

Deliverable 3: Report on Chemistry of Clean Water Effluent and WSU-Puyallup Lab Water

Report Summary

Column Construction and Experimental Setup

- Experimental columns were constructed using 6"-diameter PVC pipes containing varying depths of bioretention soil media (18", 15", 12", 9", and 6") in triplicate. Three additional columns contain 18" of soil media and serve as the clean water controls.
- A K_{sat} rate of >50 cm/hour (> 20 inches/hr) and a bulk density of 1.4 g/cm³ were targeted.

Clean Water Conditioning

- Of the metals tested, copper was the most concentrated in the effluent of clean water flushed through the experimental columns.
- 15- and 18-inch BSM treatment depths tended to leach greater concentrations of arsenic, zinc, and copper than from the 6- and 9-inch treatments.
- Nitrates (the sum of nitrate and nitrite; hereafter 'nitrate') were more concentrated than orthophosphate in effluent from all columns.
- Nitrate concentrations were significantly greater in effluent from the 6- and 9-inch BSM treatments than from the 15- and 18-inch treatments.

Baseline Saturated Hydraulic Conductivity

- The falling head method was used to determine the baseline saturated hydraulic conductivity (K_{sat}) of the experimental columns.
- K_{sat} values were greater than the target rate, most likely due to difficulties in compacting BSM to the levels needed to achieve the target bulk density.

1. Column Construction & Experimental Setup

Experimental columns were constructed at the WSU-Puyallup Aquatic Toxicology Laboratory using PVC components. PVC (6-inch diameter) was cut to lengths of 35, 32, 29, 26, and 23 inches to accommodate the various BSM depths plus 12" of gravel, 2" of mulch, approximately 3" for ponding, and 1" for air flow into each of the columns (Figure 1). Holes (8-1/4") were drilled in the top inch of each column to allow for airflow to the tops of the columns. The inside of the columns were scoured using a wire brush to deter preferential flow down the sides of the columns. The columns were lightly washed with a dilute acetone mixture (approximately 90% RO water, 10% acetone).

A PVC reducer, elbow slip, and valve slip was attached to the base of each column. All PVC components were joined using PVC primer and cement. To achieve a consistent cross-sectional area of BSM within the columns, 12-mm food-safe glass marbles were used to fill the reducer at the base of each column. Prior to placement in the columns, marbles were acid-washed in hydrochloric acid and then oven-dried at 490 °C for 6 hours. Within

the columns, marbles were placed on top of and then covered with stainless steel mesh (#20) to prevent BSM components from washing out of the system.

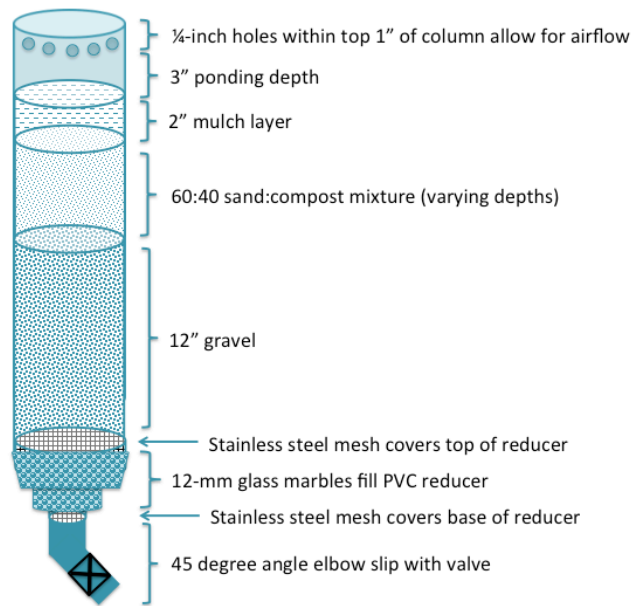


Figure 1. Experimental column construction.

Wooden bracing was constructed within the outbuilding where the columns are being housed to support the columns above the floor. Wooden shims were used to approximately level columns (Figure 2). Galvanized steel plumbers tape was then added around each of the columns to secure the columns in place. Stainless steel containers (12" x 15" x 23") were placed on the floor below the valve slip draining each column.



Figure 2. Experimental setup in temperature-controlled room.

Once columns were secured in the outbuilding, they were filled with BSM components. Compost, arborist mulch, and sand were donated by Cedar Grove Composting, Inc. (Maple Valley, WA, USA). City of Seattle type 26 drain aggregate (3/4" washed sandy gravel) was donated by Washington Rock Quarries, Inc. Each of these materials met SWMMWWW specifications for use in bioretention systems.

The various depths of 60:40 sand:compost BSM mixture were added atop 12" of gravel in each column. To obtain a consistent and well-mixed BSM, 10-L batches were individually prepared. Compost was sifted through a 1.3-cm screen (100% passing) to achieve a relatively even density. Sand and compost were proportioned into each batch by volume. Each batch was prepared in a contractor bag and shaken until well homogenized. The wet weight of each batch was recorded. Sub-samples were taken from each batch for moisture content analysis (ASTM D2216-10). Moisture content data was used to estimate the dry mass of each BSM batch. The dry mass of each batch was then used to determine the wet mass to be added to each column to achieve the target bulk density.

A K_{sat} rate of >50 cm/hour (> 20 inches/hr) was targeted. To achieve this desired K_{sat} , a bulk density of 1.4 g/cm³ was targeted when experimental columns were filled with BSM. Target bulk density was determined using a plot of saturated hydraulic conductivity as a function of soil bulk density experimentally derived by Taylor et al. (2018). As this study utilized the same BSM formulation being used in the current study, this plot was used to determine the target bulk density for the current study. As BSM was added to the columns, it was compacted every 3 inches using a 5.5-inch tamper. Following compaction, columns were covered with 2" of arborist mulch.

Three peristaltic pumps dispense water to the columns at a target rate of 38.6 mL/min per column via rainheads that were printed from polyethylene terephthalate glycol (PETG) and affixed to the top of each column. Each rainhead is approximately 4 inches in diameter and dispenses water via 19 0.8-mm holes. Water is drawn into the outbuilding from just outside of the outbuilding via four manifolds constructed of PVC components. These manifolds run the length of the outbuilding, beginning just outside the front wall, running through holes cut into the front wall of the outbuilding, and ending at the back where the pumps are located. The purpose of the manifolds was to reduce the amount of overall tubing needed and to minimize the size and number of the openings that needed to be cut into the front wall of the outbuilding. Together the manifolds consist of 18 ports. Silicone tubing connected to these ports runs through the pumps and then to each of the 18 rainheads.

2. Clean Water Conditioning

Experimental columns were flushed with clean water in order to characterize the chemical composition of water passing through the BSM prior to the application of stormwater runoff. Clean water was municipal water treated by reverse osmosis and re-constitution with salts for rearing fish at WSU-Puyallup.

A volume of three times the pore volume of the BSM for each column was applied to each column at 29-50 mL/min (avg = 38). The effluent from these three pore volumes was discarded and an additional three pore volumes of clean water was applied. Influent and

effluent waters from these next three pore volumes were sampled for chemical analyses. Three pore volumes were needed to obtain a sufficient volume for all chemical analyses. PAHs were not analyzed during column conditioning.

Metals

Copper was more concentrated than other tested metals in the effluent of clean water flushed through the experimental columns (Table 1; Figure 3). This is in contrast to the leach test, in which zinc was leached at the greatest concentration from all of the BSM components (SAM project: “Longevity of Bioretention Depths for Preventing Acute Toxicity from Urban Stormwater Runoff”, Deliverable 2). For each treatment depth, metals were detected in effluent samples in the order of copper > nickel > zinc > arsenic > lead. Aside from zinc, this order corresponds with the order of metal concentrations from individually leached bioretention components. A Kruskal-Wallis test was performed to compare medians of the treatment groups for each analyte. This test revealed statistically significant differences in concentrations of arsenic ($\chi^2(5) = 13.8, p=0.017$), zinc ($\chi^2(5) = 12.7, p=0.027$), and copper ($\chi^2(5) = 11.9, p = 0.037$) among treatment groups (BSM depths). For those analytes with a significant difference among treatment groups, a post-hoc Dunn’s test was performed to determine where differences occurred between treatment groups. The 15- and 18-inch BSM treatment depths tended to leach greater concentrations of As, Zn, and Cu than the 6- and 9-inch depth treatments. These differences could be due to the small sorption capacity of the gravel layer, the depth of which is constant in all of the columns. In the columns with the lesser depths, the majority of the metals leached from the BSM media may have sorbed to the gravel. In the larger columns, which were flushed with a greater volume of water, the sorption capacity of the gravel may have been exceeded before all of the water had been flushed through the columns. In the influent water sample, only copper and nickel were above the analytical detection limits. Cadmium was below the detection limit in all samples. Results for dissolved metals were very similar and followed the same general patterns as for total metals (Table 2).

Concentrations of metals (and of nutrients) in effluents from column conditioning with clean water were less than concentrations measured in the leach tests. This was expected because there was less contact between water and the BSM components during column conditioning than during the leach test. Additionally, the water source varied between the two tests. During column conditioning, WSU-Puyallup lab water (pH = 7.70) flowed through the BSM whereas during the leach test BSM components were completely submerged in and agitated with an acidic extraction fluid (reverse osmosis water adjusted to a pH of 5.00).

The solubility of heavy metals in soils generally increases with decreasing pH. Differences in pH between the solutions used in the leach test and column conditioning therefore likely explain differences in metal concentrations between the two tests. Differences in the order of metals leaching between the two tests may also be explained by pH differences. At neutral pH, dissolved metal concentrations in soil water extracts are dominated by DOC-metal complexes. At low pH, free ionic forms of the metals dominate (Reddy 1995). Dissolved organic matter (DOM) can form complexes with metals and increase their mobility (Christensen et al. 1996; Ashworth and Alloway 2003). Christensen et al. (1996) found that the presence of DOC lowered the adsorption-desorption

distribution coefficients (K_d) of the metals Cd, Ni, and Zn. However, DOM concentration may have less of an effect on the mobility of zinc than on other heavy metals (such as copper and nickel) (Christensen et al. 1996; Ashworth and Alloway 2003). This may explain why during column conditioning, when the pH was close to neutral, metals other than zinc dominated. During the leach tests, in which the extraction fluid had a much lower pH, metals would have leached predominantly in free ionic forms and were dominated by zinc, which is considered a highly mobile metal (Rutkowska et al. 2015). Furthermore, the dissolved/total metals ratios for zinc and lead were greater in the leach test than in effluent from column conditioning (Figure 4). During column conditioning, the dissolved/total metals ratios for copper and nickel were greater than in the leach test. Copper and nickel have a higher affinity for DOC, which is likely to complex with and increase desorption and mobility of these metals at neutral pH.

Table 1. Summary of total metal concentrations in influent (clean water) and triplicate effluent samples from each of the five treatment depths plus the clean water control (CWC). Values presented are mean (standard deviation).

Analyte	Detection Limit (µg/L)	Effluent Water (µg/L)						
		Influent Water	6"	9"	12"	15"	18"	18" CWC
Arsenic	0.05	BDL	2.1 (0.5) ^a	3 (1) ^a	6.5 (0.4) ^{ab}	7.3 (0.7) ^b	7.2 (0.7) ^b	7.6 (0.5) ^b
Cadmium	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Copper	0.2	1.3	34 (2) ^{ac}	41 (7) ^{ac}	50 (1) ^{bc}	48 (5) ^{bc}	48 (2) ^{bc}	47.1 (0.5) ^c
Lead	0.079	BDL	0.4 (0.4)	0.5 (0.5)	1.07 (0.06)	1.2 (0.2)	1.2 (0.2)	1.2 (0.4)
Nickel	0.20	0.9	14 (1)	15 (1)	17.2 (0.4)	17 (2)	17.9 (0.5)	18 (1)
Zinc	0.19	BDL	4.0 (0.6) ^a	5 (2) ^a	8.6 (0.9) ^{ab}	9.4 (0.6) ^b	9.7 (0.6) ^b	10 (2) ^b

BDL = Below Detection Limit

Note: Treatments with different superscript group labels (a, b, c) show significance at $\alpha = 0.05$ (Kruskal-Wallis with post-hoc Dunn Test).

Table 2. Summary of dissolved metal concentrations in influent (clean water) and triplicate effluent samples from each of the five treatment depth plus the clean water control (CWC). Values presented are mean (standard deviation).

Analyte	Detection Limit ($\mu\text{g/L}$)	Effluent Water ($\mu\text{g/L}$)						
		Influent water	6"	9"	12"	15"	18"	18" CWC
Arsenic	0.05	BDL	1.7 (0.4) ^a	3 (1) ^{ab}	5.9 (0.7) ^{abc}	7 (1) ^{bc}	6.9 (1.0) ^c	7.3 (0.8) ^c
Cadmium	0.05	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Copper	0.05	0.8	31 (3) ^a	36 (6) ^{ab}	45.1 (0.4) ^b	44 (3) ^b	45.1 (0.8) ^b	44 (5) ^b
Lead	0.079	BDL	BDL	BDL	BDL	BDL	BDL	BDL*
Nickel	0.20	0.90	13 (2) ^a	13.8 (0.6) ^a	15.8 (0.2) ^{ab}	15 (1) ^{ab}	16.5 (0.6) ^b	17 (2) ^b
Zinc	0.19	BDL	2.1 (0.7) ^a	2.6 (0.6) ^a	5 (1) ^b	4.6 (0.8) ^b	7 (5) ^b	7 (4) ^b
Calcium	3.4	6.5	94 (20) ^a	74 (8) ^{ab}	55.0 (0.6) ^{abc}	47 (2) ^{bc}	46 (2) ^c	44 (2) ^c
Magnesium	1.9	18.9	24 (5) ^a	19 (2) ^a	14.2 (0.2) ^{ab}	12.1 (0.3) ^b	12.6 (0.6) ^b	12.4 (0.3) ^b
Sodium	27	197	181 (10)	183 (9)	167 (6)	169 (7)	177 (9)	167 (6)

BDL = Below Detection Limit

*One replicate had a value of 1.0 $\mu\text{g/L}$. This outlier is considered detection contamination because all other samples were below the detection limit of 0.079 $\mu\text{g/L}$ and does not agree with the low inter-replicate variability in total Pb for these samples (Table 1).

Note: Treatments with different superscript group labels (a, b, c) show significance at $\alpha = 0.05$ (Kruskal-Wallis with post-hoc Dunn Test).

Metal Concentrations in Leachate and Clean Water Conditioning Experiments

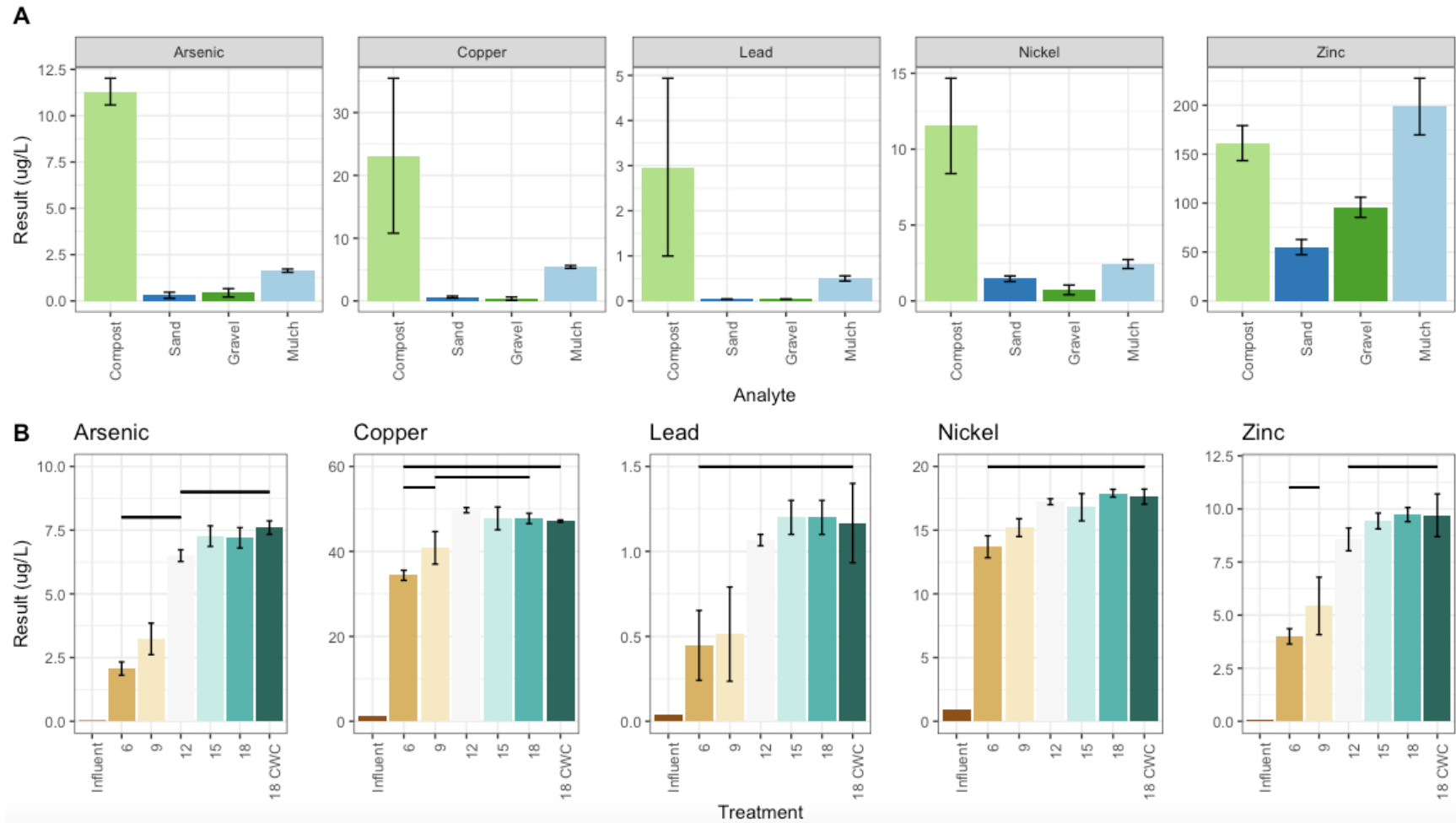


Figure 3. Comparison of A) total metal concentrations in bioretention soil media (BSM) leachate and B) total metal concentrations in influent (lab water) and triplicate samples of effluent from each of the five treatment depths (6", 9", 12", 15", 18") plus the clean water control (18" CWC) during column conditioning. Horizontal bars represent depths that share statistical significance at $\alpha = 0.05$. Error bars are one standard error of the mean.

Dissolved/Total Metal Ratios in Leachate and Clean Water Conditioning Experiments

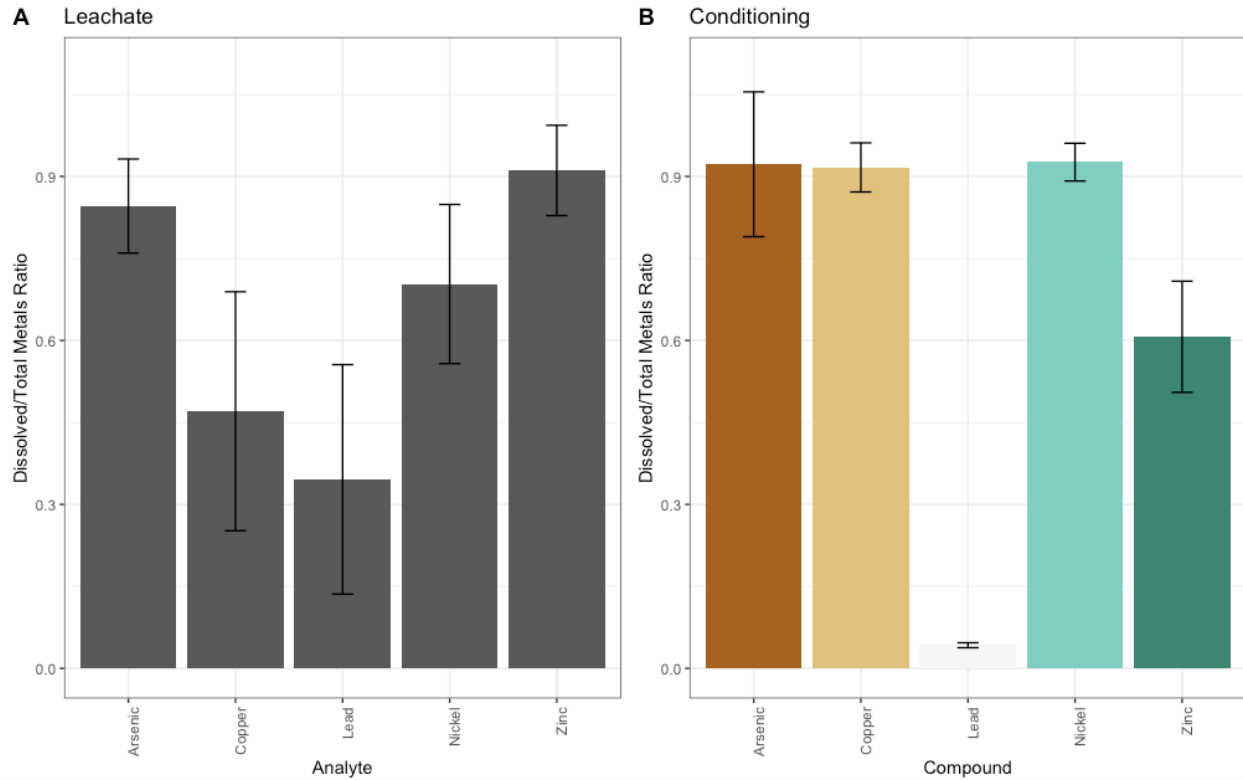


Figure 4. Comparison of A) dissolved/total metal ratios in BSM leachate (BSM components were summed in proportion to their volume in the experimental columns, using 12 inches to represent the average depth) and B) dissolved/total metal ratios averaged across treatment depths (6", 9", 12", 15", 18") plus the clean water control (18" CWC) during column conditioning. Error bars are one standard error of the mean.

Nutrients & Conventionals

Nitrates (the sum of nitrate and nitrite) were more concentrated than orthophosphate in effluent from all of the columns (Table 3). This same trend was observed in the leach test (Figure 5). The leach test further indicated that compost was the primary source of nitrates in the bioretention columns. Given this, it was surprising to see that nitrates concentrations were significantly greater in effluent from the columns with the lowest sand and compost volumes (columns with 6- and 9-inch depths of BSM) compared to those columns with a greater sand and compost volume (15- and 18-inch depths) (Table 3). This observation could be the result of greater denitrification rates in the deeper columns. A deeper saturation zone, which would encourage denitrification, may have been formed in the larger columns because of the greater volume of water flushed through these columns. Nitrate/nitrite was below the analytical detection limit in the influent water sample. Orthophosphate concentrations were significantly greater in the 15- and 18-inch columns compared to the 6- and 9-inch depths. Similar to metals, this trend may be the result of orthophosphate sorption to the gravel layer, and potential sorption site saturation in the deeper columns. However, compared to nitrates concentrations, orthophosphate concentrations were relatively low in effluent from all columns.

Table 3. Summary of nutrient and conventional parameters in influent (lab water) and triplicate effluent samples from each of the five treatment depths plus the clean water control (CWC). Values presented are mean (standard deviation).

Analyte	Detection Limit	Effluent Water						
		Influent Water	6"	9"	12"	15"	18"	18" CWC
Nitrates (mg/L)	0.003	BDL	33 (20) ^a	26 (10) ^a	9 (4) ^{ab}	5.6 (0.4) ^b	7 (2) ^b	8 (4) ^b
Orthophosphate (mg/L)	0.01	0.032	0.07 (0.03) ^a	0.15 (0.08) ^a	0.49 (0.05) ^{ab}	0.63 (0.09) ^b	0.6 (0.1) ^b	0.63 (0.06) ^b
DOC (mg/L)	0.08	0.57	38 (7)	40 (4)	47 (0.00)	44 (5)	47 (4)	46 (3)
Alkalinity (as CaCO ₃)	0.3	80	56 (8) ^a	80 (5) ^{ab}	101 (5) ^{abc}	118 (13) ^{bc}	133 (10) ^c	120 (10) ^{bc}
pH	n.a.	7.70	7.59 (0.07)	7.60 (0.06)	7.66 (0.02)	7.69 (0.03)	7.60 (0.02)	7.62 (0.02)
Conductivity (µS/cm)		1525	1893 (200)	1851 (70)	1717 (70)	1712 (30)	1767 (20)	1783 (70)
Hardness (as CaCO ₃)	calculated	0.094	0.34 (0.07) ^a	0.26 (0.03) ^{ab}	0.196 (0.002) ^{abc}	0.167 (0.006) ^{bc}	0.166 (0.006) ^c	0.162 (0.005) ^{bc}
TSS (mg/L)	0.5	0.25	7 (2)	11 (6)	20 (4)	18 (2)	19 (2)	18 (2)
Turbidity (NTU)	n.a.	0.07	11 (5) ^a	24 (1) ^{ab}	54 (9) ^b	52 (6) ^b	56 (7) ^b	52 (9) ^b
Fecal coliform (CFU/100 mL)	n.a.	<2	>1300	>1300	>6000	>6000	>6000	>6000

Note: Treatments with different superscript group labels (a, b, c) show significance at $\alpha = 0.05$ (Kruskal-Wallis with post-hoc Dunn Test).

BDL = Below Detection Limit

NTU = Nephelometric Turbidity Units

Nutrient Concentrations in Leachate and Clean Water Conditioning Experiments

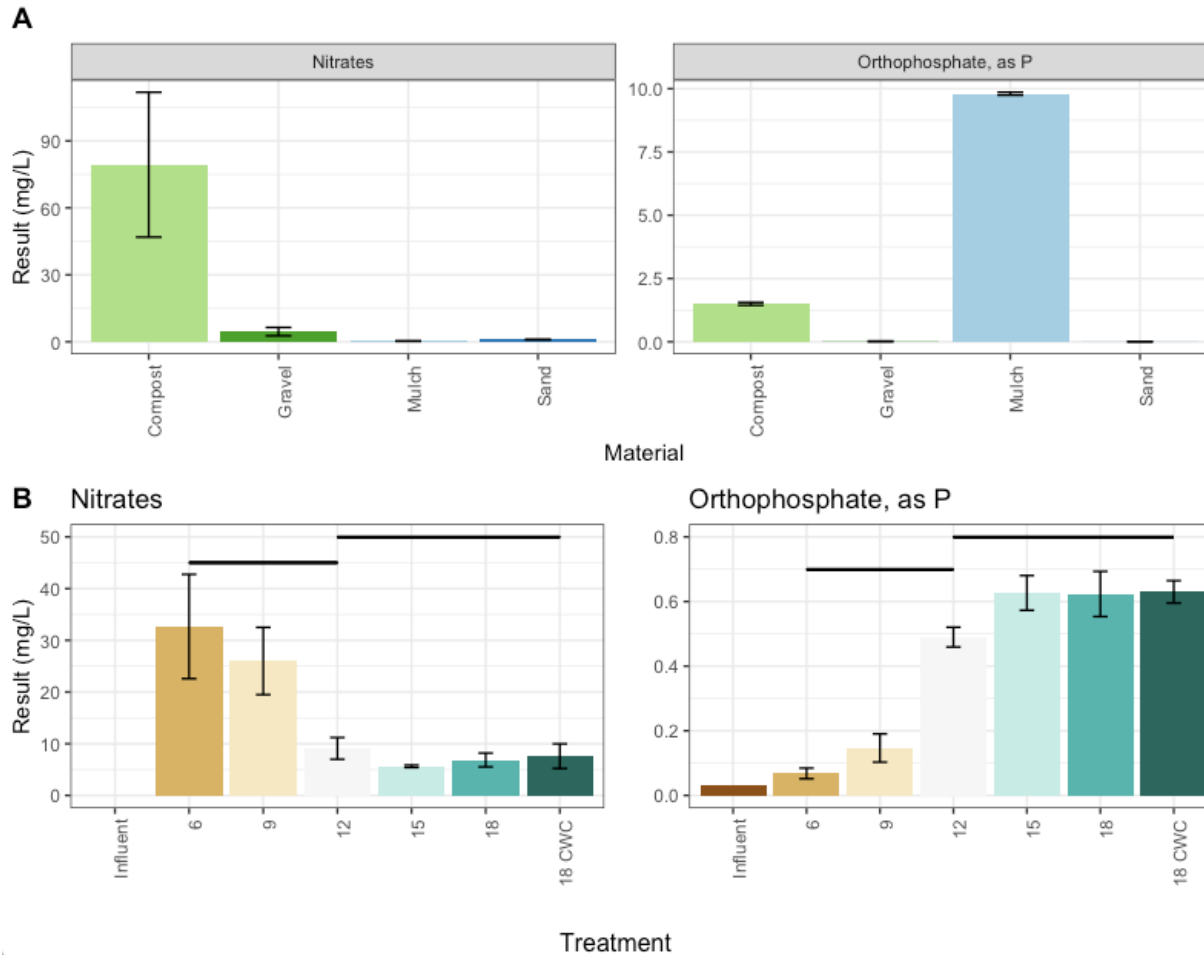


Figure 5 Comparison of A) nutrient concentrations in bioretention soil media (BSM) leachate and B) nutrient concentrations in influent (lab water) and triplicate samples of effluent from each of the five treatment depths (6", 9", 12", 15", 18") plus the clean water control (18" CWC) during column conditioning. Horizontal bars represent depths that share statistical significance at $\alpha = 0.05$. Error bars are one standard error of the mean.

3. Baseline Saturated Hydraulic Conductivity

The baseline saturated hydraulic conductivity (K_{sat}) of the experimental columns was determined for each treatment using the falling head method (Klute and Dirksen 1986). Saturation via water applied at the surface instead of through the bottom of the column was used to minimize the problematic bulk movement of fines that was observed in a previous SAM bioretention project (SAM project: “Field Test of Plants and Fungi on Bioretention Performance Over Time”). Once the columns were filled to a marked level 10 cm above the mulch layer, they were left to saturate for 24 hours. After this time period, columns for which the water level had dropped as a result of air escaping from the media were topped off with additional water. The valves at the base of each column were then opened and water was allowed to drain from the columns. The time required for the water to drain from the marked level to the soil surface was recorded. Values per column were averaged for each treatment. The following equation was used to calculate K_{sat} :

$$K_s = \frac{L}{T_1} \ln \frac{b_0 + L}{b_1 + L},$$

Where b_0 is the initial level of water ponded above the soil surface, b_1 is the end level of water above the soil surface after allowing water to drain from the columns, and L is the depth of BSM.

Due to the size of the experimental columns, boot compaction, which may have aided in achieving greater bulk density, was not feasible. Difficulties in compacting BSM to the levels needed to achieve the desired target bulk density led to actual bulk densities that were less than the target number, resulting in K_{sat} values that were greater than the target rate (Table 4). However, K_{sat} is expected to change over the lifetime of a bioretention basin as soils compress and as pores become clogged with suspended material or biological growth.

Several studies have suggested that clogging may be the greatest factor limiting the longevity of bioretention systems, which is likely to occur before breakthrough or sorption site saturation (Hatt et al. 2011; Guo et al. 2018; Li and Davis 2008). Li and Davis (2008) observed a decrease in average K_{sat} values of 86% in experimental columns due to the formation of a clogging layer. Therefore, greater initial K_{sat} values may act as a buffer against low end-of-life K_{sat} values, as were observed in a previous SAM study with progressively decreasing K_{sat} measurements over time (Taylor et al. 2018). Systems with a greater initial K_{sat} are expected to decrease substantially and at a greater rate than systems with lower initial K_{sat} , as inflow sediments fill interstitial spaces in the original media (Coustumer et al. 2008). Coustumer et al. (2008) even recommend sizing bioretention systems under the assumption that the K_{sat} is half the value of the targeted K_{sat} , to account for potential declines in hydraulic conductivity over time. Furthermore, K_{sat} values of full-scale bioretention systems will be limited by the flow rate through either the native soil or a drainpipe, neither of which are present in this study.

Table 4. Average bulk density (g/cm³) and hydraulic conductivity (K_{sat}) measurements for each treatment depth. Values presented are mean (standard deviation).

Treatment	Bulk Density (g/cm ³)	K _{sat} (cm/hr)
6"	1.05 (0.04)	423 (130)
9"	1.07 (0.03)	515 (220)
12"	1.06 (0.06)	525 (150)
15"	1.09 (0.05)	610 (31)
18"	1.13 (0.05)	391 (27)
18" CWC	1.15 (0.01)	431 (94)

References

Ashworth DJ and Alloway BJ. Soil Mobility of Sewage Sludge-Derived Dissolved Organic Matter, Copper, Nickel, and Zinc. *Environ Pollut.* 127: 137-144.

Christensen JB, Jensen DL, and Christensen TH. 1996. Effect of Dissolved Organic Carbon on the Mobility of Cadmium, Nickel and Zinc in Leachate Polluted Groundwater. *Water Res.* 30(12): 3037-3049.

Klute A and Dirksen C. 1986. Hydraulic Conductivity and Diffusivity: Laboratory Methods. In: Klute, A. Ed., *Methods of Soil Analysis - Part 1 - Physical and Mineralogical Methods*. Madison: American Society of Agronomy. p. 687-734.

Le Coustumer S, Fletcher TD, Deletic A, and Potter M. 2008. Hydraulic Performance of Biofilter Systems for Stormwater Management: Lessons from a Field Study. Report prepared for Melbourne Water by Facility for Advancing Water Biofiltration, Monash University, Melbourne, Australia.

Li H and Davis AP. 2008. Urban Particle Capture in Bioretention Media. I: Laboratory and Field Studies. *J Environ Eng.* 134(6): 409-418.

Taylor A, Wetzel J, Mudrock E, King K, Cameron J, Davis J, and McIntyre J. 2018. Engineering Analysis of Plant and Fungal Contributions to Bioretention Performance. *Water.* 10(9): (1226).

Reddy KJ. 1995. Solubility and Mobility of Copper, Zinc, and Lead in Acidic Environments. *Plant Soil.* 171: 53-58.

Rutkowska B, Szulc W, Bomze K, Gozdowski D, and Szychaj-Fabisiak E. 2015. Soil Factors Affecting Solubility and Mobility of Zinc in Contaminated Soils. *Int. J. Environ. Sci. Technol.* 12(5): 1687-1694.