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Abstract: This study investigated the effectiveness of metal and nutrient removal from stormwater in bioretention systems amended with agricultural byproducts. Both batch and column studies were conducted to evaluate three amendments: hazelnut shells, pecan shells, and spent grain from the brewing process. Batch studies using buffered synthetic water containing copper and zinc evaluated adsorptive properties of the three amendments. Of the three amendments, hazelnut shells had the highest sorption coefficient based on K_d ranges of 19,200–106,000 L/kg and 8,610–18,900 L/kg for zinc and copper, respectively. Both pecan shells and spent grain had significantly lower K_d values for zinc (2,160–6,030 L/kg and 1,702–55,932 L/kg for pecan shells and spent grain, respectively) and copper (1,090–1,760 L/kg and 1,270–2,030 L/kg for pecan shells and spent grain, respectively). However, the spent grain contained zinc that potentially could add to zinc concentrations in the stormwater. Column studies using stormwater collected from an industrial site evaluated metal and nutrient removal from stormwater. Six columns were packed with 90% bioretention soil mix and 10% hazelnut shells, pecan shells, or spent grain, and two columns were packed with 100% bioretention soil mix as a control. Five tests were conducted with stormwater collected from a nearby industrial site. Influent and effluent samples were analyzed for copper, zinc, nitrate, ammonia, total nitrogen, phosphate, and total phosphorus. The columns with pecan shells had the highest removal, with 53% removal of copper and 87% removal of zinc. Removal in the columns with hazelnut shells and spent grain was 47% and 19% for copper and 83% and 65% for zinc, respectively. All columns exported nutrients. Although hazelnut shells had the highest sorption coefficient, the pecan shells removed more metals from the stormwater. This study indicates both hazelnut and pecan shells improve metals removal potential of bioretention systems.

Introduction

Stormwater runoff in urban settings often contains high levels of metals and nutrients due to large areas of impervious surfaces, increasing the volume of stormwater runoff being managed. Accumulated particulate matter and other pollutants from streets, rooftops, and parking lots contribute to stormwater pollution (EPA 2010). Many US cities have older sewer systems that combine stormwater with wastewater, all of which is treated at a wastewater treatment plant (WWTP). During large rain events, runoff volumes exceed WWTP capacity, leading to combined sewer overflow (CSO) events in which untreated sewage and stormwater are discharged to the receiving water. To alleviate this problem, cities such as Portland, Oregon have implemented a number of low-impact strategies, including bioretention cells, infiltration basins, green roofs, disconnecting downspouts at residential houses, and installing large CSO pipe storage systems (City of Portland 2016).

In addition to decreasing the volume of stormwater that goes to the WWTP, bioretention cells passively treat stormwater as it infiltrates through engineered soil mixes. The efficacy of pollutant removal in bioretention systems has been mixed, however. Some studies have shown that bioretention significantly reduces copper and zinc from stormwater (Sun and Davis 2007; Blecken et al. 2009; Davis et al. 2003; Gülbaz et al. 2015; Liu et al. 2018; Seelsaen et al. 2006), whereas others have shown leaching of copper (Herrera Environmental Consultants 2014; Trowsdale and Simcock 2011; Li and Davis 2009). Results for nutrients have been mixed as well. Some studies have shown good removal of nitrogen and phosphorus (Clary et al. 2017; Palmer et al. 2013; Davis et al. 2006; Lucas and Greenway 2008; Li and Davis 2014), whereas others have shown an export of nitrate, phosphate, and total phosphorus (Mullane et al. 2015; Herrera Environmental Consultants 2015; Davis et al. 2006; Clary et al. 2017). Compost has been identified as the source of copper, nitrogen, and phosphorus (Mullane et al. 2015; Hurley et al. 2017). The engineered soil mixture used in bioretention systems should be altered to improve pollutant removal in bioretention systems. Some municipalities have removed compost from the bioretention soil mix (NHDES 2008; MDOE 2009; NCDEQ 2017); however, compost is needed for water-holding capacity and plant health in regions that experience hot, dry summers, such as the Western United States.

Metals typically are removed via adsorption to organic material present in the bioretention soil mix. Sorption can occur via complexation or ion exchange, and functional groups such as alcohols, aldehydes, ketones, carboxylic acid, hydroxyls, and phenols increase the metal sorption capacity of organic materials (Bilal et al. 2013; Altun and Pehlivan 2007). Although functional groups have been identified as important for sorption of metals to organic

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materials in some studies, Chowdhury et al. (2018) found that surface area was more important than functional groups for metal sorption from stormwater.

Adding agricultural byproducts to the engineered soil mixture may improve pollutant removal in bioretention systems. Agricultural byproducts often are discarded or used as a supplement to compost, and thus would be a sustainable amendment for bioretention systems. A few studies have evaluated the potential metals uptake of agricultural byproducts such as pecan shells, rice, straw, hazelnut shells, walnut shells, almond shells, and other byproducts using batch experiments (van Lienden et al. 2010; Demirbas et al. 2008; Altun and Pehlivan 2007; Lu and Gibb 2008). Van Lienden et al. (2010) studied pyrolyzed agricultural byproducts to form activated carbon and found high sorptive potential for zinc and copper. Demirbas et al. (2008) and Altun and Pehlivan (2007) also found good sorptive potential for copper with raw pulverized hazelnut and other shells. Lu and Gibb (2008) evaluated spent grain with batch and column studies, in which the column was filled with spent grain, and found it to be an effective biosorbant for removal of copper from distilling wastewater. These studies suggest that agricultural byproducts, which are low-cost, sustainable materials, have the potential to improve the uptake of metals in bioretention systems. Studies evaluating the use of agricultural byproducts in bioretention systems are needed to evaluate whether metals removal from stormwater can be improved with these materials.

This study investigated the use of agricultural byproducts to remove metals and nutrients from stormwater. Pecan shells, hazelnut shells, and spent grain from the brewing process were evaluated using batch and column studies. Each agricultural byproduct was dried and pulverized, but not pyrolyzed. Batch studies evaluated the sorption potential of each agricultural byproduct using buffered synthetic water containing copper and zinc at high but environmentally relevant concentrations, and column studies evaluated how well each byproduct removed metals and nutrients from stormwater collected from an industrial site.

Methods

Three agricultural byproducts were procured from local businesses and used as amendments in this experiment: hazelnut shells, pecan shells, and spent grain from the brewing process. The amendments were finely ground with a soil grinder and dried at 105°C for 24 h. The grain-size distribution was evaluated using a sieve analysis per ASTM D422 (ASTM 2002), and results of this characterization are shown in Fig. 1. The sieve analysis showed that pecan and hazelnut shells had very similar size distributions to each other, whereas spent grain was finer-grained. The bulk density was 0.6185 kg/L for hazelnut shells, 0.6881 kg/L for pecan shells, and 0.3431 kg/L for spent grain.

Batch Studies

Experiments were performed using relatively high but environmentally relevant concentrations of zinc and copper. Data from the National Stormwater Quality Database (NSQD) were used to determine appropriate ranges (Pitt and Maestre 2015). The NSQD reported metals concentrations in 259 samples taken from 31 locations throughout Oregon during the 1990s and early 2000s. Ten of these samples had copper concentrations exceeding 100 μg/L, and nine had zinc concentrations exceeding 600 μg/L. For this study, copper and zinc levels of 100 and 600 μg/L, respectively, were selected as high but reasonable concentrations. This aligns well with the concentrations used by van Lienden et al. (2010), who selected copper and zinc levels of 80 and 420 μg/L to represent the 90th percentile of metals concentrations in stormwater samples in California.

Because the purpose of this study was to evaluate how well agricultural byproducts can sorb metals in practical terms at environmentally relevant stormwater concentrations, only a single-concentration adsorption equilibrium experiment was conducted using each sorbent and metal. This was a useful approximation

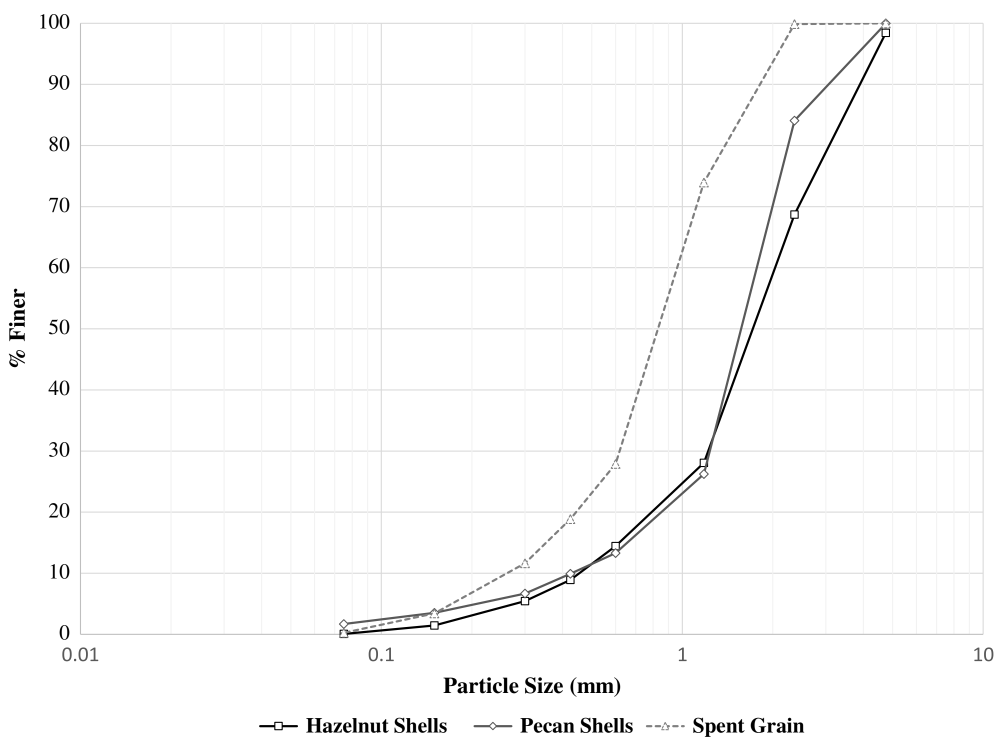

Fig. 1. Grain-size distribution of agricultural byproducts used in this study.

of the relative sorption capacity of each sorbent. That is, the purpose of the batch studies was to determine which agricultural byproducts potentially could remove copper and zinc at expected concentrations in stormwater at different pHs.

Batch studies were conducted using buffered synthetic water containing copper and zinc. A solution of 100 μg/L copper and 600 μg/L zinc was prepared using copper and zinc standard solutions (Certified Reference Material, AccuStandard, New Haven, Connecticut) and deionized water (Millipore Ultrapure System, Burlington, MA). Potassium bicarbonate (ACS Reagent 99.7%, Sigma-Aldrich, St. Louis, Missouri) was added to this solution to reach an alkalinity of 200 mg/L as $CaCO_3$. The pH was adjusted to the desired levels using either potassium bicarbonate or nitric acid (Trace Metals Grade, Sigma-Aldrich, St. Louis, Missouri). Three solutions were prepared, at pH 6, 7, and 8 respectively, each with enough solution for at least 12 samples. Additionally, a control solution was prepared, containing only buffered synthetic water (200 mg/L at $CaCO_3$ alkalinity) without metal pollutants of concern.

Sorbent samples were added to prewashed 125 mL HDPE bottles. Four sorbent treatments (hazelnuts, pecans, grain, and no sorbent) and four solution treatments (pH 6 + metals spike, pH 7 + metals spike, pH 8 + metals spike, and deionized water) were tested. All the tests were conducted in triplicate. The samples containing grain and hazelnuts each received 100 mg of sorbent, whereas the samples containing pecans received 250 mg of sorbent. These quantities had been determined previously in range-finding experiments to produce metals concentrations ideal for the purposes of these experiments. Then 100 mL of the appropriate solution was added to each sample before they were placed in a custom-built tumbler for 72 h.

After tumbling, aliquots of each sample were taken by passing the solution through a 0.45-μm polyvinyl difluoride (PVDF) syringe filter. These aliquots then were preserved by adding nitric acid until the pH was ≤2 according to standard methods (Rice et al. 2012) and analyzed in an atomic absorption spectrophotometer (Shimadzu AA-7000, Columbia, Maryland) for copper and zinc.

Based on the copper and zinc results, the solid–water distribution coefficient (K_d) was computed for each sample. The K_d is defined as

$$K_d = \frac{q_e}{C_e} \tag{1}$$

where K_d = solid–water distribution coefficient (L solution/kg sorbent); q_e = sorbed metal concentration on adsorbent at equilibrium (mg metal/kg sorbent); and C_e = metal concentration in water at equilibrium (mg metal/L solution) (Schwarzenbach et al. 2003). In this study, q_e was calculated using the conservation of mass principle and C_e according to the equation

$$q_e = \frac{M_T - C_e V_w}{M_s} = \frac{V_w}{M_s} \times (C_0 - C_e) \tag{2}$$

where M_T = total initial mass of metal added to each bottle; V_w = volume of water in each bottle; M_S = mass of sorbent in each bottle; and C_0 = initial concentration in each bottle (equivalent to M_T/V_w) (Mihelcic and Zimmerman 2014). Higher values of K_d thus indicated a higher affinity of the sorbent for the metal.

Column Studies

A total of eight 30.5-cm-diameter, 97.5-cm-tall PVC columns were used for testing (Fig. 2): two columns for each of the three types of agricultural byproducts, and two columns for the control. Each column had a 30.5-cm (12-in.) drainage layer mix of river rock and

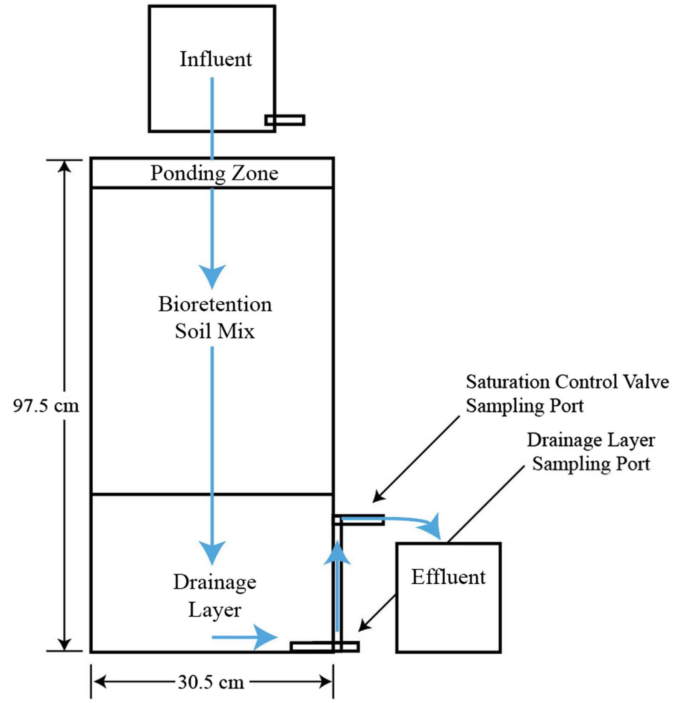

Fig. 2. Experimental setup for column study.

1.9-cm (¾-in.) gravel rock, a 61-cm (24-in.) layer of bioretention soil mix, and 15.2-cm (6-in.) layer for ponding on the top (City of Portland 2016). A riser pipe with a valve 30.5 cm above the bottom of the column was used to create a saturated zone in the gravel layer, which was connected to a slotted 1.9-cm-diameter PVC pipe at the bottom of the column. The amended columns were packed with a mixture of 90% City of Portland bioretention soil mix (BSM) and 10% agricultural byproduct, whereas the control columns were packed with 100% BSM.

The City of Portland bioretention design storm [2.1 cm (0.83 in)], which is the 6-month, 24-h storm; a drainage area ratio of 10:1; and a runoff ratio of 0.9 were used to determine the runoff volume with the rational method (City of Portland 2016). Stormwater was collected during multiple storms from a 24.3-ha (60-acre) industrial site, where activities include ship building and repair and fabrication of bridge, aerospace, and steel structure components. Stormwater was stored in 227-L (60-gal.) high-density polyethylene (HDPE) containers, which were agitated to resuspend particles before testing. A sump pump (Little Giant Model NK-1, Fort Wayne, Indiana) was placed at the bottom of the HDPE container to pump water to 25-L polypropylene stormwater containers used for testing. A trial test of the untreated stormwater indicated copper concentrations were lower than typical for stormwater; therefore, copper chloride (Reagent Grade, Sigma-Aldrich, St. Louis, Missouri) was added to the stormwater two days before testing to ensure that the added copper was fully dissolved before testing. The resulting influent copper concentrations were 9–16 μg/L. A total of five tests were conducted with approximately one week between tests to mimic typical stormwater patterns in Portland, Oregon. Influent water quality for all of the tests is listed in Table 1.

The columns were placed in a greenhouse to control environmental conditions. During each test, 13.6 L of stormwater was applied to the top of each column from 25-L polypropylene stormwater containers using a ball valve attached to flexible tubing with a flow spreader. Runoff rate was controlled using the ball valve to maintain 5 cm of ponding. A polypropylene container was placed

Table 1. Influent water quality during all tests

	Constituent (mg/L)							
Test	NO_3^-	NH_3	TN	PO_4^{3-}	TP	TOC	Copper	Zinc
1	0.9	0.10	ND	0.04	0.11	1.8	0.011	0.067
2	0.6	0.07	1.3	0.05	0.09	2.1	0.009	0.068
3	0.6	0.04	0.6	0.04	0.11	2.1	0.013	0.095
4	0.3	0.04	ND	0.03	0.08	2.0	0.016	0.091
5	0.7	ND	ND	0.02	0.12	3.2	0.016	0.105

Note: ND = concentrations below detection limit.

under the outflow valve of each column to collect the effluent. Using a stopwatch and a graduated cylinder, the infiltration rates were recorded. Once the effluent slowed to a drip, composite samples were collected using 250-mL HDPE bottles. All containers and sample bottles were acid-washed according to standard methods (Rice et al. 2012). Turbidity and pH were recorded for both the influent and effluent samples. Total volume of effluent also was measured for each column.

Sample Analysis

All water quality samples were analyzed in duplicate to ensure quality control. Metal analysis was completed for both column and batch studies using an atomic absorption spectrophotometer (Shimadzu AA-7000) according to Standard methods 3500-Zn B and 3500-Cu C for zinc and copper, respectively (Rice et al. 2012). Samples from the batch studies were analyzed for dissolved zinc and copper, and samples for column studies were analyzed for total zinc and copper.

In addition, samples from the column studies were analyzed for total phosphorus (TP), phosphate (PO_4^{3-}), total nitrogen (TN), nitrate (NO_3^-), and ammonia (NH_3) concentrations using Standard method 4000 (Rice et al. 2012). The persulfate method was used to analyze TP and TN (4500-P B and 4500-N, respectively), and the colorimetric method was used to analyze all nutrients (4500-NO_3^-, 4500-NH_3, and 4500-P H). Reagents used for nutrient analysis were obtained from HACH (Loveland, Colorado) and were all reagent grade. Total organic carbon (TOC) was determined using a TOC analyzer (Sievers M5310 C, Trevose, Pennsylvania) following Standard method 5310 B (Rice et al. 2012).

For column studies, influent and effluent nutrient and metal concentrations from the five tests, as well as the different treatments (hazelnut shells, pecan shells, spent grain, and control) were compared using the Kruskal–Wallis and Wilcoxon signed rank tests. The Kruskal–Wallis is a statistical test to determine if there are differences between three or more independently sampled groups (McKnight and Najab 2010), and the Wilcoxon signed rank test is an effective method for comparing paired data (Lamorte 2017). The Kruskal–Wallis test was used first in analysis to determine if there was a statistical difference between all columns and tests. If the Kruskal–Wallis test indicated a statistical difference, the Wilcoxon signed rank Test then was used to compare two data sets at a time. Microsoft Excel (2016 version) was used to conduct both tests. Error bars shown in all figures described subsequently represent one standard deviation of replicates.

Results and Discussion

Batch Studies

Distribution coefficients (K_d) of Cu and Zn at different pH values for the three byproducts are shown in Figs. 3 and 4, respectively.

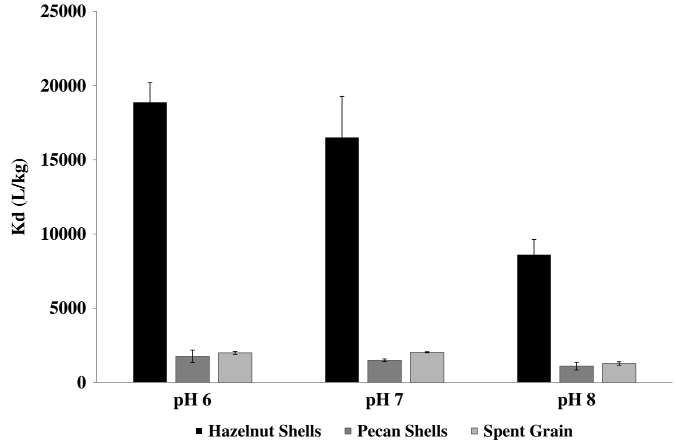

Fig. 3. Batch test results of K_d for copper using hazelnut shells, pecan shells, and spent grain at pH 6, 7, and 8. Error bars represent the standard deviation between replicates.

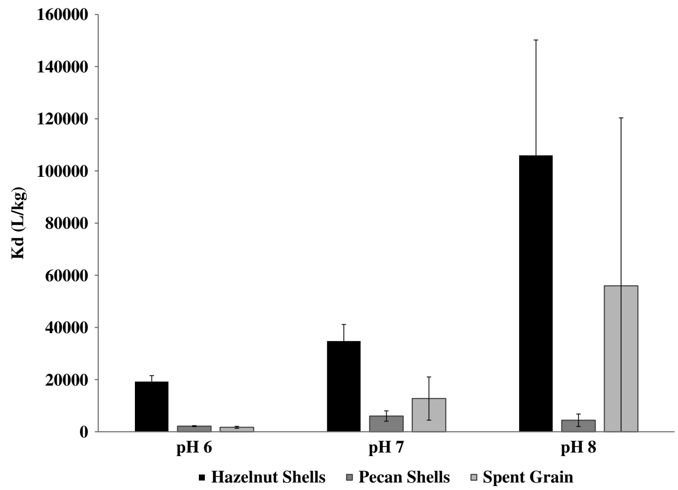

Fig. 4. Batch test results of K_d for zinc using hazelnut shells, pecan shells, and spent grain at pH 6, 7, and 8. Error bars represent the standard deviation between replicates.

Experimental data are summarized in Table 2. Hazelnut shells consistently had higher affinities for both copper and zinc than did the other byproducts, exhibiting sorption coefficients 5–10 times higher than the spent grain and pecan shells. The K_d for hazelnuts ranged from 19,200 to 106,000 L/kg for zinc, and from 8,610 to 18,900 L/kg for copper. Because the hazelnut and pecan shells had similar grain-size distributions (Fig. 1), and the spent grain generally was finer, it is unlikely that the higher sorption coefficient was due to surface area differences between the materials. The higher sorption coefficient may be due to additional binding sites or different functional groups in the ground hazelnut shells, although more research is needed for verification.

Sorption capacity can vary with pH for a number of reasons, such as the occurrence of metal surface precipitation on the adsorbent with the pH change, electrostatic interaction at different pH, and pH-dependent metal speciation. For hazelnut shells, the K_d decreased as pH increased for copper, whereas for zinc the K_d increased at higher pH. The results for zinc, showing increased sorption with increasing pH, generally agreed with those of previous studies for adsorption onto activated carbon (Marzal et al. 1996, Alvarez-Merino et al. 2005). However, the results for copper

Table 2. Solid–water distribution coefficient and standard deviation for batch tests

	Solid–water distribution coefficient (K_d) ± standard deviation (L/kg)					
	Copper			Zinc		
Treatment	pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
Hazelnut shells	18,900 ± 1,310	16,500 ± 2,770	8,610 ± 1,010	19,200 ± 2,280	34,800 ± 6,390	106,000 ± 44,200
Pecan shells	1,760 ± 420	1,500 ± 80	1,090 ± 260	2,160 ± 190	6,030 ± 1,990	4,410 ± 2,390
Spent grain	1,990 ± 100	2,030 ± 30	1,280 ± 120	1,700 ± 390	12,700 ± 8,290	55,900 ± 64,400

(decreasing sorption with increasing pH, particularly for hazelnut shells) were inconsistent with those found by Demirbas et al. (2008), who also evaluated hazelnut shells. The different observations likely were caused by the different pH ranges of the two studies. pH 3–7 was used by Demirbas et al.(2008), whereas pH 6–8 was tested in this study.

The affinity for copper and zinc was similar for the pecan shells and spent grain, although the range of K_d values for the spent grain was larger, particularly for zinc. The K_d for the pecan shells ranged from 2,160 to 6,030 L/kg for zinc and from 1,090 to 1,760 L/kg for copper, whereas the K_d for spent grain ranged from 1,703 to 55,934 L/kg for zinc and from 1,270 to 2,030 L/kg for copper. The higher K_d range for the spent grain may be due to native zinc present in the spent grain, because blanks containing spent grain without a metals spike showed high levels of zinc. This potentially led to high K_d results for zinc in the pH 7 and 8 samples. The recovery in the lab control spikes (samples containing the metals solution without sorbent) was 55%–73%, with generally lower recoveries at higher pHs. This suggests that at high pH, the metals are more likely to precipitate out of solution or sorb to the walls of the sample bottles. This likely contributed to the higher variability between replicates for zinc at pH 8. Thus, although determination of the specific mechanisms controlling sorption at different pHs was beyond the scope of this study, results provide evidence supporting the role of zinc precipitation, particularly at high pH, in zinc removal.

The K_d values for hazelnut shells were higher than those in other studies. However, most previous batch sorbent studies used concentrations of copper and zinc much larger than those used in this study. Shuguang and Gibb (2008) studied the ability of spent grain from the brewing process to remove copper from water at initial concentrations between 20 and 75 mg/L. Interpolation from a Langmuir model fitted to their data yielded a K_d value of 93 L/kg at an equilibrium concentration of 100 μg/L or 168 L/kg at an equilibrium concentration of 50 μg/L. However, these results may not be environmentally relevant due to the fact that these copper concentrations are more than 200 times higher than the concentrations typically found in stormwater in the United States.

Demirbas et al. (2008) studied the ability of ground raw hazelnut shells (similar to the present study) to remove copper from water at initial concentrations between 1 and 92 mg/L. The data were fitted to both the Langmuir and Freundlich models. Interpolation from the Langmuir model yielded a K_d value of 820 L/kg at an equilibrium concentration of 100 μg/L or 830 L/kg at 50 μg/L. Interpolation from the Freundlich model yielded K_d values of 4,880 L/kg and 7,170 L/kg at concentrations of 100 μg/L and 50 μg/L respectively. Although the present study found somewhat higher K_d values, the Demirbas et al. study exhibited K_d values via the Freundlich model of a similar order of magnitude.

Van Lienden et al. (2010) studied the ability of commercial activated carbon, as well as activated carbon materials made by pyrolyzing pecan shells and other agricultural byproducts, to remove copper and zinc from water. In their experiments, copper and zinc had initial concentrations of 80 and 420 μg/L, respectively. They found that the K_d for copper removal was about 700 L/kg, and the K_d for zinc removal was less than 100 L/kg. Van Lienden et al. used similar concentrations to those in the present study, but pyrolyzed the materials and did not study hazelnut shells. Other than the K_d for zinc at pH 8, all results in the present study were within the range of findings of van Lienden et al. for rice straw, husk, and almond shells. The K_d values for pecan shells for both zinc and copper in the present study were higher than the K_d for activated carbon made with pecan shells in van Lienden et al. (2010).

Column Studies

The average infiltration rate for all columns was 131 cm/h (51 in./h). Of the total volume applied, an average of 17% was retained in each column. Average pH in the effluent was consistently between 5.8 and 6.6 for all tests and columns, which was significantly lower than the influent pH of 8.4 ($p < 0.005$). Turbidity was significantly higher in the effluent of all columns than in the influent ($p < 0.005$), particularly for the columns with spent grain. Average turbidity in effluent from the columns with spent grain was 180 nephelometric turbidity units (NTU) compared with 2.33 NTU in the influent. Average turbidity was 11.9 NTU in effluent from the other columns. TOC concentrations in the effluent were higher than in the influent ($p < 0.005$). Average influent TOC was 2.2 mg/L, whereas average effluent TOC was 28.0 mg/L. This trend of higher turbidity and TOC in the effluent may be due to unexpected leaching of the compost that was present in all columns.

Average effluent water quality for each treatment is given in Table 3, and average removal of metals and nutrients is listed in Table 4. Total effluent concentrations of metals, nitrate, and ammonia for all tests and treatments (control, and each of three amendments: pecan shells, hazelnut shells, and spent grain) are shown in Figs. 5–8.

Metals

Effluent copper concentrations generally were lower than influent concentrations when using agricultural byproducts. The greatest reduction in copper concentrations was observed in the columns with pecan shells, with an average 53% removal over all tests. An average removal of 47% and 19% was observed in the columns with hazelnuts and spent grain, respectively. The average removal in the columns with hazelnut and pecan shells was 48% ($p < 0.01$) and 65% higher ($p < 0.005$) than the removal observed in the control, respectively. Copper removal in the columns with spent grain was statistically the same as the removal in the control. This was much lower than the 91%–98% removal of copper observed by Davis et al. (2003). The difference likely was due to the different experimental conditions. Davis et al. used a higher influent concentration (140 μg/L, compared with 13 μg/L for the present study) and also used plants and mulch in the bioretention boxes, which were excluded in the present study. In addition, copper was exported from the control columns during four of the five tests, and the standard deviation was higher for the control columns than for columns with

Table 3. Average effluent water quality with standard deviation for all treatments

Treatment	Concentration ± standard deviation (mg/L)							
	NO_3^-	NH_3	TN	PO_4^{3-}	TP	TOC	Copper	Zinc
Control	0.6 ± 0.3	0.28 ± 0.19	2.5 ± 1.2	1.9 ± 1.0	2.8 ± 1.5[a]	24.1 ± 1.7	0.018 ± 0.011	0.017 ± 0.028
Hazelnut shells	0.5 ± 0.2	0.34 ± 0.02[a]	2.9 ± 1.1	3.0 ± 0.8	4.5 ± 1.0	25.3 ± 1.1	0.009 ± 0.0038[a]	0.016 ± 0.019
Pecan shells	0.6 ± 0.3	0.23 ± 0.05	2.9 ± 1.3	3.3 ± 0.7	6.3 ± 2.3	24.9 ± 1.4	0.006 ± 0.0031[a]	0.012 ± 0.020[a]
Spent grain	13.3 ± 12.6[a]	0.62 ± 0.20[a]	94.0 ± 38.8[a]	4.6 ± 0.7	12.5 ± 1.2[a]	37.6 ± 6.5[a]	0.010 ± 0.0053	0.031 ± 0.031

[a]Differences were statistically significant from the control.

Table 4. Average percentage reduction for all treatments

Treatment	Reduction (%)							
	NO_3^-	NH_3	TN	PO_4^{3-}	TP	TOC	Copper	Zinc
Control	5	−10	−300	−7,300	−2,600	−1,000	−36	84
Hazelnut shells	19	−36	−360	−11,300	−4,300	−1,020	47	83
Pecan shells	11	8	−350	−12,500	−6,041	−1,010	53	87
Spent grain	−2,048	−148	−14,700	−17,600	−12,117	−1,600	19	65

Note: Negative values indicate export.

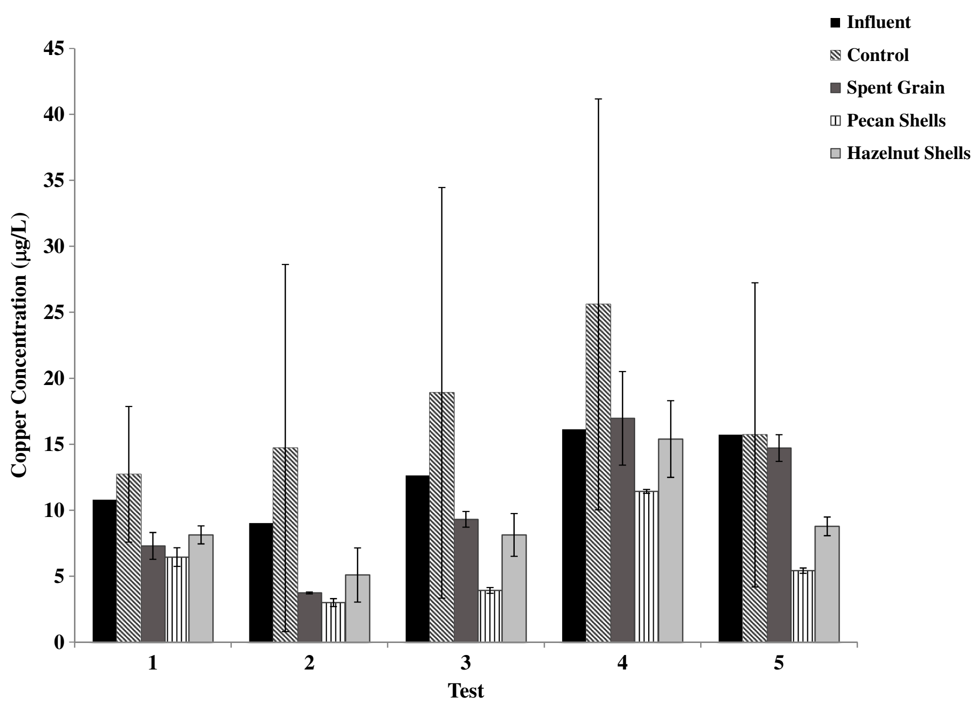

Fig. 5. Copper concentrations compared among the three treatments (spent grain, pecan shells, and hazelnut shells), control, and influent for all column five tests. Error bars represent the standard deviation between replicates.

agricultural byproducts. The control columns contained only BSM; therefore this increase may be due to the presence of copper in the BSM, which likely reduced removal efficiencies. Other studies observed copper export from the BSM and identified compost as its source (Mullane et al. 2015; Herrera Environmental Consultants 2014). The high standard deviation may be due to the natural variation of native copper in the BSM to and the variability in natural systems in general.

Zinc removal was significant for all columns compared with the influent concentration. Similar to the copper results, the greatest reduction in zinc concentrations was observed in the columns with pecan shells, with an average 87% removal over all tests ($p < 0.01$). An average removal of 83% and 65% was observed in the columns with hazelnut shells and spent grain, respectively ($p < 0.01$ and $p < 0.01$, respectively). Low removal and high standard deviation from the columns with spent grain may be due to the native zinc observed in the spent grain, which would have some natural variability. Similar removal was observed from the control column with an average 84% removal of zinc ($p < 0.007$). Concentrations were below the detection limit for the hazelnut and pecan shells during Tests 3 and 4, and for the control during Test 4 (Fig. 6). Zinc removal was lower and standard deviation was higher between replicates during Test 5. It is not clear why effluent zinc concentrations were higher during Test 5. It may be due to preferential flowpaths

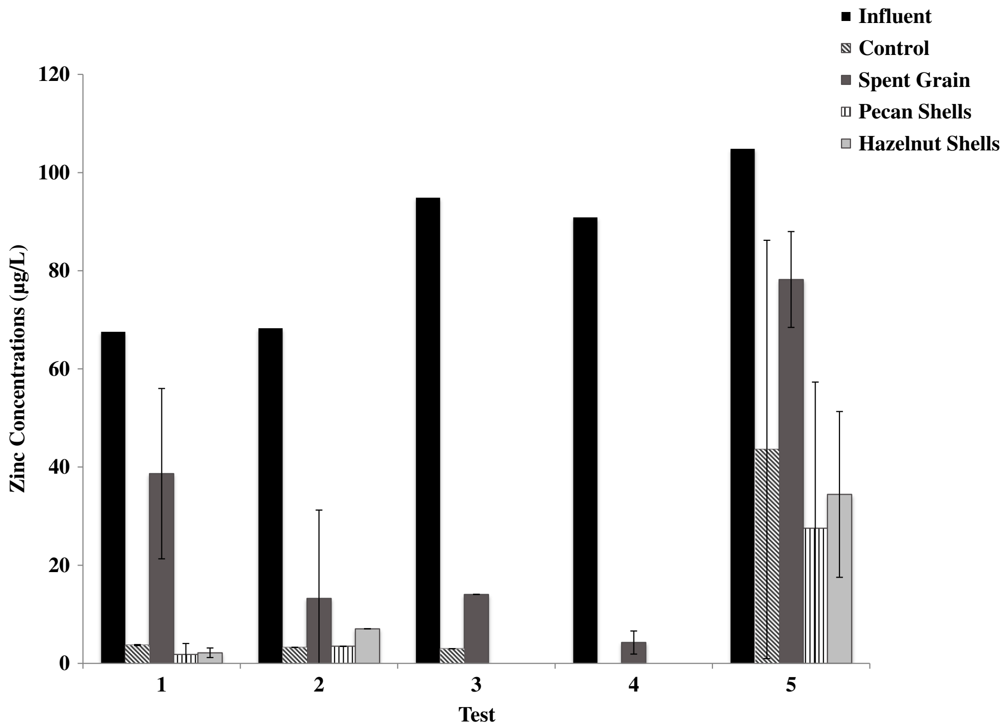

Fig. 6. Zinc concentrations compared among the three treatments (spent grain, pecan shells, and hazelnut shells), control, and influent for all five column tests. Error bars represent the standard deviation between replicates.

forming in the columns, although effluent copper concentrations were similar for Test 5 compared with other tests. High standard deviation and higher effluent zinc concentrations also may be due to breakthrough of zinc. Saturation of zinc and subsequent leaching could occur at different rates due to the natural variability of the soil, microbial population, agricultural byproducts, and so forth. These results are comparable to the findings of Liu et al. (2018), who observed 77%–78% removal of zinc from bioretention beds, but lower than the 93%–96% removal observed by Davis et al. (2003). The difference in results likely was due to the higher

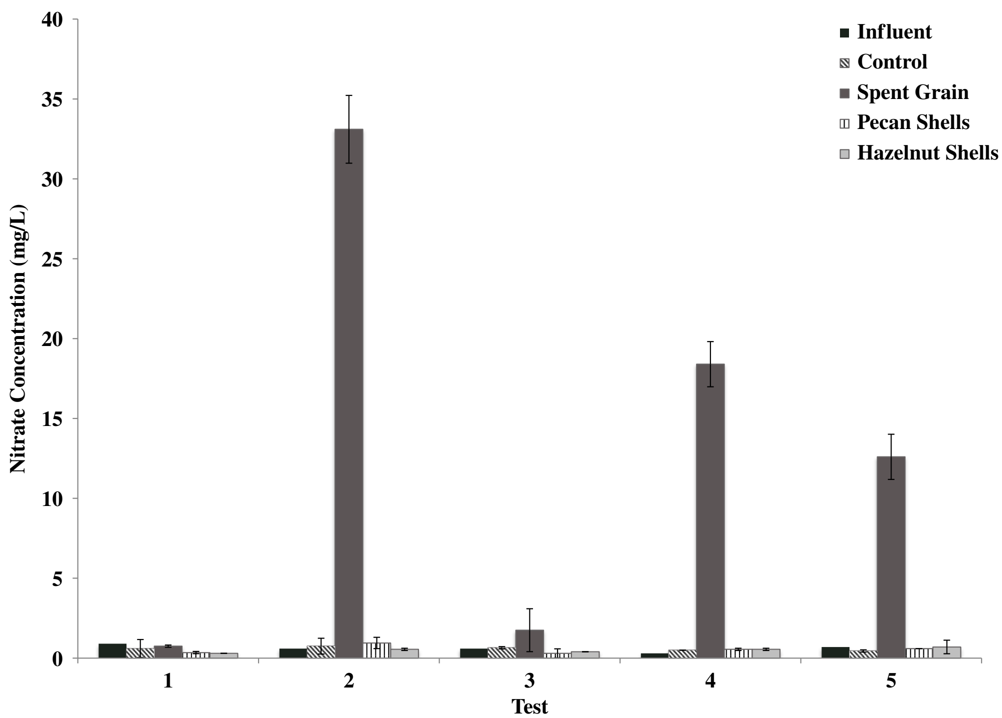

Fig. 7. Nitrate concentrations compared among the three treatments (spent grain, pecan shells, and hazelnut shells), control, and influent for all five column tests. Error bars represent the standard deviation between replicates.

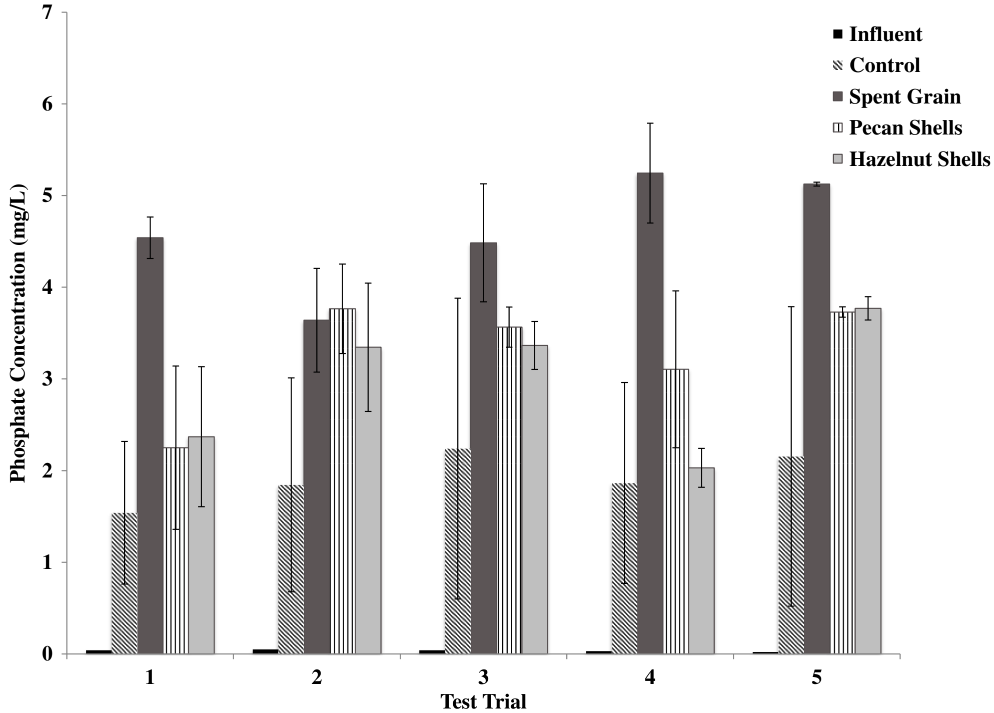

Fig. 8. Ammonia concentrations compared among the three treatments (spent grain, pecan shells, and hazelnut shells), control, and influent for all five column tests. Error bars represent the standard deviation between replicates.

influent concentrations used by Davis et al. (2003) (600 μg/L, compared with 57–105 μg/L in the present study), which may have resulted in higher removal percentages.

Results were promising in columns with pecan and hazelnut shells for enhancing copper and zinc removal in bioretention systems, indicating that hazelnut and pecan shells are effective without pyrolysis of materials. The columns with hazelnut and pecan shells had significantly higher removal of copper than did the control, but zinc had results similar to those of the control. The high sorptive capacity observed for hazelnut shells in this study and other studies (Altun and Pehlivan 2007; Demirbas et al. 2008) was consistent with the additional removal observed in the column studies. Furthermore, the additional removal observed with pecan shells was consistent with the results of van Lienden et al. (2010), who observed a high sorption coefficient for activated carbon made with pecan shells. The different adsorptive behaviors of spent grain and the shells may be due to their different chemical structures. It is possible that more binding sites and functional groups are present in the shells. More research is needed to verify the removal mechanisms occurring in bioretention systems amended with agricultural byproducts.

Nutrients

Nitrate, total nitrogen, ammonia, total phosphorus, and phosphate concentrations were about the same or higher in the effluent compared with the influent (Tables 1 and 3, and Figs. 7 and 8). Nutrient concentrations in the effluent were much higher from the columns with spent grain compared with the control, pecan, and hazelnut shell columns. Average effluent nitrate concentrations from the columns with pecan and hazelnut shells were 11% and 19% lower than the influent concentration, and 7% and 15% lower than those of the control, respectively; however, these average removals were not statistically significant. Average effluent nitrate concentrations from the columns with spent grain were 20.5% ($p < 0.008$) and 21.5% ($p < 0.006$) higher than the influent concentrations and effluent concentrations from the control, respectively. Average effluent phosphate concentrations from the columns with pecan and hazelnut shells were 12,500% and 11,300% higher than the influent concentration, and 70% and 54% higher than those of the control, respectively. Average export of phosphate was 17,600% and 138% higher for the columns with spent grain compared with the influent and control, respectively.

Export of nutrients has been observed in other studies (Palmer et al. 2013; Mullane et al. 2015; Herrera Environmental Consultants 2015). Although it is expected that nutrient export from compost will decrease over time, this has not been observed in bioretention systems or green roofs (Poor and Kube 2019; Okita et al. 2018). Nutrient concentrations have been observed to be more cyclical and to vary seasonally. In addition, many bioretention studies in the Northeast have shown removal of nutrients (i.e., Davis et al. 2006) with a negligible variation over time, which is in contrast to studies in the Northwest, where export has been observed. The byproducts tested in this study were all plant products that contained nutrients, which thus added to the nutrients already present in the BSM. This study did not include plants, which may help retain nitrogen and phosphorus via plant uptake (Poor et al. 2018; Palmer et al. 2013). Additional amendments such as water treatment residuals (WTRs) also can be added to retain phosphorus (Poor et al. 2019; Palmer et al. 2013). The addition of nutrients should be considered if agricultural byproducts are added to the BSM, particularly if an underdrain is used to carry treated stormwater to a sensitive waterway.

Conclusion

The following conclusions were made as a result of this study:

1. Hazelnut shells, which are a common agricultural byproduct in Oregon, could be very useful as an additive to bioretention soil

mixes to remove copper and zinc from stormwater. Batch tests showed that hazelnut shells had a high sorption coefficient.
2. Pecan shells, although not as effective as hazelnut shells, also could provide treatment benefits when added to bioretention soil mixes
3. Spent grain from the brewing process was not effective for removing metals and exported significant amounts of nutrients. In addition, spent grain is not very useful as an amendment, because it has native zinc that could contribute to zinc concentrations in runoff.
4. In general, all agricultural byproducts tested in this study exported nutrients. This may be a concern in areas with sensitive receiving waters and in bioretention systems with underdrains.

More work is needed to determine when the sorption capacity is reached and the hazelnut/pecan shells need to be replaced to maintain treatment efficacy, as well as the impacts of scaling up to a full-scale bioretention system. Testing with other amendments, such as WTRs, and plants is necessary to limit nutrient leaching if used in bioretention systems with an underdrain. Pecan and hazelnut shells have the potential to reduce the amount of metals in stormwater that eventually reach receiving waters.

Data Availability Statement

All data generated during the study are available from the corresponding author by request, including water quality analysis and hydraulics data.

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