Assessing Zeolite Amended Bioretention Media for Removal of Nutrients and Metals from Stormwater

by

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Abstract

Bioretention cells are installed to treat stormwater through physical, biological, and chemical processes facilitated by a permeable soil media. The soil media is commonly composed of sand, silt, clay, and organic matter, but alternative materials may improve cell performance. Zeolites, an aluminosilicate mineral group, have properties including high hydraulic conductivity and cation exchange capacity (CEC) that may increase pollutant removal while maintaining appropriate hydrologic conditions. The objectives of this study were to design and characterize three bioretention soil mixtures that incorporate a zeolite mineral, perform column studies to compare the nutrient and metal removal capabilities of the mixtures, and evaluate the longevity of the mixtures. A standard bioretention mixture of 85% sand, 11% fines, and 4% organic matter by volume (ALMIX) was altered by replacing sand with Ecolite, a commercially available zeolite product. Mixtures were created with 2% (AUMIX), 10% (AUMIX10), and 20% (AUMIX20) volume of Ecolite, and a control of 100% sand was included. The addition of Ecolite decreased maximum bulk density and particle density, F(3,4)= 25.38, p= 0.005. Estimated CEC increased with increasing Ecolite addition, F(4,5)= 100.97, p< 0.001. Saturated hydraulic conductivities of mixtures containing Ecolite were significantly higher than or similar to ALMIX, F(4,55)= 319.03, p< 0.001. All mixtures were placed in columns, and four storm events were simulated by running synthetic stormwater containing copper, zinc, phosphorus, ammonium, and nitrate through the columns. Pollutant concentrations in collected effluent were measured by inductively coupled plasma mass spectrometry and catalytic reduction with colorimetric readings. There was no significant difference in effluent concentrations among mixtures or storm events for zinc, F(12,57)= 0.90, p= 0.65, or copper, F(12,57)= 0.76, p=0.68. All non-control mixtures had statistically lower effluent phosphorus than the control, F(12,57)=

1.9, $p = 0.04$. Mixtures containing Ecolite yielded significantly lower ammonium concentrations than ALMIX, but this difference decreased over time, $F(12,60) = 5.18$, $p < 0.001$. All non-control mixtures had increases in effluent nitrate concentration, but mixtures containing Ecolite had significantly lower effluent nitrate than ALMIX, $F(12,60) = 2.38$, $p = 0.014$. Amending bioretention media with Ecolite did not appear to affect longevity as compared to ALMIX.

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List of Abbreviations

CEC	Cation Exchange Capacity

Chapter 1: The Utilization of Column Studies to Test Bioretention Cell Media Pollutant Removal Performance

Stormwater Runoff

Metropolitan areas in the United States have undergone significant expansion in the last seven decades (USEPA, 2013). As cities have grown, the additions of suburbs and connecting roads have spread development outward, and the increase in urbanized land area has outpaced the growth of the population (USEPA, 2013). Stormwater results when precipitation cannot fully infiltrate in the ground, and the excess precipitation moves over pavement, rooftops, and other surfaces, washing pollutants directly into water bodies. Urban expansion affects stormwater infiltration through addition of impervious surfaces, removal of floodplain area, and rerouting of natural water channels for infrastructure purposes (Shuster et al., 2005). Increases in impervious surfaces can increase the amount of runoff, the peak discharge rate, and the concentration of pollutants in runoff (Shuster et al., 2005). Pollutants in stormwater include heavy metals, nutrients, and hydrocarbons. The first inch of a storm, commonly called the first flush, typically has a higher concentration of pollutants than the rest of the storm (Hatch & Burton, 1999).

Common metals in stormwater include copper, lead, cadmium, nickel, and zinc, and stormwater chemistry affects which forms of the metals are present (Clary et al., 2011). Depending on the pH, redox potential, and other present compounds, metals may be found in dissolved, particulate, or colloidal forms (Clary et al., 2011). Metals in stormwater are primarily present in particulate form. However, dissolved metals still warrant concern, because they are more bioavailable than particulate metals, and some metals, such as copper and lead, are typically dissolved (LeFevre et al., 2014). Many metals are naturally occurring, but high metal concentrations are usually a result of urban pollution (Boyd, 2015). Urban and suburban sources include the combustion of fossil fuels and lubricating oils, the wear of automobile parts, metal corrosion, and industrial emissions (Makepeace et al., 1995). Heavy metals can be highly persistent when they enter environments, leading to bioaccumulations in organisms and decreases in aquatic diversity (Beasley & Kneale, 2002; Dorchin & Shanas, 2013; Mayer et al., 2011; McIntyre et al., 2014).

Stormwater may also contain excess nutrients. Nitrogen and phosphorus are essential nutrients for organisms, but anthropogenic additions of these nutrients into systems can have detrimental consequences. Dissolved forms of nutrients in stormwater include nitrate, nitrite, ammonia, ammonium, dissolved organic nitrogen, inorganic orthophosphate, and dissolved organic phosphorus (LeFevre et al., 2014; River & Richardson, 2018). Particulate forms of nutrients include particulate organic nitrogen and particulate organic phosphorus. Nitrogen in stormwater is most commonly present in dissolved forms, and its transformations are biologically mediated (Taylor et al., 2005). Phosphorus is more commonly particulate bound in stormwater, and its transformations are chemically driven (Uusitalo et al., 2003). Point sources such as sewage can contribute to nutrient pollution, but nonpoint sources including fertilizers, animal wastes, and atmospheric deposition are more frequent contributors (Anderson et al., 2002). Together, nitrogen and phosphorus can trigger harmful algal blooms capable of producing toxins and decreasing dissolved oxygen (Anderson et al., 2002). Additionally, high concentrations of nitrogen in the form of ammonia or nitrite can be toxic to aquatic organisms. High concentrations of phosphorus are not toxic to aquatic organisms (Boyd, 2015).

Bioretention Cells

Green infrastructure measures take inspiration from natural landscapes and are designed to improve stormwater quality by replicating ecosystem services in urban settings. By installing measures such as permeable pavements, urban trees, green roofs, and bioretention cells, stormwater toxicity can be addressed by reducing the quantity of excess water and transforming pollutants into less harmful forms. Bioretention cells are designed to filter the first flush of stormwater before it enters surface water or groundwater. These structures are depressed landscape features topped by mulch and planted with native vegetation. An inlet brings stormwater into the cell, and the water is filtered through permeable media. After passing through the cell, stormwater may exfiltrate into the surrounding soils or be transported by an outlet structure (Roy-Poirier et al., 2010). This increase in stormwater retention may reduce the amount of runoff, peak discharge rate, and concentration of pollutants (Trowsdale & Simcock, 2011). Further advantages of incorporating bioretention cells as stormwater practices include cost effectiveness and increased aesthetic value (Roy-Poirier et al., 2010).

Well-designed bioretention soil media must incorporate aspects of both soil physics and soil chemistry. To achieve proper infiltration, the media needs a high hydraulic conductivity. Additionally, physical processes such as filtration and settling are principally responsible for removal of particulate pollutants (Davis et al., 2010; LeFevre et al., 2014). These objectives are achieved by composing the media primarily of sand sized particles (0.05 - 2 mm) (Hsieh & Davis, 2005). In contrast, dissolved pollutants are largely removed by chemical and biological processes, such as adsorption, precipitation, ion exchange, and nitrification (Davis et al., 2009; LeFevre et al., 2014). These can be achieved by adding chemically active particles, such as negatively charged clay particles or organic matter, which raise the cation exchange capacity

(CEC) of soil media. However, if the clay percentage is too high, the media may swell when wetted, and organic matter can leach nutrients in the effluent (Hsieh & Davis, 2005). Therefore, media design requires finding a balance between hydraulic and chemical performance. The recommended composition of the media is variable among states and city green infrastructure handbooks. Although most of the handbooks recommend a texture of sandy loam, loamy sand, or sand, the specifications differ in media depth, sand percentage, silt percentage, clay percentage, organic matter percentage, and organic matter sources. Sizing methods of the cell also vary by state and may be based on peak runoff, the impervious drainage area, or the local water quality standards (Roy-Poirier et al., 2010). Recommendations in Alabama are that bioretention cells have an area that is 5-8% of the impervious drainage area (Dylewski et al., 2013).

Laboratory Bioretention Studies

Bioretention studies have occurred in field and laboratory settings. Whereas field settings may provide a more realistic view of how the cell performs in a particular environment, laboratory settings simplify the comparison of numerous bioretention mixtures under constant environmental conditions. This is frequently accomplished by performing column studies (Lewis & Sjöstrom, 2010). Packed soil columns are created by enclosing a homogenous mixture inside of a solid material. Researchers can then regulate or measure the rate of infiltration, as well as collect the effluent at the bottom of the column and model one-dimensional flow (Lewis & Sjöstrom, 2010). By packing the columns, researchers can create reproducible columns with identical bulk densities and dispersivities, but care must be taken to avoid the creation of preferential flow paths (Lewis & Sjöstrom, 2010).

Once a media has been designed for use in a column experiment, its physical and chemical properties are typically analyzed. Physical properties such as texture, bulk density, porosity, hydraulic conductivity, and hydraulic residence time provide measurements relevant to the material's ability to drain the stormwater. Some chemical measurements affect how well the media can remove pollutants, including pH and cation exchange capacity. Chemical measurements also include concentrations of metals and nutrients in the soil, including copper, zinc, aluminum, iron, manganese, plant available metals, total nitrogen, total phosphorus, total calcium, total potassium, total magnesium, total carbon, inorganic nitrogen, and plant extractable phosphorus (Davis et al., 2001; Hsieh & Davis, 2005; Ippolito, 2015; Jay et al., 2019; Liu et al., 2014). It is important to know these concentrations because these elements can leach into the stormwater effluent and affect the interpretation of the results. Additionally, many of these nutrients need to be present in small amounts to support the bioretention cell's native plant growth (Liu et al., 2014).

The use of synthetic stormwater is common in bioretention studies (Davis et al., 2001; Feng et al., 2012; Hsieh & Davis, 2005). Passing water through multiple columns can require large quantities of water. From a practical standpoint, making synthetic stormwater provides the needed volume, which may be large, with known pollutant concentrations (Feng et al., 2012). This also minimizes the differences in pollutants from affecting the reported pollutant removal (Hsieh & Davis, 2005). Synthetic stormwater is typically created by dechlorinating tap water or using distilled water and adding desired compounds to simulate concentrations found in stormwater (Table 1). The method by which the stormwater is added to the column varies. Stormwater can be added by maintaining a constant head above the media (Hsieh & Davis, 2005), pumping (Liu et al., 2014) or pouring (Jay et al., 2019) volumes based on rainfall events onto the media, or passing the water upward through the column (Davis et al., 2001). Once the stormwater has passed through the media, it is often transported through tubes (Davis et al., 2001; Liu et al., 2014) or simply allowed to drain (Ippolito, 2015) into containers. The pollutant concentrations and often the pH and dissolved oxygen concentration are also measured.

Table 1. Examples of common additives in synthetic stormwater.

Pollutant	**Source**	**Concentration**
		mg/L
Total dissolved solids*†	$CaCl_2$	120
Suspended solids†	Soil sieved to 0.59 mm	150
Phosphorus†	Na_2HPO_4	3 (as P)
Nitrate*†	$NaNO_3$	2 (as N)
Ammonium†	NH_4Cl	2 (as N)
Organic nitrogen*	NH_2CH_2COOH	4 (as N)
Copper*	$CuSO_4$	0.08
Lead*	$PbCl_2$	0.08
Zinc*	$ZnCl_2$	0.6
Motor Oil†	Oil from car garage	20

*Davis et al., 2001
†Hsieh and Davis, 2005

Evaluating the effectiveness of bioretention cells is complex. Environmental factors including temperature, pH, and availability of oxygen can affect performance (LeFevre et al., 2014). In field experiments, performance is noted to change depending on the season. Warmer months have higher rates of evapotranspiration, meaning outflow may be higher in colder months (Hunt et al., 2006). Furthermore, effectiveness has been reported in multiple formats. Many studies have reported effectiveness as a pollutant reduction percentage, but this can change in response to the initial concentration of pollutants in stormwater. For example, a bioretention cell would display a lower reduction percentage if the incoming stormwater had lower pollutant concentrations as compared to a highly contaminated inflow (Roy-Poirier et al., 2010). Therefore, it is preferred to maintain a consistent influent concentration of pollutants or to report effectiveness as a removal percentage on a mass basis (Roy-Poirier et al., 2010).

Metals have generally been shown to have high removal rates in bioretention cells, while nutrients are more variable. Multiple studies were performed with a sandy loam media (averaging 76% sand, 10% clay, and 14% silt from four samples) to evaluate the ability of a bioretention system to remove pollutants from a synthetic stormwater solution (Davis et al., 2001). Copper, lead, and zinc were selected as representative heavy metals, and the system yielded at least 98% mass removal for all three metals (Davis et al., 2003). However, other metals, including cadmium, iron, chromium, and aluminum, may have lower removal efficiencies (Glass & Bissouma, 2005). Davis et al. (2006) documented high phosphorus removal (82% by mass, 70-85% by concentration) but variable nitrogen removal. The form of nitrogen is an important factor in removal, as total Kjeldahl nitrogen (TKN) (organic nitrogen, ammonia, and ammonium) had an average mass removal of 86% (55-65% by concentration), but nitrate had a poor removal of less than 20% by concentration or often increased in concentration (Davis et al., 2006). This is likely due to the high mobility of nitrate in soil from lack of adsorption to soil particles and aerobic conditions in the bioretention cell that would allow for nitrification to produce nitrate (Roy-Poirier et al., 2010).

Table 2. Examples of previous bioretention research utilizing column studies.

Study	Column Information	Media Used	Hydraulic Properties of Media	Stormwater Used	Water Addition	Average Pollutant Removal	Notes
Hsieh and Davis, 2005	Plexiglas, Height 110 cm, Diameter 19.1 cm	54% sand, 43% sandy loam soil, 3% mulch*	Infiltration rate: 0.48 ± 0.02 cm/min	Synthetic	Water was pumped into top of column with 15 cm constant head	Total suspended solids (TSS): >96% Oil and grease (O/G): >96% Pb: >98% Total phosphorus (TP): 83 ± 1.4% Nitrate: 13 ± 59% Ammonium: 26 ± 2.6%	N/A
Hsieh and Davis, 2005	Plexiglas, Height 110 cm, Diameter 19.1 cm	81% sand, 17% sandy loam, 2% mulch*	Infiltration rate: 5.40 ± 0.15 cm/min	Synthetic	Water was pumped into top of column with 15 cm constant head	TSS: >96% O/G: >96% Pb: 97 ± 0.2% TP: 24 ± 3.8% Nitrate: 6 ± 1.5% Ammonium: 26 ± 0.6 %	N/A
Sun and Davis, 2007	Pot, Height 31 cm, Diameter 31 cm	50% sand, 30% silt loam planting soil, 20% leaf mulch†	Not given	Synthetic	Water was applied to pot from plastic drums	Zn: 93 ± 4% Cu: 88 ± 4.5% Pb: 95 ± 2% Cd: >95%	Top 5 cm were 50% silt loam planting soil and 50% leaf mulch†, Plants were included
Feng et al., 2012	PVC pipe, Height 91 cm, Diameter 37.5 cm	80% sandy loam soil, 10% leaf compost, 10% mulch†	Not given	Semi-synthetic	Water was applied using jugs	Fe: 92% (4) Pb: 97% (2) Cu: 90% (7) Cr: 83% (8) Zn: 99% (0) Al: 87% (6)	Plants were included
Bratieres et al., 2008	PVC pipe, Height 91 cm, Diameter 37.5 cm	80% sandy loam soil, 10% leaf compost, 10% mulch†	Not given	Semi-synthetic	Water was applied using jugs	TSS: 98% (0.5) Total nitrogen (TN): -101% (>100) NO_x: -158% (>100) TP: 38% (78) Phosphate: -78% (>100)	Plants were included
Hong et al., 2006	Porcelain Büchner funnel, Height 11 cm, Diameter 25.3 cm	Leaf compost mulch	Not given	Synthetic	Water was pumped onto mulch surface	Dissolved naphthalene: ~90% Dissolved toluene: ~83% Dissolved motor oil: ~80% Particulate naphthalene: ~97%	N/A

All removal percentages represent reductions in concentration.
*Percentage by mass
†Percentage by volume
() Denotes coefficient of variation
± Denotes standard deviation

Zeolite

Although bioretention media traditionally mixes sand, silt, clay, and organic matter, modified mixtures may incorporate alternative materials. The purpose of this is to add charged material with high cation exchange capacity while subsequently attempting to raise or maintain hydraulic conductivity and water holding capacity (Vijayaraghavan & Praveen, 2016). Commonly researched alternative materials have included water treatment residuals (Chun-bo Jiang et al., 2018; Li et al., 2018), coconut materials (Chun-bo Jiang et al., 2018; Li et al., 2018; Vijayaraghavan & Praveen, 2016), and fly ash (Chun-bo Jiang et al., 2018; Li et al., 2018). Zeolites, a group of natural and synthetic aluminosilicate and microporous minerals, are also potential additives for bioretention mixtures.

Zeolites can modify soil structure by increasing the pore volume and lowering the bulk density (Nakhli et al., 2017). A study by Xiubin and Zhanbin (2001) showed that applying a zeolite (Mordenite) to soil with gentle slopes increased infiltration by 7-30%, and a study by Mu et al. (2006) concluded that a zeolite (lignin and natural zeolite) was capable of decreasing runoff, indicating that infiltration had increased. In contrast, Al-Busaidi et al. (2008) concluded that the micropores in their synthetic zeolite (Ca^{2+}-type) decreased infiltration rate.

The channels in the structure of zeolites allow them to also alter hydraulic conductivity (Nakhli et al., 2017). When Githinji et al. (2011) compared a zeolite's (Ecolite) hydraulic conductivity to sand, they found that it was greater than three times higher, and a mixture of the zeolite and sand had higher hydraulic conductivity than sand alone. However, attention must be given to particle size. If the zeolite's particles are smaller than sand, too much zeolite can decrease the hydraulic conductivity (Nakhli et al., 2017).

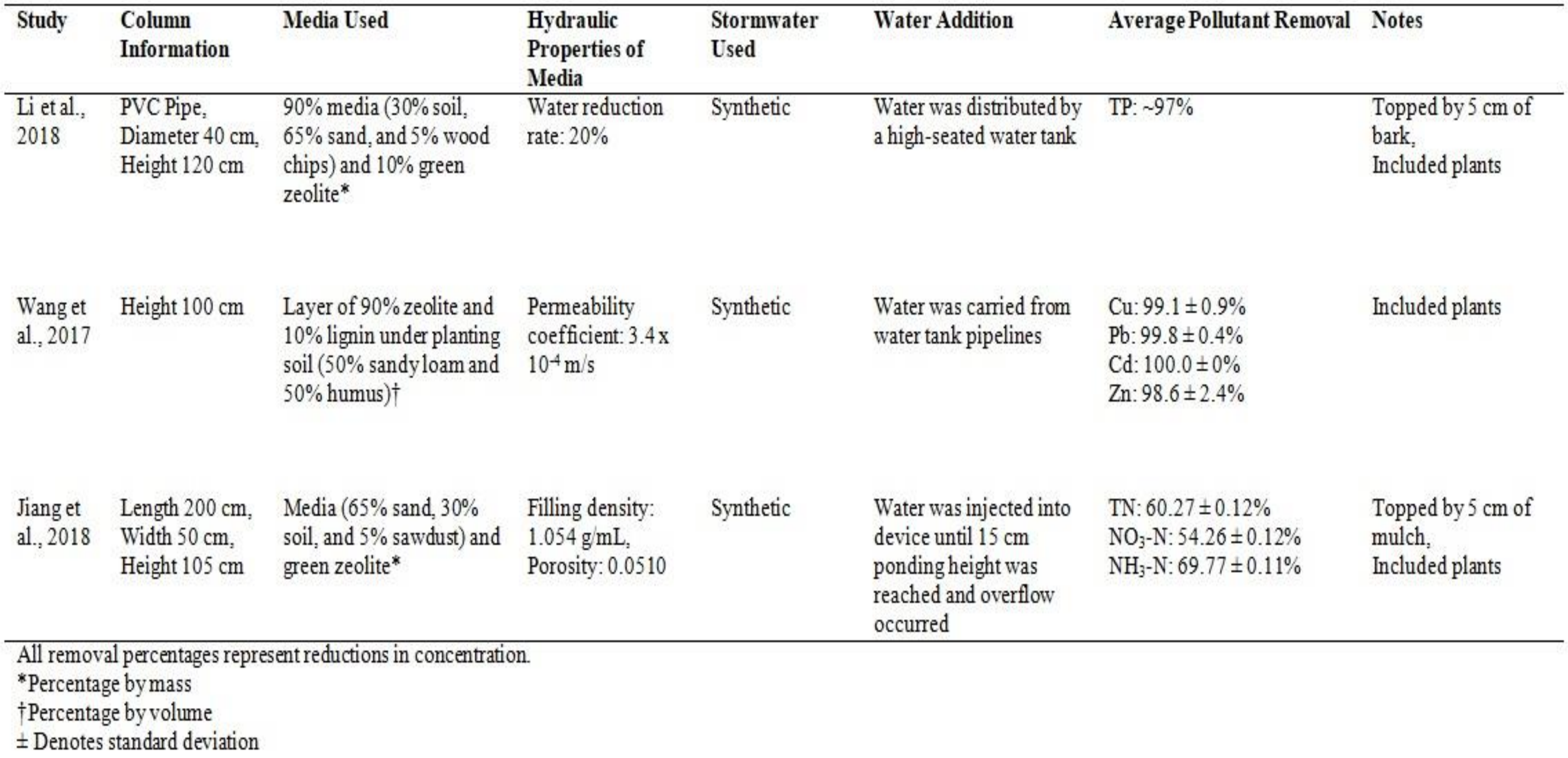
Adding zeolites to soil can increase water holding capacity, as bulk density is decreased and porosity is increased (Nakhli et al., 2017). de Campos Bernardi et al. (2013) added a zeolite (Stilbite) in increasing amounts to a sandy soil and found that their highest rate of application (10% w w^{-1}) increased water content by 67%. Bigelow et al. (2001) added 10% v v^{-1} of a zeolite (Ecolite) to a sandy soil and increased the volumetric water content by 20%. Within this same study, inclusion of the zeolite increased CEC from 0.8 cmol/kg to 1.6 cmol/kg (Bigelow et al., 2001).

Because zeolites can increase a soil's water holding capacity, infiltration rate, saturated hydraulic conductivity, and CEC, they have conventionally been used in agricultural and turf grass fields for amending or remediating soil and have industrial purposes as molecular sieves, catalysts, and ion exchangers (Nakhli et al., 2017). These services could prove useful in a bioretention cell, and existing research has yielded some success (Table 3). However, most papers have only focused on one type of pollutant, and the effectiveness of zeolite can change with the type of zeolite used and the blend of bioretention mixture selected (Nakhli et al., 2017).

Study Goals

The purpose of this study was to assess the potential of Ecolite, a commercially available form of zeolite, as a soil amendment in bioretention media. Research objectives were to (1) design three bioretention mixtures that incorporate a zeolite mineral and identify physical and chemicals properties of the mixtures, (2) perform column studies to compare the nutrient and metal removal capabilities of the mixtures, and (3) evaluate the longevity of the mixtures by pollutant removal.

Table 3. A summary of previous research investigating the use of zeolite in bioretention cells.



Study	Column Information	Media Used	Hydraulic Properties of Media	Stormwater Used	Water Addition	Average Pollutant Removal	Notes
Li et al., 2018	PVC Pipe, Diameter 40 cm, Height 120 cm	90% media (30% soil, 65% sand, and 5% wood chips) and 10% green zeolite*	Water reduction rate: 20%	Synthetic	Water was distributed by a high-seated water tank	TP: ~97%	Topped by 5 cm of bark, Included plants
Wang et al., 2017	Height 100 cm	Layer of 90% zeolite and 10% lignin under planting soil (50% sandy loam and 50% humus)†	Permeability coefficient: 3.4 x 10^{-4} m/s	Synthetic	Water was carried from water tank pipelines	Cu: 99.1 ± 0.9% Pb: 99.8 ± 0.4% Cd: 100.0 ± 0% Zn: 98.6 ± 2.4%	Included plants
Jiang et al., 2018	Length 200 cm, Width 50 cm, Height 105 cm	Media (65% sand, 30% soil, and 5% sawdust) and green zeolite*	Filling density: 1.054 g/mL, Porosity: 0.0510	Synthetic	Water was injected into device until 15 cm ponding height was reached and overflow occurred	TN: 60.27 ± 0.12% NO_3-N: 54.26 ± 0.12% NH_3-N: 69.77 ± 0.11%	Topped by 5 cm of mulch, Included plants

All removal percentages represent reductions in concentration.

*Percentage by mass

†Percentage by volume

± Denotes standard deviation

Chapter 2: Design and Characterization of Bioretention Mixtures Containing Zeolite

Abstract

Three bioretention mixtures were designed based on the Low Impact Development Handbook for the State of Alabama recommended mixture of 85% sand, 11% fines, and 4% organic matter by volume (ALMIX) (Dylewski et al., 2013). This mixture was altered by replacing volumes of sand with a zeolite (Ecolite) as 2% (AUMIX2), 10% (AUMIX10), and 20% (AUMIX20) of the total mixture volume. Sand, topsoil, peat moss, and Ecolite were used to create the mixtures, ALMIX, and a control of 100% sand. The media were characterized by determining maximum bulk density, particle density, estimated cation exchange capacity (CEC), and saturated hydraulic conductivity, and the data were analyzed by ANOVAs in R statistical software. ALMIX had the highest maximum bulk density of 1.77 g/cm^3 and AUMIX20 had the lowest of 1.69 g/cm^3. AUMIX20 had a mean particle density of 2.55 g/cm^3 and was significantly lower than the other mixtures, $F(3,4)= 25.38$, $p= 0.005$. AUMIX10 and AUMIX20 had significantly higher mean estimated CECs than the other mixtures, 3.00 and 3.15 cmol/kg, respectively, $F(4,5)= 100.97$, $p< 0.001$. CONTROL had a mean saturated hydraulic conductivity of 2.77 cm/min that was significantly higher than all other mixtures. AUMIX2 and AUMIX20 had significantly higher mean saturated hydraulic conductivities than ALMIX , $F(4,55)= 319.03$, $p<0.001$. The effects of these properties on bioretention performance will be further analyzed in a column study.

Introduction

Bioretention cells address urban and suburban stormwater pollution by filtering the water through a soil mixture. The composition of the soil mixture heavily determines the pollution removal capability and hydrologic performance of the cell. Larger sized particles can provide for adequate infiltration and removal of particulate pollutants. Finer materials, like silt and clay, can increase mixture CEC and the removal of dissolved pollutants but decrease the hydraulic conductivity. Organic matter is often included as compost, peat moss, or mulch to increase moisture retention, carbon supplies for microbial processes in the soil, and support for the native vegetation planted in the cell (Hills et al., 2016). However, too much organic matter can leach excess nutrients in the effluent stormwater (Jay et al., 2019).

Across city and state green infrastructure handbooks and published research, the recommended configuration of bioretention cells and the composition of bioretention media varies greatly. The ideal bioretention cell is not necessarily universal and may depend on the targeted pollutants desired for removal from the watershed. For example, Wang et al. (2019) built a database of results from bioretention studies and concluded that suspended solids are well removed by mixtures with sandy loam filters, and organic matter may impair the removal of nutrients. Additionally, system components such as the inclusion of internal water storage layers or vegetation and high media depth can increase nutrient removal.

However, prior research includes some general suggestions for the composition of bioretention media. The selected media should be paired with a configuration that appropriately utilizes the media design. For example, Davis et al. (2005) suggested two cell designs that each utilizes a different mixture and configuration. One design is coarse sand and 20-70% sandy loam soil by mass. The plants are planted directly in the mulch and filtration media, so the percentage of soil must meet the requirements of the plant. The second design includes a planting layer above the filtration media, so the media does not have to support vegetation. The mixture can therefore be 50% coarse sand and 50% sandy loam soil by mass. After comparing three bioretention blends for the removal of nitrogen and phosphorus, Liu et al. (2014) provided recommendations for bioretention media composition. The mixtures should contain less than 10% fines to ensure adequate infiltration, at least 3-5% low nutrient carbon material (organic matter) by volume, and minimal soil nitrogen and phosphorus as needed for plant establishment.

Zeolites, an aluminosilicate mineral group, have potential attributes including improved hydraulic conductivity, CEC, and water holding capacity (Nakhli et al., 2017) that could make them effective amendments in bioretention media that increase pollutant removal while maintaining required infiltration. Research on the inclusion of zeolites in bioretention media is limited, and the effects of a zeolite may change as the form of zeolite and the soil texture change. Previous research has incorporated zeolites into cells in multiple ways. Li et al. (2018) incorporated 10% green zeolite by mass into a mixture of 30% soil, 65% sand, and 5% woodchips. Wang et al. (2017) incorporated the zeolite as a layer of 90% zeolite and 10% lignin by volume under a planting soil of 50% sandy loam and 50% humus.

The objective of this research was to design and characterize bioretention mixtures containing a zeolite mineral. Designing the bioretention mixtures required selecting a zeolite source, deciding the volumes of zeolite to incorporate into the mixtures, and selecting a commonly utilized bioretention mixture to compare with the designed mixtures. Measuring the selected physical and chemical properties provided values necessary for experimental design and future result interpretation. Maximum bulk density and particle density values were used when designing the column study. CEC values and saturated hydraulic conductivity would aid result interpretation from the column study.

Ecolite, a naturally occurring and commercially available zeolite product composed of clinoptilolite was selected as the zeolite source. This soil amendment was chosen due to its high reported CEC and its reported ability to adsorb ammonium ions. Reports of the CEC differ, as the Ecolite tech sheet claims 200 meq/100g (“Ecolite Physical Soil Amendment,”) and Wehtje et al. (2000) reported 71.4 meq/100 g.

Methods

Media Design

The design of the three amended bioretention mixtures was based on the media recommendation in the Low Impact Development Handbook for the State of Alabama: 85-88% sand, 8-12% fines, and 3-5% organic matter by volume (Dylewski et al., 2013). This media was modified by lowering the volume of sand and replacing it with varying amounts of Ecolite. The percentages of Ecolite added were based on previous recommendations from Bigelow (2004). While researching the incorporation of Ecolite in the root zone of turfgrass, their highest application of 20% by volume resulted in the lowest ammonium loss (7.8%), but Bigelow recommended 10% as a more cost-effective solution. Using this as a guide, the designed mixtures contained 2%, 10%, and 20% zeolite (Table 4).

Table 4. Composition of mixtures used in study.

Mixture	**Sand**	**Fines**	**Organic Matter**	**Ecolite**
	% volume			
ALMIX	85	11	4	0
AUMIX2	83	11	4	2
AUMIX10	75	11	4	10
AUMIX20	65	11	4	20
CONTROL	100	0	0	0

Media Creation

The mixtures were created by mixing calculated volumes of sand, topsoil, peat moss, and Ecolite. Topsoil was collected twice from the edge of a pivot irrigation plot at E.V. Smith Research Center in Shorter, AL. The samples were processed by air drying, sieving to 2 mm, and combining the collections together. Texture was determined by Pipette Analysis 3A1a (Burt, 2014) as silt loam (25% sand, 49% silt, and 26% clay). Sand was collected from the Auburn University Turfgrass Research Unit. Earthworks Ecolite was purchased as the zeolite source, and Majestic Earth Sphagnum peat moss was purchased for the organic matter source.

Media Characterization

After mixture creation, ALMIX, AUMIX2, AUMIX10, and AUMIX20 were used for Proctor compaction tests following ASTM D 698 – 07 (ASTM International, 2007). Samples were brought to multiple moisture contents and compacted with 600 kN-m/m^3 of effort into a cylindrical mold of 10.16 cm diameter. Dry weight of the soil and cylinder volume were used to determine the bulk density of each sample. Compaction curves were created by plotting the bulk density of samples over their molding water content (Figure 1). The peaks of the curves were used to identify the maximum bulk density of each mixture.

Particle densities for ALMIX, AUMIX2, AUMIX10, and AUMIX20 were determined by the pycnometer method ASTM D854 – 14 (ASTM International, 2014). Pycnometers of 25 mL volume were used, water was boiled to remove entrapped air, and three repetitions occurred for every mixture. Cation exchange capacity values for ALMIX, AUMIX2, AUMIX10, AUMIX20, CONTROL, Ecolite, and the EV Smith topsoil were estimated based on Mehlich-extractable base cations and pH by Waters Agricultural Laboratories in Camilla, GA.

Saturated hydraulic conductivity (K_s) values were determined after the column studies were completed (see column set up in Chapter 3). Tap water was ponded 13 cm above the material in the column and the time to drain 5 cm was recorded. Saturated hydraulic conductivity values were calculated as follows:

$$K_s = \frac{\text{media depth}}{\text{drain time}} \times \ln \frac{\text{initial height of water above media+media depth}}{\text{final height of water above media+media depth}} : \textbf{Equation 1.}$$

Particle density, estimated CEC, and log transformed saturated hydraulic conductivity values were analyzed in R statistical software. The values for each property were compared between mixtures by ANOVAs. Tukey HSD tests were used to further identify the significant differences.

Results

Maximum bulk density and particle density decreased with increasing volume of Ecolite (Figure 1Figure 1. The compaction curve resulting from the Proctor compaction test for each mixture., Table 5). Particle density was significantly affected by mixture, and AUMIX20's mean particle density of 2.551 g/cm^3 was significantly higher than all other mixtures, $F(3,4) = 25.38$, $p = 0.005$.

CEC was significantly affected by mixture, $F(4,5) = 100.97$, $p < 0.001$. AUMIX 20 had the highest mean CEC at 3.15 cmol/kg and was significantly higher than CONTROL, ALMIX, and AUMIX2. AUMIX2 and ALMIX were significantly higher than CONTROL (Table 5).

Saturated hydraulic conductivity was also significantly affected by mixture, $F(4,55) = 319.01$, $p < 0.001$. CONTROL had the highest mean saturated hydraulic conductivity at 2.77 cm/min and was significantly higher than all other mixtures. AUMIX2 and AUMIX20's saturated hydraulic conductivities were significantly higher than that of ALMIX (Table 5).

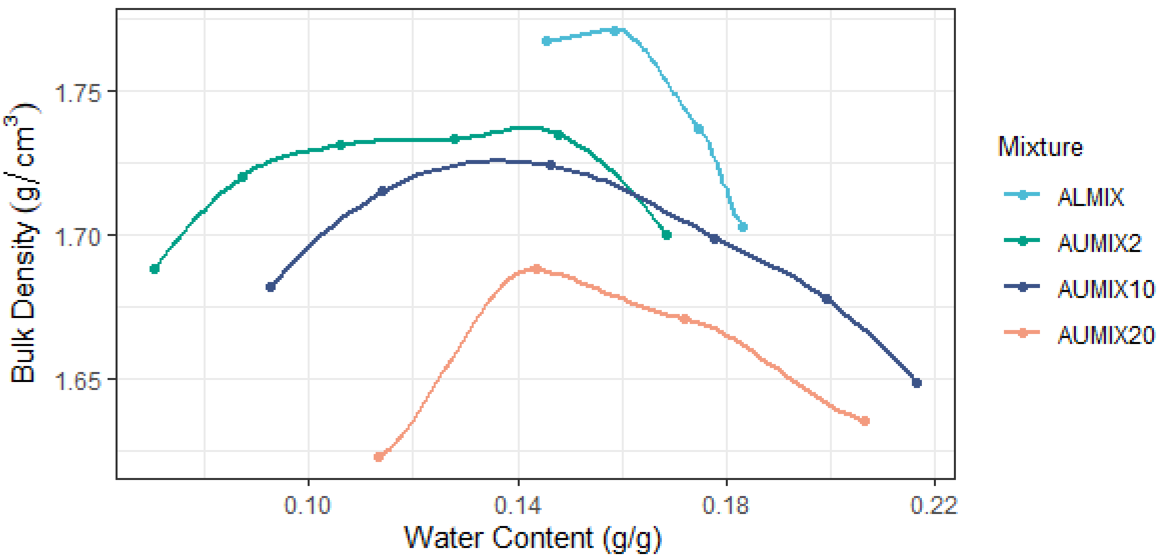


Figure 1. The compaction curve resulting from the Proctor compaction test for each mixture.

Table 5. Values resulting from Proctor compaction, particle density, cation exchange capacity, and saturated hydraulic conductivity tests.

Mixture	**Maximum Bulk Density**	**Particle Density**	**Cation Exchange Capacity***	**Saturated Hydraulic Conductivity**
	g/cm^3		cmol/kg	cm/min
ALMIX	1.772	2.675 ± 0.02 ^{a}	2.05 ± 0.07 ^{b}	0.20 ± 0.03 ^{c}
AUMIX2	1.735	2.643 ± 0.01 ^{a}	2.05 ± 0.21 ^{b}	0.33 ± 0.12 ^{b}
AUMIX10	1.727	2.622 ± 0.01 ^{a}	3.0 ± 0.14 ^{a}	0.25 ± 0.03 ^{bc}
AUMIX20	1.688	2.551 ± 0.02 ^{b}	3.15 ± 0.07 ^{a}	0.31 ± 0.06 ^{b}
CONTROL	NA	NA	0.7 ± 0.14 ^{c}	2.77 ± 0.37 ^{a}
n	1	3	2	3

* Estimated
± Standard Deviation
^{a,b,c} Denote significance groups

Discussion

Maximum Bulk Density and Particle Density

Maximum bulk density can be used to determine a goal bulk density for bioretention cell compaction. Additionally, bulk density and particle density are used to calculate the porosity of a soil. Based on these results, it is assumed there will be some variation among mixtures in the determined goal bulk densities and porosities, and therefore, the amount of media compacted in the columns.

Addition of zeolites in soil is commonly reported to decrease soil bulk density (Nakhli et al., 2017; Ramesh et al., 2011). Githinji et al. (2011) amended sand with Ecolite and Clinolite as 15% of the mixture volume. The bulk density of the sand was 1.67 g/cm^3, and the Ecolite and Clinolite amended mixtures had bulk densities of 1.56 g/cm^3 and 1.57 g/cm^3, respectively. Bigelow et al. (2001) amended sand with Ecolite as 10% of the volume, and the bulk density decreased from 1.66 g/cm^3 to 1.60 g/cm^3.

CEC

High CEC can aid in chemical removal of positively charged pollutants from stormwater. Because AUMIX10 and AUMIX20 had significantly higher CECs than the other mixtures, they may have the potential to remove some pollutants better than the other mixtures. However, because AUMIX10 and AUMIX20 do not have significantly different CECs, the addition of 20% Ecolite may not have a significant improvement over a 10% addition.

The increase in soil CEC with addition of zeolite minerals is extensively reported (Inglezakis et al., 2016; Nakhli et al., 2017) and a major factor of their use in agriculture and industry. When Bigelow et al. (2001) incorporated Ecolite with quartz sand at 10% volume, the CEC doubled from 0.8 cmol/kg to 1.6 cmol/kg.

Saturated Hydraulic Conductivity

Bioretention cells require sufficient hydraulic conductivity to drain the incoming stormwater at a rate that avoids ponding and excessive flow through but allows adequate exposure to the media. Because CONTROL is 100% sand, it was expected that it would have the highest saturated hydraulic conductivity. It was also expected that mixtures containing Ecolite may have significantly higher saturated hydraulic conductivities than ALMIX. Except for AUMIX10, this was true. The hydraulic conductivity of standard media was improved by greater than 50% when comprised of 2% and 20% Ecolite. Hydraulic conductivity is a highly variable property, and it is possible that column conditions attributed to AUMIX10 not being statistically different than ALMIX.

Zeolites are generally considered to have the potential to increase saturated hydraulic conductivity, but the effect highly relies on soil texture. If the zeolite particles are smaller than sand, too much zeolite may decrease the saturated hydraulic conductivity (Nakhli et al., 2017). When Githinji et al. (2011) incorporated Ecolite and Clinolite at 15% volume to sand, the saturated hydraulic conductivity increased from 0.683 cm/min to 1.27 cm/min and 1.30 cm/min, respectively. These results agree with the result of this study, as the hydraulic conductivity of the standard ALMIX was improved as the sand portion was replaced with amounts of Ecolite.

Similar to this study, Razmi and Sepaskhah (2012) and Gholizadeh-Sarabi and Sepaskhah (2013) reported increases and decreases in saturated hydraulic conductivity with increasing amounts of zeolite. Razmi and Sepaskhah (2012) utilized soil with a high fine content (5% sand, 49% silt, and 46% clay) and applied zeolite at rates of 4, 8, and 12 g zeolite/kg soil. The soil had a saturated hydraulic conductivity of 0.0030 cm/min, slightly decreased at the 4 g/kg soil rate, increased to 0.0070 cm/min at the 8 g/kg soil rate, and decreased again to 0.0023 cm/min at the 12 g/kg soil rate. Gholizadeh-Sarabi and Sepaskhah (2013) applied rates of 4, 8, and 16 g zeolite/kg soil to sandy loam soil. The saturated hydraulic conductivity of the sandy loam soil measured 0.162 cm/min. This decreased with applications of 4 and 8 g/kg of soil to 0.076 cm/min and 0.053 cm/min, and it increased to 0.091 cm/min at the 16 g/kg soil rate.

Conclusion

Adding a zeolite mineral (as soil amendment Ecolite) significantly changed some physical and chemical characteristics of a conventional bioretention mixture containing 85% sand, 11% fines, and 4% organic matter. Mixtures containing Ecolite had lower maximum bulk density. Comprising the mixture with 20% Ecolite significantly decreased the mixture particle density from 2.68 g/cm^3 to 2.55 g/cm^3. Estimated CEC was significantly increased when adding 10% or more of Ecolite. Adding Ecolite to the soil yielded variable saturated hydraulic conductivity values, but mixtures with 2% and 20% Ecolite had significantly higher values than the standard mixture.

Chapter 3: Column Study Comparing Mixture Pollutant Removal Capabilities

Abstract

Bioretention cells are landscape practices designed to treat the first, most polluted flush of stormwater runoff and are typically installed in urban and suburban watersheds. A column study was conducted to evaluate pollutant removal capabilities of a standard bioretention mixture recommended in Alabama, three mixtures containing varying amounts of a zeolite mineral (Ecolite), and one control of 100% sand. Four storm events were simulated to assess pollutant removal and the longevity of Ecolite amended media. Synthetic stormwater containing copper, zinc, phosphorus, nitrate, and ammonium was added to the columns with Mariotte bottles and the effluent was tested by inductively coupled plasma mass spectrometry and catalytic reduction with colorimetric readings. Effluent concentrations were log transformed and analyzed in R statistical software by analysis of variance and Tukey's honest significant difference test. ALMIX had the highest average zinc removal, but there was no significant difference among mixtures or storm events, F(12, 57)= 0.80, p= 0.65. ALMIX and AUMIX10 had the highest average copper removal, but there was no significant difference among mixtures or storm events, F(12,57)= 0.76, p= 0.68. ALMIX had the highest average phosphorus removal, but it was not significantly different from any of the mixtures containing Ecolite, F(12,57)= 1.9, p= 0.04. AUMIX10 and AUMIX20 had significantly higher removal of ammonium than ALMIX and CONTROL, F(12,60)= 5.18, p< 0.001. ALMIX, AUMIX2, AUMIX10, and AUMIX20 all had increases in the effluent nitrate concentration. CONTROL had significantly lower values of effluent nitrate concentrations than all other mixtures, F(12,60)= 2.38, p= 0.014. Amending media with Ecolite did not appear to affect longevity as compared to the ALMIX.

Introduction

Bioretention cells are installed in urban environments to filter the first flush of stormwater through a permeable soil media. Physical processes, including filtration and settling, and chemical processes, including adsorption and ion exchange, promote the removal of particulate and dissolved pollutants from stormwater. The media is typically designed to balance the proportions of sand, silt, clay, and organic matter to allow for adequate infiltration rates and the removal of a suite of common stormwater pollutants. Bioretention research has included alternative cell designs, such as the addition of an internal water storage layer (R. A. Brown & Hunt, 2011) and separation of the cell into layers to create specific conditions for pollutant removal (Khorsha & Davis, 2017b). Studies have also included the amendment of bioretention media with alternative materials including water treatment residuals (Chun-bo Jiang et al., 2018; Li et al., 2018), coconut materials (Chun-bo Jiang et al., 2018; Li et al., 2018; Vijayaraghavan & Praveen, 2016), fly ash (Chun-bo Jiang et al., 2018; Li et al., 2018), and zeolites.

Soil amended with zeolites have previously shown increased hydraulic conductivity (Githinji et al., 2011) and CEC (Bigelow et al., 2001) of soil. Previous bioretention studies have not shown notable improvement of metal or phosphorus removal as compared to conventional mixtures (Li et al., 2018; J. Wang et al., 2017) but have shown potential for increased nitrogen removal (Chun-bo Jiang et al., 2018). However, many studies have only focused on one type of pollutant and the effectiveness of adding zeolites may change as the zeolite source and soil mixture composition change. Additionally, no previous research utilizing Ecolite as the zeolite source in bioretention media was found.

The objective of this study was to assess the potential of a zeolite mineral (Ecolite) as a soil amendment in bioretention media by performing column studies that compare pollutant removal and media longevity. Column studies allow replication of multiple simulated storm events through bioretention mixtures under constant conditions. Performing multiple storm events supplies data for proper mixture comparison and assessment of the longevity of amended media. Mixture longevity is considered because bioretention cells have a system capacity for pollutant retention. As a bioretention cell filters stormwater, pollutants build up in the media over time. Surpassing the capacity can decrease the system’s ability to remove pollutants and lead to leaching of stored pollutants (Roy-Poirier et al., 2010). Comparing the longevity of an amended mixture to standard recommended mixture is beneficial, because replacing the media in a cell can be costly and time consuming.

Methods

Column Set Up

Four wooden structures were constructed to hold columns while providing space under the columns to collect effluent. Each column was made of 10.16 cm (4 in) diameter polyvinyl chloride (PVC) pipe cut to a length of 60.96 cm (24 in). The insides of the columns were roughened with 60-grit sandpaper to decrease preferential side flow. Fine metal mesh was cut to fit the openings of the columns and epoxied to the bottoms (Figure 2). Holes were drilled into 10.16 cm PVC caps, and plumbing fittings were epoxied into the holes to allow effluent to drain (Figure 2). The caps were then placed on the bottoms of the columns.

Figure 2. The mesh covering and the cap placed on the bottom of the columns.

Top Fin aquarium gravel was placed in the bottom of each column at a thickness of 2.5 cm to mimic the inclusion of pea gravel in actual bioretention cells, which prevents fine sediment from clogging the cell. Bioretention mixtures were then added to calculated heights that ensured the volume of stormwater added was at least three times larger than the media pore volume in the columns. This was done to reduce the effects of hydrodynamic dispersion, which could disrupt the solute distribution patterns of the influent stormwater. These calculations were based on the bulk density and porosity of each mixture. Bioretention media is often installed based on its maximum bulk density, which was determined from the proctor compaction tests. The porosity of each mixture was calculated (**Error! Reference source not found.**) using 80% of the maximum bulk densities and the experimentally determined particle densities.

$$\text{porosity} = 1 - \frac{\text{bulk density}}{\text{particle density}} : \textbf{Equation 2.}$$

The pore volume for each column was 1.2 L. To achieve this, porosity values were used to calculate the volume of each mixture necessary to have 1.2 L of pore space (Table 6). Each mixture was added in 2 cm increments of calculated weights to achieve the desired bulk density throughout the column. For the control columns, 200 mL of sand were added every 2 cm. Once the media was at the desired volume, it was topped with 5 cm of peat moss to minimize disturbance of the soil from influent water and mimic the use of mulch on top of bioretention cells. The finished columns were placed in the wooden structures following a randomized complete block design (Figure 11, Appendix).

Table 6. Calculations to determine media volume in columns.

Mixture	80% Maximum Bulk Density	Porosity	Desired Pore Volume	Required Media Volume	Required Media Height
	g/cm^3	%	cm^3		cm
ALMIX	1.418	47.0	1200	2552.8	31.49
AUMIX2	1.388	47.5	1200	2527.7	31.18
AUMIX10	1.382	47.3	1200	2536.2	31.28
AUMIX20	1.350	47.1	1200	2549.5	31.45

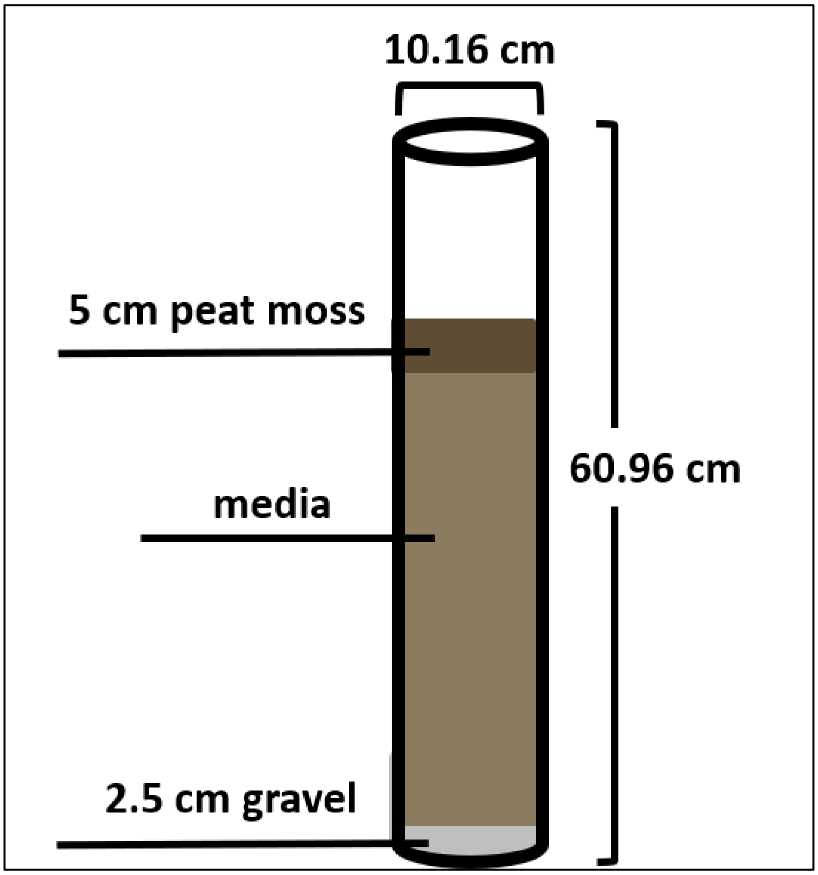


Figure 3. A diagram of the inside of a column.

Synthetic Stormwater

Synthetic stormwater (Table 7) was created based on the pollutant concentrations of Davis et al. (2001) and Hsieh and Davis (2005). A 1:250 stock solution containing phosphorus, nitrate, ammonium, copper, and zinc was created by mixing selected compounds with distilled water. The stock was kept covered in a dark location at room temperature.

Table 7. Concentration of pollutants in the synthetic stormwater.

Pollutant	Source	Concentration
		mg/L
Phosphorus	Na_2HPO_4	3 (as P)
Nitrate	$NaNO_3$	2 (as N)
Ammonium	NH_4Cl	2 (as N)
Copper	$CuSO_4$	0.08
Zinc	$ZnCl_2$	0.6

Water Distribution and Effluent Collection

Five glass bottles with spigots were used to distribute water to the columns one block at a time. Each bottle was plugged with a stopper holding a glass tube to establish a Mariotte system (Figure 4). The same constant head was created in all bottles by placing the tubes the same distance away from the spigot of the bottle. This allowed for a constant rate of flow from the bottles.

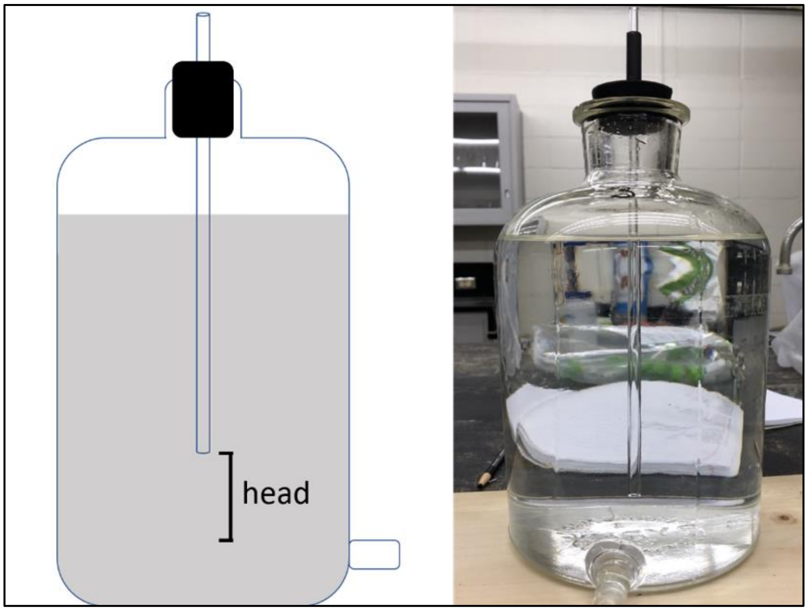


Figure 4. A diagram of the Mariotte bottle and a bottle used in the study.

When a storm event was applied to a block, the Mariotte bottles were placed above the columns (Figure 5), and tubing attached to the spigots directed water into the columns at an average rate of 42 mL/min. Effluent was collected until the columns stopped flowing. The total effluent per column was mixed well in a 4 L glass bottle. Two samples from each mixture were filtered by Whatman Grade 42 filter paper and placed into centrifuge tubes. One tube was stored at 1.1° C for later ICP (inductively coupled plasma) analysis and one was stored at 0° C for later nitrogen analysis.

Before running pollutants through the columns, 4 L of distilled water with enough calcium chloride to match the ionic strength of the synthetic stormwater, calculated as 6.099×10^{-4} M, was applied to each column to determine the potential contribution of the media to effluent pollutant concentrations (Table 15, Appendix). Four storm events were then simulated by applying synthetic stormwater. Following the last storm event, 4 L of 0.01 M $CaCl_2$ solution were added to the columns to extract the retained pollutants and determine their concentrations in the soil (Table 13). ICP analysis of zinc, copper, and phosphorus were performed by Waters Agricultural Lab in Camilla, GA. Nitrate and ammonium analysis were performed at Auburn University with catalytic reduction and colorimetric readings (Crutchfield & Grove, 2011).

Figure 5. A block setup for a storm event.

Data Analyses

The effluent pollutant concentrations were log transformed and used in ANOVAs in R statistical software to determine if mixture and storm event had effects on pollutant removal. Tukey HSD tests were used to further identify significant differences.

Results

Zinc

ALMIX had the highest average zinc removal, but there was no significant difference among mixtures or storm events, F(12, 57)= 0.80, p= 0.65 (Table 8, Figure 6).

Table 8. Mean effluent concentrations (mg/L) of zinc from columns by mixture and storm event. Mean reductions in concentrations are displayed in parentheses.

	CONTROL	**ALMIX**	**AUMIX2**	**AUMIX10**	**AUMIX20**
All Storms	0.01 ± 0.0 (98.0%)	0.01 ± 0.01 (98.13%)	0.01 ± 0.0 (98.0%)	0.01 ± 0.01 (98.02%)	0.01 ± 0.01 (98.11%)
Storm 1	0.01 ± 0.0 (98.33%)	0.01 ± 0.0 (98.33%)	0.01 ± 0.0 (97.92%)	0.02 ± 0.01 (97.5%)	0.01 ± 0.0 (98.33%)
Storm 2	0.01 ± 0.01 (97.92%)	0.02 ± 0.01 (97.5%)	0.01 ± 0.01 (97.92%)	0.01 ± 0.00 (98.33%)	0.01 ± 0.0 (98.33%)
Storm 3	0.01 ± 0.01 (97.92%)	0.01 ± 0.0 (98.33%)	0.01 ± 0.01 (97.92%)	0.01 ± 0.0 (98.33%)	0.02 ± 0.01 (97.5%)
Storm 4	0.01 ± 0.01 (97.78%)	0.01 ± 0.0 (98.33%)	0.01 ± 0.0 (98.33%)	0.01 ± 0.01 (97.92%)	0.01 ± 0.0 (98.33%)

± Standard Deviation

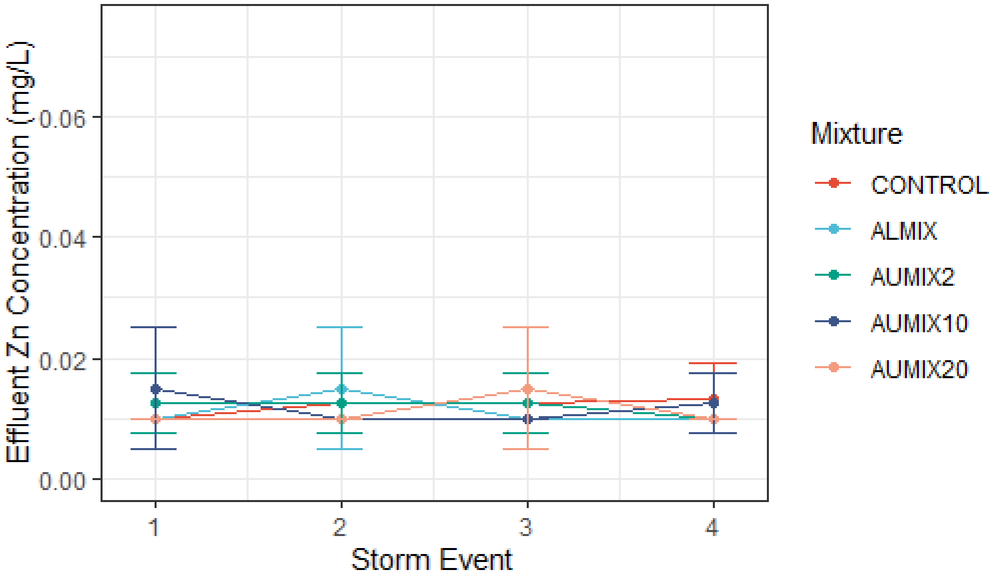


Figure 6. Mean effluent concentration of zinc by storm and mixture. Bars display standard deviation.

Copper

ALMIX and AUMIX10 had the highest average copper removal, but there was no significant difference between mixtures or storm events, F(12,57)= 0.76, p= 0.68 (Table 9, Figure 7).

Table 9. Mean effluent concentrations (mg/L) of copper from columns by mixture and storm event. Mean reductions in concentrations are displayed in parentheses.

	CONTROL	**ALMIX**	**AUMIX2**	**AUMIX10**	**AUMIX20**
All Storms	0.01 ± 0.01 (85%)	0.01 ± 0.01 (85.94%)	0.01 ± 0.01 (84.17%)	0.01 ± 0.003 (85.94%)	0.01 ± 0.01 (85%)
Storm 1	0.01 ± 0.0 (87.5%)	0.02 ± 0.01 (81.25%)	0.02 ± 0.01 (81.25%)	0.02 ± 0.01 (81.25%)	0.01 ± 0.0 (87.5%)
Storm 2	0.01 ± 0.01 (84.38%)	0.01 ± 0.0 (87.5%)	0.02 ± 0.01 (81.25%)	0.01 ± 0.0 (87.5%)	0.02 ± 0.01 (81.25%)
Storm 3	0.02 ± 0.01 (81. 25%)	0.01 ± 0.0 (87.5%)	0.01 ± 0.0 87.5%	0.01 ± 0.0 (87.5%)	0.01 ± 0.01 (84.38%)
Storm 4	0.01 ± 0.0 (87.5%)	0.01 ± 0.0 (87.5%)	0.01 ± 0.0 87.5%	0.01 ± 0.0 (87.5%)	0.01 ± 0.0 (87.5%)

± Standard Deviation

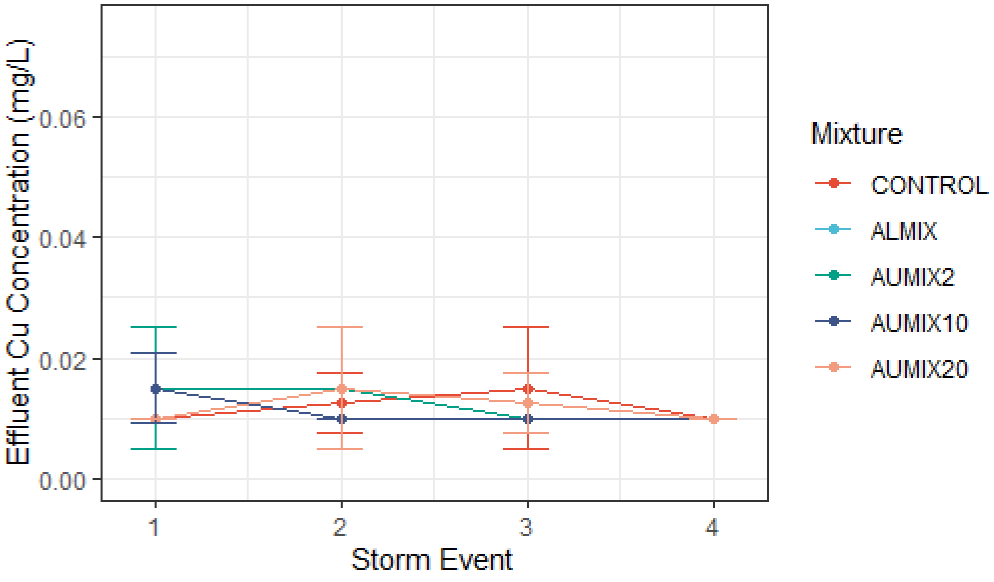


Figure 7. Mean effluent concentration of copper by storm and mixture. Bars display standard deviation.

Phosphorus

ALMIX had the highest average phosphorus removal, but it was not significantly different from any of the mixtures containing Ecolite. CONTROL had significantly higher effluent phosphorus than the other mixtures. ALMIX, AUMIX2, AUMIX10, and AUMIX20 all had significant increases in effluent phosphorus between the first and fourth storm events, F(12,57)= 1.9, p= 0.04 (Table 10, Figure 8).

Table 10. Mean effluent concentrations (mg/L) of phosphorus from columns by mixture and storm event. Mean reductions in concentrations are displayed in parentheses.

	CONTROL	**ALMIX**	**AUMIX2**	**AUMIX10**	**AUMIX20**
All Storms	2.39 ± 0.35	0.08 + 0.12	0.13 ± 0.15	0.10 ± 0.12	0.16 ± 0.15
	(20.22%)	(97.27%)	(95.64%)	(96.77%)	(94.73%)
Storm 1	1.91 ± 0.08	0.01 ± 0.0	0.02 ± 0.01	0.01 ± 0.0	0.04 ± 0.06
	(36.5%)	(99.67%)	(99.42%)	(99.67%)	(98.75%)
Storm 2	2.34 ± 0.05	0.01 ± 0.0	0.04 ± 0.02	0.02 ± 0.01	0.05 ± 0.03
	(22.17%)	(99.67%)	(98.83%)	(99.5%)	(98.42%)
Storm 3	2.65 ± 0.06	0.09 ± 0.07	0.20 ± 0.11	0.11 ± 0.07	0.24 ± 0.11
	(11.67%)	(97.0%)	(93.25%)	(96.42%)	(92.08%)
Storm 4	2.78 ± 0.02	0.22 ± 0.19	0.31 ± 0.16	0.26 ± 0.14	0.36 ± 0.07
	(7.33%)	(92.75%)	(89.56%)	(91.5%)	(88.0%)

± Standard Deviation

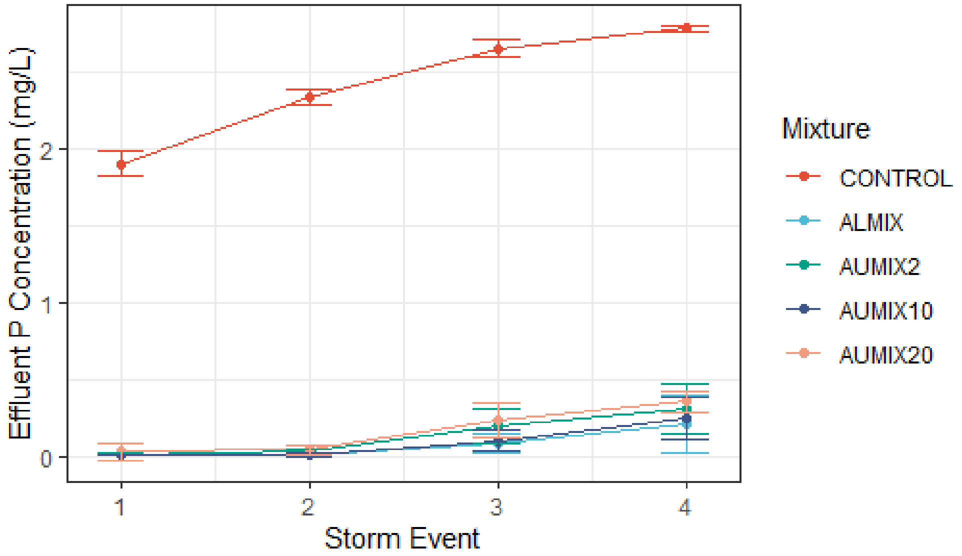


Figure 8. Mean effluent concentration of phosphorus by storm and mixture. Bars display standard deviation.

Ammonium

AUMIX10 and AUMIX20 had significantly higher removal of ammonium than ALMIX and CONTROL, but the difference between ALMIX decreased over time. ALMIX, AUMIX2, AUMIX10, and AUMIX20 all had significant decreases in effluent ammonium concentrations between the first and fourth storm events, F(12,60)= 5.18, p< 0.001 (Table 11, Figure 9).

Table 11. Mean effluent concentrations (mg/L) of ammonium from columns by mixture and storm event. Mean reductions in concentrations are displayed in parentheses.

	CONTROL	ALMIX	AUMIX2	AUMIX10	AUMIX20
All Storms	1.52 ± 0.18 (23.78%)	0.59 ± 0.41 (70.40%)	0.40 ± 0.18 (80.03%)	0.28 ± 0.14 (86.23%)	0.26 ± 0.13 (86.96%)
Storm 1	1.38 ± 0.03 (31.10%)	1.18 ± 0.23 (41.08%)	0.59 ± 0.07 (70.51%)	0.38 ± 0.03 (80.87%)	0.35 ± 0.01 (82.41%)
Storm 2	1.59 ± 0.05 (20.73%)	0.60 ± 0.10 (70.12%)	0.44 ± 0.03 (77.80%)	0.36 ± 0.04 (82.02%)	0.32 ± 0.03 (84.20%)
Storm 3	1.77 ± 0.06 (11.39%)	0.45 ± 0.10 (77.54%)	0.43 ± 0.05 (78.57%)	0.31 ± 0.01 (84.58%)	0.32 ± 0.03 (84.07%)
Storm 4	1.36 ± 0.07 (31.90%)	0.14 ± 0.09 (92.85%)	0.13 ± 0.08 (93.26%)	0.05 ± 0.05 (97.47%)	0.06 ± 0.03 (97.15%)

± Standard Deviation

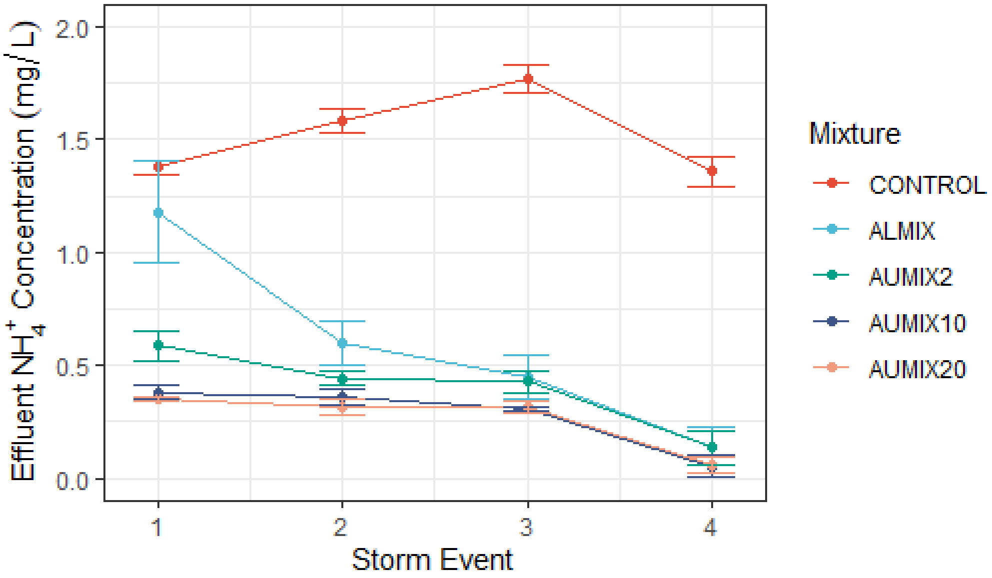


Figure 9. Mean effluent concentration of ammonium by storm and mixture. Bars display standard deviation.

Nitrate

CONTROL had significantly lower values of effluent nitrate concentrations than all other mixtures. ALMIX, AUMIX2, AUMIX10, and AUMIX20 all had increases in the effluent nitrate concentration. However, by the fourth storm, all mixtures containing Ecolite had significantly lower nitrate concentrations than ALMIX, F(12,60)= 2.38, p= 0.014 (Table 12, Figure 10).

Table 12. Mean effluent concentrations (mg/L) of nitrate from columns by mixture and storm event. Mean reductions in concentrations are displayed in parentheses.

Event	**CONTROL**	**ALMIX**	**AUMIX2**	**AUMIX10**	**AUMIX20**
All Storms	1.88 ± 0.17 (5.87%)	3.55 ± 0.64 (-77.38%)	2.83 ± 0.37 (-41.45%)	2.64 ± 0.22 (-31.78%)	2.60 ± 0.29 (-30.22%)
Storm 1	1.63 ± 0.07 (18.59%)	2.99 ± 0.24 (-49.40%)	2.49 ± 0.16 (-24.49%)	2.49 ± 0.17 (-24.26%)	2.51 ± 0.15 (-25.36%)
Storm 2	1.91 ± 0.06 (4.68%)	3.17 ± 0.31 (-58.17%)	2.70 ± 0.30 (-34.93%)	2.55 ± 0.19 (-27.34%)	2.50 ± 0.23 (-24.89%)
Storm 3	2.01 ± 0.03 (-0.54%)	3.63 ± 0.49 (-81.34%)	2.80 ± 0.18 (-40.23%)	2.62 ± 0.21 (-30.82%)	2.52 ± 0.26 (-26.00%)
Storm 4	1.99 ± 0.10 (0.73%)	4.41 ± 0.15 (-120.62%)	3.32 ± 0.23 (-66.13%)	2.89 ± 0.12 (-44.70%)	2.89 ± 0.37 (-44.61%)

± Standard Deviation

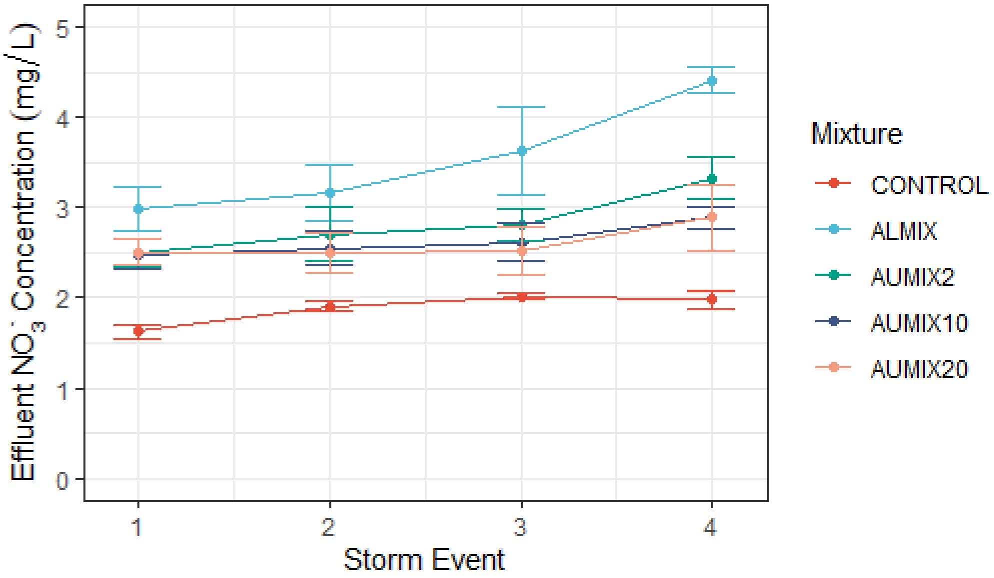


Figure 10. Mean effluent concentration of nitrate by storm and mixture. Bars display standard deviation.

Post-Storms Extraction

The extraction pollutant concentrations (Table 13) suggested ALMIX, AUMIX2, AUMIX10, and AUMIX20 are storing low concentrations of ammonium and high concentrations of nitrate.

Table 13. Mean outflow concentrations of the extraction following the storm events.

Mixture	Zinc	Copper	Phosphorus	Ammonium	Nitrate
	mg/L				
CONTROL	0.758 ± 0.20	0.193 ± 0.11	0.370 ± 0.05	1.43 ± 0.19	0.525 ± 0.03
ALMIX	0.133 ± 0.12	0.048 ± 0.03	0.010 ± 0.0	1.51 ± 0.64	6.15 ± 0.07
AUMIX2	0.083 ± 0.10	0.045 ± 0.02	0.010 ± 0.0	1.12 ± 0.62	7.78 ± 0.30
AUMIX10	0.010 ± 0.0	0.010 ±0.0	0.010 ± 0.0	0.347 ± 0.12	8.01 ± 0.37
AUMIX20	0.010 ± 0.0	0.010 ± 0.0	0.013 ± 0.01	0.206 ± 0.14	7.82 ± 1.12

± Standard Deviation

Discussion

Zinc and Copper

For both copper and zinc, there was no significant difference in effluent concentration among mixtures or storms. Addition of fine materials and Ecolite to sand did not yield improved or worsened metal removal. This suggests that primarily physical removal processes were occurring. Furthermore, the number of storm events did not have a significant impact on effluent removal, so the longevity for metal removal of the Ecolite amended media was not different from the ALMIX longevity in this study.

The mean zinc removal of 98% by all mixtures is similar to or better than those reported in previous bioretention research. Sun and Davis (2007) and Feng et al. (2012) reported zinc reductions of 93 ± 4% and 99%, respectively. The Wang et al. (2017) study containing a layer of zeolite yielded a zinc reduction of 98.6 ± 2.4%.

The mean copper removal of 85% by all mixtures is similar to the results of previous bioretention studies. Sun and Davis (2007) and Feng et al. (2012) yielded reductions in copper concentrations of 88 ± 4.5% and 90%, respectively. However, both included plants in their study, which could increase metal removal through plant uptake. Wang et al. (2017) used a media of 50% sandy loam and 50% humus with a layer of 90% zeolite. Plants were also included. This resulted in a copper removal of 99.1 ± 0.9%. The higher uptake of copper could be a result of their column being taller (100 cm of media), the inclusion of the plants, or the exposure provided by the layer of 90% zeolite.

Phosphorus

All mixtures had significantly lower effluent phosphorus than CONTROL. Mixtures containing fine materials in addition to sand yielded improved phosphorus removal, but further addition of Ecolite did not improve or worsen removal. ALMIX and the mixtures containing Ecolite significantly decreased in the ability to remove phosphorus over four storms, and their effluent phosphorus concentrations from the fourth storm were not significantly different. Therefore, the longevity for phosphorus removal of the Ecolite amended media was not different than the ALMIX longevity in this study.

The mean phosphorus reduction of 96% by ALMIX, AUMIX2, AUMIX10, and AUMIX20 is similar to or higher than previous bioretention studies. Two mixtures from Hsieh and Davis (2005) resulted in total phosphorus reductions of 24 ± 3.8% and 83 ± 1.4%. Their primary difference was the amount of fine materials included, with increased fine material yielding increased phosphorus removal. Bratieres et al. (2008) included plants in the study and had a mean phosphorus reduction of 38%. Similar to this Ecolite study, Li et al. (2018) included

10% green zeolite in a mixture and reported an average phosphorus reduction of approximately 97%. Plants were included in this study.

Ammonium and Nitrate

AUMIX10 and AUMIX20 demonstrated the capability to yield significantly lower effluent ammonium concentrations than ALMIX and CONTROL. However, the effluent concentration of ammonium from ALMIX decreased significantly over time. Mixtures containing fine materials and Ecolite yielded higher removal of ammonium in this study. All mixtures except CONTROL significantly decreased in effluent ammonium concentration over four storms.

The mean ammonium reduction of 86% by AUMIX10 and AUMIX20 is higher than many in previously reported studies. The two aforementioned mixtures from Hsieh and Davis (2005) yielded percentage reductions of 26 ± 2.6% and 11 ± 0.6%. Jiang et al. (2019) compared their bioretention soil media to an amended version containing 10% green zeolite by mass. The original bioretention media reduced the ammonium concentration by 71.0 ± 11.6%, and the mixture containing green zeolite reduced ammonium by 73.0 ± 14.6%.

CONTROL was the only mixture that did not have higher effluent nitrate compared to the synthetic stormwater. The addition of fine materials and Ecolite to sand did not yield improved nitrate removal. However, AUMIX10 and AUMIX20 demonstrated significantly lower concentrations of effluent nitrate than ALMIX. Additionally, ALMIX and AUMIX2 significantly increased in effluent nitrate over four storms, but AUMIX10 and AUMIX20 did not change significantly. This suggests that even if Ecolite does not contribute to removal of nitrate from stormwater, inclusion in a bioretention cell may yield less effluent nitrate than a standard mixture such as ALMIX.

The study yielded a wide range of nitrate removal percentages, with CONTROL displaying an average removal of 5.87%. It is likely that CONTROL did not remove this much nitrate, and the effluent from storm 1 contained residual water from the initial blank run that did not contain nitrate. ALMIX averaged -77.38% removal, and additions of Ecolite improved this with AUMIX20 averaging -30.22% removal. Previous bioretention studies also display large differences in nitrate. The Hsieh and Davis (2005) mixtures removed 13 ± 59% and 6 ± 1.5%. Bratieres et al. (2008) reported an increase in nitrate, with an average removal of -158%. Jiang et al. (2018) reported a nitrate removal of 54.26 ± 0.12%. Jiang et al. (2019). The standard media in Jiang et al. (2019) yielded a removal of 56.2 ± 13.2%, and the mixture containing green zeolite removed 56.6 ± 13.6%. Nitrate does not adsorb to soil particles well, so the high removal percentages from the Jiang et al. studies could be due to plant uptake of nitrate by the plants included in the studies.

When ammonium entered the columns, it could adsorb to the media or be converted to nitrate through nitrification. The extraction values following the storms suggested ALMIX and Ecolite amended mixtures were storing low concentrations of ammonium and high concentrations of nitrate in the columns. However, the $CaCl_2$ extraction may not have been effective at extracting ammonium. These data, along with the effluent ammonium and nitrate values from the storm events, suggest that nitrification occurred in the columns. Brown et al. (2013) noted that ammonium trapped in the media may be converted to nitrate between storm events and flushed out in subsequent events. This likely occurred in the columns and explains effluent nitrate values that were higher than the input of nitrate.

Application

The results of this research could be utilized by stormwater managers for consideration when designing and installing bioretention cells. Adding Ecolite into a bioretention mixture will increase the cost, so it is not recommended that Ecolite be included in every bioretention cell. Specifically, the results may be most beneficial to managers targeting areas with impaired watersheds and streams on their environmental state agency's list of impaired waters, the 303(d) list, due to nitrogen pollution. If stormwater managers chose to incorporate an alternative material in a conventional bioretention cell, this research is useful for determination of Ecolite volume in the cell. Since the effluent ammonium and nitrate concentrations from AUMIX10 and AUMIX20 were not significantly different, adding more than 10% Ecolite by volume is likely not worth the financial cost.

However, based on the nitrogen results of this study, Ecolite would likely serve better in bioretention cells with alternative designs, such as those proposed by Brown and Hunt (2011) and Khorsha and Davis (2017b). Brown and Hunt (2011) proposed to alter the drainage system by creating an elbow in the outflow pipe. This would create an internal water storage layer with anoxic conditions that would allow for denitrification of nitrate to nitrogen gas. Khorsha and Davis (2017b) further elaborated a design that includes three layers. The top layer would capture organic nitrogen and convert it to ammonium, the second layer would capture ammonium and convert it to nitrate, and the third layer would be anoxic for denitrification.

The inclusion of a zeolite mineral in nitrogen-focused stormwater control measures was also proposed by Khorsha and Davis (2017a). In their study, they tested ammonium retainment with a 50:50 mixture of Bear River zeolite and sand. This may be more expensive than the suggested media in this research of 90% conventional bioretention materials and 10% Ecolite.

Researchers may also find this study interesting for future studies. Different minerals of zeolite may continue to be tested, but it is also worth noting that other common bioretention mixtures may respond differently and therefore could also be tested with Ecolite. Additionally, the procedure described for building the columns and simulating storm events is easily replicated with accessible materials and can be applied for other bioretention studies.

Conclusions

The purpose of this study was to assess the potential of a commercially available form of zeolite to improve the performance of bioretention media. A standard bioretention mixture for the state of Alabama was altered by replacing sand contents with Ecolite, a zeolite soil amendment, as 2%, 10%, and 20% of mixture volume. Following mixture characterization, the mixtures and a control of 100% sand were utilized in a column study for removal of pollutants from synthetic stormwater.

Replacing sand with Ecolite at up to 20% volume did not improve the removal of copper, zinc, or phosphorus. The inclusion of 10% and greater Ecolite removed more ammonium than the standard Alabama mixture, although this difference decreased over time. It did not improve nitrate removal, as the standard and all mixtures containing Ecolite resulted in increases in the concentration of effluent nitrate. This is likely due to the conversion of ammonium to nitrate within the columns. However, mixtures containing Ecolite leached less nitrate than the Alabama standard. Amending the soil with Ecolite did not appear to change longevity as compared to the Alabama standard.

Based on these results, stormwater managers may consider inclusion of 10% Ecolite in bioretention cells specifically targeted for nitrogen-impaired watersheds. Ecolite could also be considered for bioretention cells designed specifically for conversion of organic nitrogen, ammonium, and nitrate to nitrogen gas. It would be contained in an aerobic layer for conversion of ammonium to nitrate before denitrification in an internal water storage layer.

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Appendix A. Additional Information.

Table 14. Additional cation exchange capacity values.

Material	Cation Exchange Capacity*
	cmol/kg
Ecolite	7.7
EV Smith Topsoil	8.5

* Estimated

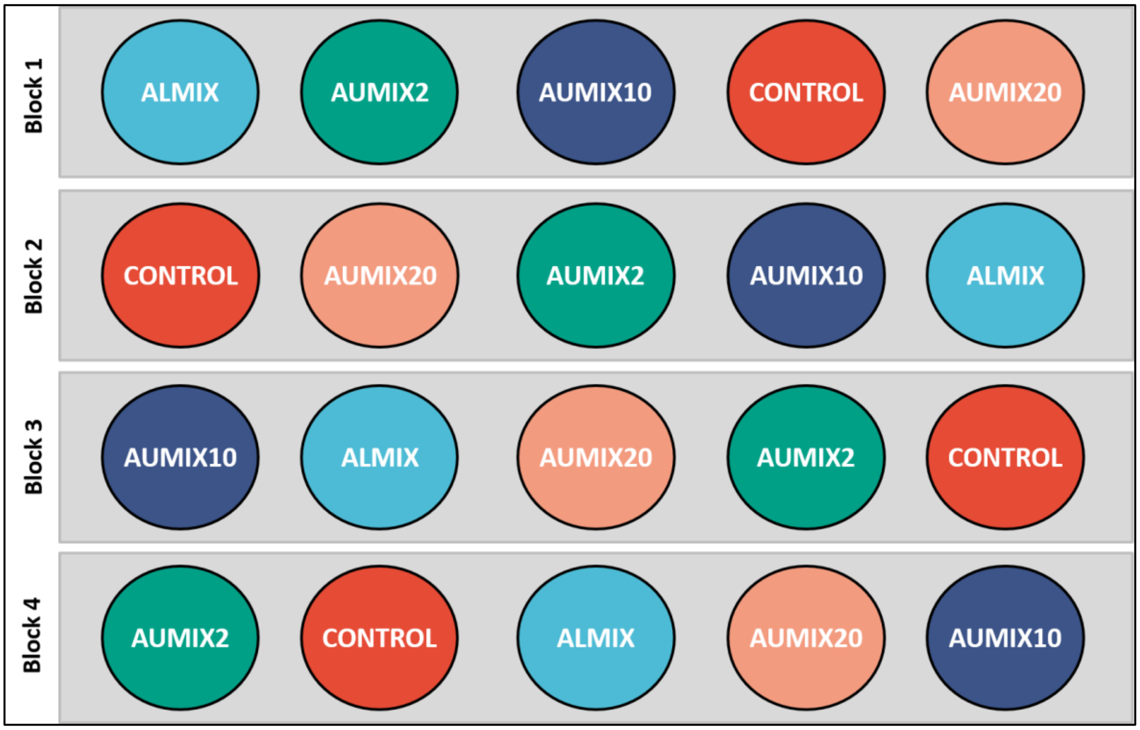

Figure 11. The randomized complete block design of mixtures in columns.

Table 15. Mean outflow concentrations of the blank run before the storm events.

Mixture	Zinc	Copper	Phosphorus	Ammonium	Nitrate
			mg/L		
CONTROL	0.013 ± 0.01	0.010 ± 0.00	0.013 ± 0.01	0.564 ± 0.12	0.068 ± 0.03
ALMIX	0.015 ± 0.01	0.013 ± 0.01	0.033 ± 0.01	1.03 ± 0.24	2.08 ± 0.19
AUMIX2	0.010 ± 0.0	0.018 ± 0.01	0.050 ± 0.03	0.766 ± 0.12	1.89 ± 0.13
AUMIX10	0.010 ± 0.0	0.018 ± 0.02	0.083 ± 0.03	0.702 ± 0.13	2.72 ± 0.31
AUMIX20	0.013 ± 0.01	0.010 ± 0.0	0.073 ±0.01	0.666 ± 0.11	3.21 ± 0.11

± Standard Deviation