli	Enterococci	
Influent	A				B	A		B
Sand	A	B			B	A	A	
Sand + biochar	A	B	C	A	B	A		B
Sand + iron	A	B	C		B	A		B
Stalite	A	B	C	A	B	A		B
Stalite + biochar		B	C	A		A		B
Stalite + biochar + iron			C	A	B	A		B
Stalite + iron		B	C	A	B	A		B

*Levels not connected by the same letter are significantly different ($p<0.05$).

A28. Phase 4.5 - UVA and SUVA Influent

UV-254 and SUVA are both low, ranging from 0.715 to 1.071 cm-1 and 0.135 to 0.298 L/mg-M, respectively (Table A30).

Table A30. Phase 4.5 spiked stormwater influent data – UV-254 and SUVA.

	Minimum	Median	Maximum
UV-254 (cm-1)	0.715	0.764	1.07
SUVA (L/mg-M)	0.135	0.225	0.298

A29. Phase 4.5 - UVA and SUVA Effluent

For UVA, all stormwater filtration column effluent displayed significantly different values except for sand + iron and Stalite column effluent, which was similar to the influent UVA value (Figure A13). Between columns, sand and sand + biochar filtration column effluent displayed significantly greater UVA values than the remaining filtration columns, while Stalite + biochar + iron displayed the lowest UVA values (Table A31).

For SUVA, all stormwater filtration column effluent displayed similar values except for sand and sand + biochar, which were significantly greater than the influent SUVA values. Between columns, sand and sand + biochar displayed significantly greater SUVA values while Stalite +biochar + iron displayed the lowest SUVA values.

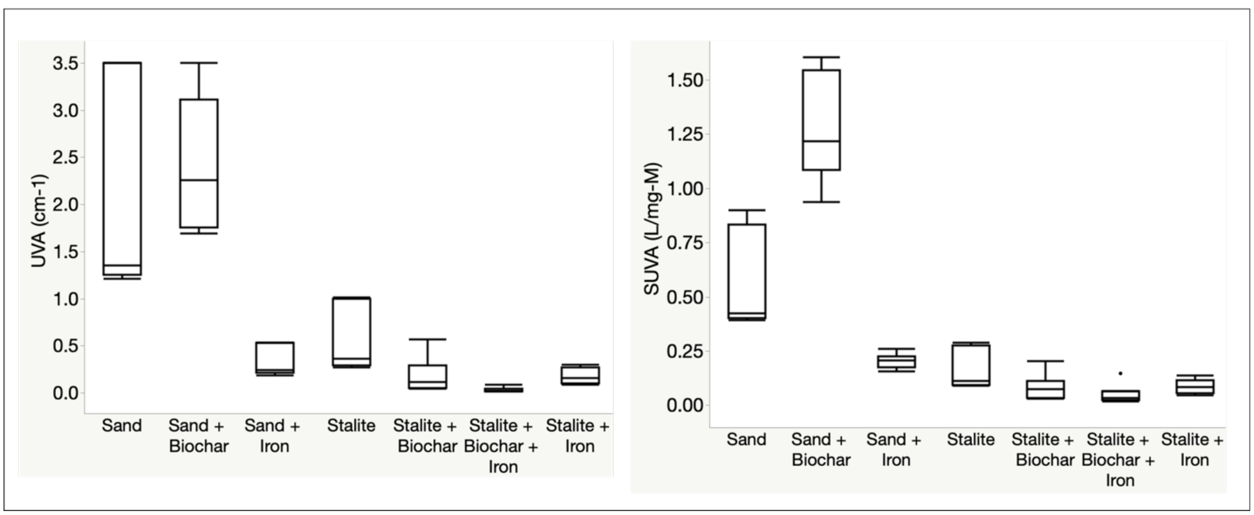

Figure A13. Phase 4.5 spiked stormwater effluent – UV-254 and SUVA.

Table A31. Phase 4.5 spiked stormwater effluent connecting letters report – UV-254 and SUVA.

	UV-254			SUVA			
Influent		B				C	
Sand	A				B		
Sand + biochar	A			A			
Sand + iron		B	C			C	
Stalite		B	C			C	D
Stalite + biochar			C			C	D
Stalite + biochar + iron			C				D
Stalite + iron			C			C	D

*Levels not connected by the same letter are significantly different ($p<0.05$).

A30. Phase 4.5 – DOC Influent

Dissolved organic carbon was analyzed in the spiked stormwater column influent (Table A32). Influent concentrations ranged from approximately 3 to 5 mg/L.

Table A32. Phase 4.5 spiked stormwater influent data – Dissolved organic carbon.

	Minimum	Median	Maximum
DOC (mg/L)	3.06	3.66	5.29

A31. Phase 4.5 - DOC Effluent

Dissolved organic carbon was analyzed in the spiked stormwater column influent for comparison to effluent concentrations (Figure 14). All stormwater filtration columns except for sand and Stalite displayed significantly lower DOC concentrations than the influent (Table A33). Between columns, sand displayed the greater DOC concentrations while Stalite + biochar + iron displayed the lowest DOC concentrations.

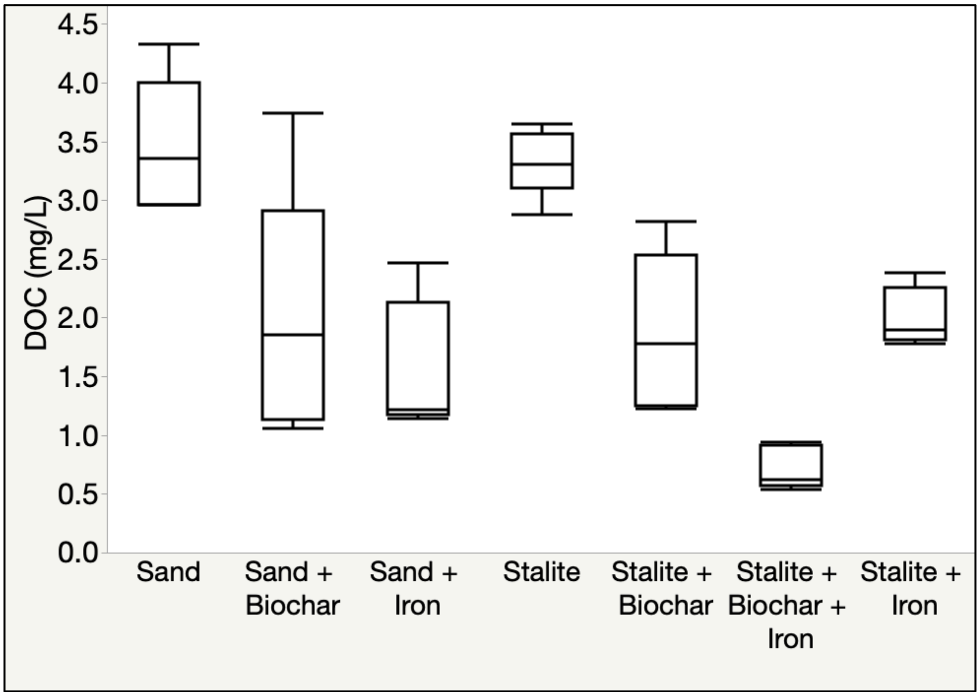

Figure A14. Phase 4.5 spiked stormwater effluent – DOC.

Table A33. Phase 4.5 spiked stormwater effluent connecting letters report – DOC.

	DOC		
Influent	A		
Sand	A		
Sand + biochar		B	
Sand + iron		B	
Stalite	A		
Stalite + biochar		B	
Stalite + biochar + iron			C
Stalite + iron		B	

*Levels not connected by the same letter are significantly different ($p<0.05$).