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EVALUATION OF STORMWATER TREATMENT BY VARIOUS REACTIVE
MEDIA FOR BIORETENTION CELL DESIGN CONSIDERATIONS

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A THESIS APPROVED FOR THE
SCHOOL OF CIVIL ENGINEERING AND ENVIRONMENTAL SCIENCE

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This thesis is dedicated to my parents who were forced to leave their country and work endlessly to give me an advantage in my education, an opportunity they not were not able to have. *Con yêu Má với Pá rất nhiều.*

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Abstract

Bioretention cells (BRC) can be effective at filtering particulate pollutants from stormwater runoff, but substantial removal of the dissolved pollutant fraction is challenging. Various reactive treatment media for BRCs were evaluated to address nitrate (NO_3^-) and dissolved fractions of phosphorus (P), copper (Cu^{2+}), lead (Pb^{2+}), and zinc (Zn^{2+}) removal in BRCs. Fly ash (FA) and iron oxyhydroxide mine drainage residuals (MDR) were blended with sand at 5% (FA5.0) and 7.5% (MDR7.5) by mass. Additionally, APTsorb (APT) and bioAPT (BIO), commercially available granulated and hardened peat products, were evaluated as treatment media, each with a sand layer to augment hydraulic retention time. Pollutant removal performance was evaluated by pumping synthetic stormwater (SS) through packed up-flow columns. 100% sand (SAND) was used as the control media. SS had target concentrations of NO_3^- at 1.5 milligrams per liter (mg/L) as N, phosphate (PO_4^{3-}) at 0.5 mg/L as P, Cu^{2+} at 25 $\mu\text{g/L}$, Pb^{2+} at 30 $\mu\text{g/L}$, and Zn^{2+} at 100 $\mu\text{g/L}$. FA5.0 and MDR7.5 both removed over 84% of P. SAND, APT, and BIO had limited TP and TDP removal rates with BIO showing net export. All proposed media had Cu^{2+} and Zn^{2+} removal rates of over 75% and 89%, respectively. APT showed the highest Pb^{2+} removal at over 84%. FA5.0 and MDR7.5 were the most cost-effective options that did not show export of pollutants, therefore they are recommended as amendments to BRC media.

CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Urban stormwater management practices are typically developed to minimize flood risk by shunting water from the landscape to the nearest receiving water body using impervious surfaces, such as rooftops, pavement, and stormwater drainage systems (Walsh et al., 2012). Unlike natural surfaces that allow for infiltration, rainfall onto impervious surfaces results in greater amounts of stormwater that “runs off,” thereby increasing water volume and peak flow (Vogel and Moore, 2016). Additionally, runoff from impervious surfaces collects and conveys pollutants, which degrade downstream water quality (Liu et al., 2014). Common pollutants in urban runoff include total suspended solids (TSS), trace metals, nutrients, pathogens, and organic compounds (Liu et al., 2014).

Low-impact development (LID) technologies, such as the bioretention cell (BRC), are widely used to capture runoff, control water quantity and water quality, and decrease or negate the effects of impervious infrastructure characteristically associated with urban development (Dietz et al., 2007; Roy-Poirier et al., 2010; Payne et al., 2014; LeFevre et al., 2015; Vogel et al., 2015; Holzbauer-Schweitzer, 2016). BRCs function by capturing upstream runoff from impervious and saturated surfaces for treatment using vegetated, treatment media (usually sand-based), with a drainage layer below consisting of gravel and a drainage pipe for discharge (Payne et al., 2015). The pollutant removal performance of BRCs have been variable, ranging from high to poor pollutant removal and net production in some cases (Roy-Poirier et al., 2010; Payne et al., 2014, Holzbauer-

Schweitzer, 2016). BRCs do well to remove TSS and particulate fractions of pollutants, but still leave a significant portion of the dissolved fractions to be addressed (LeFevre et al., 2015). Soils high in organic matter (OM) and incorporating compost can remove organic pollutants and the dissolved fraction of metals by forming OM-metal complexes; however, the usage of compost results in mediocre nutrient removal performance, where net production of nitrogen (N) and P is common (Roy-Poirier et al., 2010; Graves et al., 2014; Payne et al., 2014; LeFevre et al., 2015). For example, the discharge at the Trailwoods residential rain gardens in Norman, Oklahoma resulted in P export, which was attributed to residential applications of fertilizer and the compost mix of 10 percent (%) OM (Holzbauer-Schweitzer, 2016).

This study proposed the use of various reactive materials as BRC media in to address the removal of dissolved pollutants, while minimizing nutrient leaching. These reactive media included mine drainage residuals (MDR), Class C fly ash (FA), and two manufactured peat-based sorptive media, APTsorb (APT), and bioAPT (BIO). An MDR-sand mix (MDR7.5) was used at 7.5% MDR with 92.5% sand to increase hydraulic conductivity of MDRs. Similarly, the FA-sand mix (FA5.0) was composed of 5.0% FA and 95% sand. APT and BIO were not used as amendments but were used as the layer with sand as the second layer, at a one-to-three peat-to-sand ratio. This research evaluated the pollutant removal performance of the reactive media for NO_3^- , PO_4^{3-} , Cu^{2+} , Pb^{2+} , and Zn^{2+} in laboratory up-flow treatment columns. SS was pumped upward through columns packed with the reactive media. Performance was evaluated based on net changes in pollutant concentrations in column effluents. Results of the performance evaluation

determined if the potential application of each media in BRCs could enhance water treatment performance.

1.2 Literature Review

1.2.1 Urban Stormwater Runoff

Runoff is excess precipitation that flows over, or “runs off,” a surface. Runoff occurs when natural surfaces have reached saturation or when precipitation falls on impervious surfaces, characteristically associated with urban development. As a result, the urban runoff volume is greater than runoff from natural or undeveloped environments (Vogel and Moore, 2016). Traditional stormwater management plans are primarily designed to minimize flood risk by quickly draining runoff directly to the nearest receiving water body, via impervious infrastructure (EPA, 1983; Walsh et al., 2012). Gutters, concrete channels, and roadways are major components of traditional drainage systems, which increase runoff volume and peak discharge into receiving water bodies (Walsh et al., 2012). Furthermore, conventional stormwater drainage is considered the chief contributor to stream degradation (Walsh et al., 2012; Liu et al., 2014; LeFevre et al., 2015). The increased water velocities in receiving streams cause channels to erode, which then increases water turbidity and sediment deposition clogs infrastructure, and suffocates aquatic biota (EPA, 1983).

In addition to physical degradation, runoff transports pollutants existing on surfaces to receiving water bodies (Liu et al., 2014). The United States Environmental Protection Agency (EPA) identifies urban runoff as nonpoint source pollution (NPS), naming it as

the leading cause of water quality impairment (Dressing et al., 2016). Urban runoff affects rivers and streams, oceans and coastal waters, lacustrine waters, and wetlands (Dressing et al., 2016). Water quality degradation is attributed to runoff conveyance of sediment, nutrients, metals, pathogens, and pesticides (Liu et al., 2014; LeFevre et al., 2015; Dressing et al., 2016).

1.2.1.1 Runoff Water Quality Characterization

In 1983, the EPA released the first national urban runoff water quality characterization report, compiling five years of data collected by the EPA's Nationwide Urban Runoff Program (NURP). Maestre and Pitt (2005), in partnership with the EPA, compiled the original National Stormwater Quality Database (NSQD) using water quality data from NURP and the EPA's National Pollutant Discharge Elimination System (NPDES). Today, the database (NSQDv4.02) includes data from the previous versions of the NSQD, the United States Geological Survey (USGS), and the International Stormwater Best Management Practices (BMP) Database, the new base for the NSQD (BMP Database, 2015). National runoff water quality data for residential land uses are summarized in Table 1. Several additional parameters not previously discussed were documented, including total dissolved solids (TDS), five-day biochemical oxygen demand (BOD₅), chemical oxygen demand (COD), total nitrogen (TN), total Kjeldahl nitrogen (TKN), ammonia (NH₃), nitrite (NO₂⁻), total phosphorus (TP), total dissolved phosphorus (TDP), arsenic (As), cadmium (Cd), chromium (Cr), and nickel (Ni). The data are presented as mean concentrations with associated standard deviation values. This table illustrates the amount of variability in pollutant species and concentrations.

Table 1: Select water quality data for residential and mixed residential land use categories, summarized from the NSQDv4.02 (BMP Database, 2015).

Constituent	Units	Mean concentration	Standard Deviation
pH	-	7.08	0.84
TDS	mg/L	140	520
TSS	mg/L	140	320
BOD ₅	mg/L as O ₂	13	20
COD	mg/L as O ₂	73	82
Fecal Coliform	colonies/100 mL	85,000	350,000
TN	mg/L	3.34	4.85
TKN	mg/L	2.03	2.41
NH ₃	mg/L	0.662	0.887
NO ₃ ⁻	mg/L as N	1.2	1.8
NO ₂ ⁻	mg/L as N	0.2	0.5
TP	mg/L	0.44	0.72
TDP	mg/L	0.23	0.54
Total As	µg/L	5.5	10.4
Total Filtered As	µg/L	7.5	14.0
Total Cd	µg/L	3.2	15.4
Total Filtered Cd	µg/L	0.7	0.8
Total Cr	µg/L	8.9	12.0
Total Filtered Cr	µg/L	3.8	3.5
Total Cu	µg/L	29	48
Total Filtered Cu	µg/L	13	18
Total Pb*	µg/L	24	41
Total Filtered Pb*	µg/L	15	27
Total Ni	µg/L	10	10
Total Filtered Ni	µg/L	6.3	5.1
Total Zn	µg/L	135	380
Total Filtered Zn	µg/L	85	116

*Data taken after 1984

The “first flush” refers to the phenomenon where runoff pollutant loads are typically greatest at the beginning of a storm event because surface pollutants get “flushed,” which decreases concentrations in runoff over time (Hunt and White, 2001; Maestre and Pitt, 2005). The first flush effect tends to occur in small watersheds rather than large watersheds, though the opposite observation can occur as well (Maestre and Pitt, 2005). In large watersheds, the greatest pollutant concentrations are often observed at times of peak flow, though elevated concentrations can occur after peak flow as well (Maestre and

Pitt, 2005). Hunt and White (2001) generalize the first flush to be the runoff generated by the first inch of rainfall. Because of these elevated pollutant concentrations, especially in the first flush, stormwater treatment must be addressed (Walsh et al., 2012; Liu et al., 2014; LeFevre et al., 2015). Low impact development (LID) technologies are often used as alternative stormwater management, with many geared toward addressing both water quantity and quality issues (Hunt and Lord, 2006; Dietz et al., 2007; LeFevre et al., 2015; Payne et al., 2015; Vogel et al., 2015).

1.2.1.2 Low Impact Development

LID is an alternative approach to stormwater management that revolves around the goal of reproducing the pre-development hydrology of a site by alleviating the adverse effects of impervious infrastructure associated with urbanization in a cost-effective way (Dietz, 2007; Vogel et al., 2015). The implementation of green infrastructure, which integrate LID technologies such as BRCs, green roofs, and permeable pavements in the urban environment, attempts to meet this goal (Dietz, 2007; Vogel et al., 2015). The use of these LID technologies can maintain local hydrologic functionality and promote biodiversity (Vogel et al., 2015).

BRCs, which also include rain gardens, are often used in residential and commercial landscaping and have been shown to function hydrologically to decrease peak flows of one-year storm events by approximately 80% (Dietz, 2007; Payne et al., 2015). BRCs are traditionally vegetated land depressions filled with highly permeable growing media (Payne et al., 2015). BRCs are advantageous because pollutant removal can be

implemented with proper vegetation and media selection (Vogel et al., 2015). As the focus of this thesis, BRCs will be discussed in greater detail later in following sections.

Green roofs are traditionally vegetated soil layers that often require additional structural support (Dietz, 2007). However, green roof technology is now using thinner and lighter media as well as a larger variety of vegetation (Dietz, 2007). Green roofs can retain about 60% to 70% of water from rain events (Dietz, 2007). More recent developments include containerized green roofs that allow for removability and flexibility, which are not present in intensive green roofs (Vogel et al., 2015).

Permeable pavements, designed with voids to allow for infiltration, include pre-cast concrete or plastic products, pervious asphalt, and pervious concrete (Dietz, 2007). Pervious asphalt and concrete are made with little or no fine-sand aggregates to provide larger pore spaces for permeability (Dietz, 2007). Permeable pavements can be designed with water treatment characteristics to address TSS, metals, and some N and P removal (Dietz, 2007; Vogel et al., 2015). Although permeable pavements can effectively decrease runoff volumes and provide some water treatment, they are easily clogged by TSS and require consistent cleaning to uphold function (Dietz, 2007; Vogel et al., 2015).

1.2.2 An Overview of Bioretention Cell Design

1.2.2.1 Bioretention Cell Components and Sizing

Over the past few decades, the use of bioretention systems has gained widespread attention as an alternative to traditional stormwater management (Roy-Poirier et al., 2010;

Vogel et al., 2015). A BRC is a shallow depression in the landscape that was excavated and backfilled with permeable media, such as sandy soils, to allow for the infiltration of stormwater (Hunt and White, 2001, Roy-Poirier et al., 2010; Payne et al., 2015). They allow for the infiltration of stormwater, effectively decreasing runoff volumes and filtering the water (Payne et al., 2015). The BRC is strategically placed to intercept runoff at the low-point of the topography, where most of the water converges (Hunt and White, 2001, Roy-Poirier et al., 2010; Payne et al., 2015). The media is vegetated with species selected based on local origin, resistance to local environmental stresses, and aesthetics (Hunt and White, 2001; Roy-Poirier et al., 2010). The permeable media, also the water treatment layer, is often covered with a layer of mulch to keep the material in place (Roy-Poirier et al., 2010). If the parent soil at a site does not allow for adequate drainage to infiltration water within 24-48 hours, a drainage layer below the treatment media is used to allow for discharge via an underdrain (Roy-Poirier et al., 2010). A schematic of a simplified design of a BRC is shown in Figure 1.

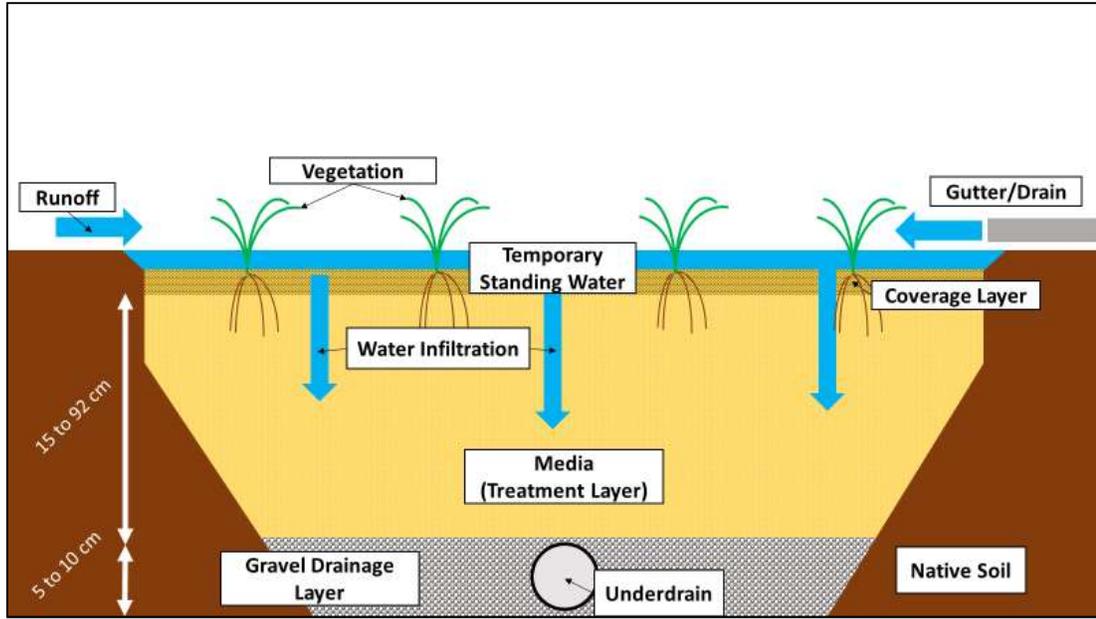


Figure 1: A simplified cross-section of a typical bioretention cell showing its layers.

Hunt and White (2001) and Chavez (2015) recommend that the area of the BRC be about 5% to 7% of the runoff area, depending on the degree of impervious coverage. Hunt and White (2001) refer to the USDA-NRCS Curve Number method, typically used for small urban watersheds, to calculate runoff produced by a given surface area:

$$R = \frac{(P-0.2S)^2}{P+0.8S} \quad (1)$$

R = runoff depth in inches

P = precipitation (assume 1 inch for treatment of first flush)

S = $1,000 \div \text{CN} - 10$

CN = curve number (standard curve number of 98 for sandy soils)

The curve number is a measure of water infiltration of a soil for a storm event (USDA, 1986). The calculated runoff depth can then be used to calculate the amount of runoff to be captured using a volume equation:

$$V = A \times \frac{R}{12} \quad (2)$$

V = runoff volume (ft³)

A = runoff area (ft²)

R = runoff depth (in)

The resulting volume will determine the amount of water the BRC is designed to capture (Hunt and White, 2001; Franti and Rodie, 2007a; McLemore et al., 2017). This sizing method for volume capture is consistently used across several different bioretention design manuals (Franti and Rodie, 2007a; Franti and Rodie, 2007b; ISP, 2009; Jaber et al., 2012). Although bioretention designs typically call for a nine-inch water holding depth, the depth can vary between from six up to 36 inches (Hunt and Lord, 2006; Franti and Rodie, 2007a; McLemore et al., 2017). Because bioretention systems are typically designed to treat runoff from the first flush (usually the first inch of precipitation), they will often require flow diversion to address flooding for a given geographical area (Hunt and White, 2001).

Because bioretention system research is rapidly evolving, various terminology has been used somewhat interchangeably. “Rain garden” is common terminology used by the public in the United States to refer to a BRC for residences (EPA, 2016a). Biofilters and biofiltration systems have traditionally been associated with wastewater treatment outside

of the United States (Payne et al., 2015). Recently they have been extensively applied in stormwater management, becoming almost synonymous with rain gardens. Bioswales, which are like rain gardens, are vegetated channels that convey infiltrate and treat stormwater (EPA, 2016a). Bioswales are linear in design and are ideal features for streets and parking lots. These systems have coevolved through similar research, one system often developing improvements for the others.

1.2.2.2 Bioretention Cell Media Selection

BRCs are designed to hold water and to facilitate pollutant removal processes. The media used for the treatment layer of bioretention systems should balance high permeability and adequate retention (Roy-Poirier et al., 2010). Sandy loam or loamy sand textured media are suggested as fill materials for the treatment layer to provide adequate permeability (Hunt and White, 2001; Hunt and White, 2006; Payne et al., 2015). The recommended hydraulic conductivity is a minimum of approximately 2.54 centimeters (1.0 inch) per hour (Hunt and White 2001; Hunt and Lord, 2006; Chavez, 2015). Adequate drainage will also prevent disease vectors from breeding in standing water (Roy-Poirier et al., 2010). Liu et al. (2014) suggested the use of a loamy sand media with low organic content of 3% to 5% as the optimal balance to provide minimum vegetation requirements and limit nutrient leaching risks. In addition to water quantity functions, BRCs can facilitate a variety of pollutant removal processes such as settling, filtration, sorption, vegetative uptake, microbial metabolism, and redox reactions (Hunt and Lord, 2006; LeFevre et al., 2015; Payne et al., 2015).

Recent research has proven that small modifications to bioretention systems, such as using reactive amendments or adding a saturated zone, can improve and enhance the metals and nutrients treatment processes previously described (Payne et al., 2015; Vogel et al., 2015). Many types of reactive materials suggested for BRCs use have had previous success in applications involving highly concentrated pollutants (Zhang et al., 2006; Zhang et al., 2008a; O'Neill and Davis, 2012; Erickson et al., 2012; Erickson et al., 2016). For example, FA, a coal combustion byproduct, is often used as an alternative for Portland cement in concrete production but has been widely used as a P coprecipitate (due to lime content in many sources of FA) and adsorbent for trace metals in wastewater (Nairn and Mercer, 2000; Ahmaruzzaman, 2010). Pollutant removal properties of FA have been applied to stormwater applications for P, trace metals, and microbial removal (Zhang et al., 2006; Zhang et al., 2008a; Zhang et al., 2008b; Chavez, 2015; Kandel et al., 2017; Youngblood et al., 2017). This thesis studied FA and MDRs as BRC amendments, and APT and BIO as media in BRCs.

1.2.2.3 Bioretention Cell Vegetation

The best types of vegetation used for plant coverage in BRCs must withstand cycling of wet and dry periods (Hunt and White, 2001; McLemore et al., 2017). Avoiding the use of obligate wetland and obligate upland species is important to sustain vegetative life (Hunt and White, 2001). Native plants may often grow better than others because of their adaptation to local climate. The usage of native and tolerant species is an important part of BRC design because they can decrease maintenance costs and effort. An important consideration for clay soils is the relative inaccessibility to water compared to sandy soils

(Hunt and White, 2001; Franti and Rodie, 2007a; McLemore et al., 2017). Clay soils are often recommended to be avoided, not just for hydraulic conductivity issues, but vegetation (Hunt and White, 2001; Franti and Rodie, 2007a; McLemore et al., 2017). Trees and shrubs with aggressive root growth will constantly attempt to grow deeper to find water, thus creating the potential to clog drainage pipes (Hunt and White, 2001). Clogged pipes will increase the required maintenance frequency. Therefore, clayey soils, soils with poor permeability, and soil compaction should be avoided with respect to vegetation.

1.2.3 Variable Bioretention Cell Performance Issues

1.2.3.1 Lack of Focus on Dissolved Pollutants

Pollutants are present in stormwater in the dissolved fraction or particulate fraction. Metals typically associated with stormwater are largely present in dissolved forms, where portions of Pb and Zn are both present at approximately 63% and Cu at 46% dissolved (BMP Database, 2015). Dissolved forms of P can be present in stormwater at 45% and even up to 90% (LeFevre et al., 2015). Although the proportions of pollutants in the particulate form are significant, their removal is usually associated with TSS removal via settling and filtration (Liu et al., 2014; LeFevre et al., 2015). Addressing the removal of dissolved pollutants is important because they are more bioavailable, therefore affecting receiving water bodies more quickly than particle-associated pollutants (LeFevre et al., 2015). LeFevre et al. (2015) concluded that little bioretention research has focused on removal of the soluble fraction of pollutants compared to particulate removal. However,

the use of reactive media enhances the ability of BRCs to remove dissolved pollutants via sorption and precipitation processes (LeFevre et al., 2015).

1.2.3.2 Nutrient Export from Bioretention Cells

An important water quality concern in LID technologies is nutrient export (Dietz, 2007). Nutrient removal in BRCs is highly variable and often mediocre (Payne et al., 2014; LeFevre et al., 2015; Holzbauer-Schweitzer, 2016). Variability in N and P removal, in some cases including export, may be attributed to diverse properties of different soils, especially those with high OM (Payne et al., 2014; LeFevre et al., 2015). Compost or soils rich in OM are internal sources of N and P (Payne et al., 2014; LeFevre et al., 2015). Liu et al. (2014) suggested soil compositions with more than 5% OM can cause nutrient leaching problems. Although highly organic soils can effectively retain metals, nutrient leaching remains a problem (LeFevre et al., 2015). Recommendations for the use of soil mixes containing 30% to 50% compost in several bioretention design manuals may explain why increases in N and P in BRC discharges are common (Franti and Rodie, 2007a; Franti and Rodie, 2007b; ISP, 2009; Jaber et al., 2012). Ironically, the Iowa Stormwater Partnership (ISP) lists common mistakes of bioretention implementation, which include the use of fertilizer (ISP, 2009). However, they recommend soil mixtures of 50% compost and more than 5% OM.

1.2.4 Reactive Media

1.2.4.1 “Class C” Fly Ash Amendment

FA is a captured coal combustion byproduct produced when inorganic impurities in coal are suspended in the combustion chamber and treated, along with flue gas, for sulfur dioxide (SO₂) emissions, using flue gas desulfurization (FGD) (Kalyoncu, 2001). “Class C” FA is designated as such by meeting a total silica (SiO₂), aluminum oxide (Al₂O₃), and iron oxide (Fe₂O₃) composition between 50% and 70%; it is typically comprised of approximately 20% CaO (ASTM C618). FA has proved to be an effective BRC media amendment for Cu, Pb, Zn, and P removal using sand amended with Class C FA (Zhang et al., 2006; Zhang et al., 2008a; Zhang et al., 2008b). Zhang et al. (2006) observed 94.2% decrease in P concentrations using sand amended with FA, which comprised 5% of the total mass of the mixture. The primary removal mechanism for phosphate was coprecipitation with calcium (Ca), as hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂), due to the abundance of lime in Class C FA (Zhang et al., 2006). Metals removal was attributed to sorption onto Al₂O₃ and Fe₂O₃ at circumneutral pH and precipitation as metal oxides (Zhang et al., 2008a).

The main trade-off to using FA as an amendment is the exponential drop in hydraulic conductivity as the percentage of FA composition increases (Zhang et al., 2006). Zhang et al. (2006) determined that a blend of sand should limit FA amendments at 5.8% by mass for adequate runoff infiltration. Although FA is pozzolanic and hardens in water, the 5% FA amendment still exhibited hydraulic conductivity of 0.91 centimeters per hour after 28 days of saturation (Hewlett, 2003; Zhang et al., 2006).

1.2.4.2 Iron Oxyhydroxide Mine Drainage Residuals Amendment

MDRs are comprised of several iron oxide forms, which come from a three-step process, which includes oxidation then hydrolysis, and finally precipitation (Watzlaf et al., 2004). When mine drainage is exposed to oxidizing conditions, naturally occurring pyrite (FeS_2) dissolves and releases aqueous Fe^{2+} (Watzlaf et al., 2004). Fe^{2+} oxidizes to ferric iron (Fe^{3+}) in the presence of atmospheric oxygen (O_2), then hydrolyzes and precipitates as iron oxyhydroxide ($\text{FeO}(\text{OH})$) (Watzlaf et al., 2004). Generally, MDRs are comprised of different forms of oxidized iron such as, but not limited to, goethite being the most common, ferrihydrite, and hematite (Wendling et al., 2013).

Iron oxides have had a great deal of attention in agricultural context because of their important role in phosphorus immobilization in soil (Fink et al., 2016). Phosphorus occurs naturally in soil primarily as apatite-group minerals and anthropogenically as PO_4^{3-} fertilizers (Fink et al., 2016). Iron oxides can occur naturally and abundantly in soil and have a high affinity for phosphorus, attributed to preferential adsorption of phosphate to the hydroxyl groups of iron oxides (Fink et al., 2016). PO_4^{3-} preferences for different iron oxide series follow the order of highest to lowest preference: ferrihydrite>goethite>hematite (Wendling et al., 2013). Kang et al. (2003) compared the performance of synthetic ferrihydrite, goethite, and hematite on treatment of wastewater effluent and synthetic P solutions in a series of batch studies. By adding 25 mg of ferrihydrite to one L of solution dose at 2.7 mg/L as P, they found greater than 60% P removal and greater than 80% P removal when adding 150 mg. Goethite removed less

than 10% of P at 25 mg of Fe and greater than 40% of P at 150 mg. However, hematite removed less than 15% of P at all Fe additions.

Iron oxides are known to adsorb metals well, except for complexed species (Benjamin and Sletten, 1996). The presence of the hydroxyl group on some iron oxide forms, such as goethite, is a major adsorption site for divalent trace metals such as Cu^{2+} , Pb^{2+} , Cd^{2+} , and Zn^{2+} (Swedlund et al., 2009). These divalent cations can form hydroxyl bridges with the surface (Forbes et al., 1976). The affinity for metals adsorption onto goethite follows, $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$ (Forbes et al., 1976). These metals also follow the general trend of increased adsorption with increased system pH, with near complete removal of all metals species except Cd above pH 8.0 (Forbes et al., 1976). With decreasing pH, competition for the adsorption sites seems to increase due to increased surface charge on goethite from excess hydrogen ions (H^+) (Forbes et al., 1976).

1.2.4.3 APTsorb and bioAPT

American Peat Technology distributes APTsorb and bioAPT, which are granular materials made from reed-sedge peat resources in Aitkin, Minnesota. Reed-sedge peat consists of mainly lignin, hemicellulose, cellulose, and humic substances, which feature an extensive list of functional groups that readily interact with metal cations (American Peat Technology, 2017a). These products are processed via “granulation and low temperature hardening,” which allows for the granulated peat to maintain structure when wetted (Eger et al., 2015a). Raw harvested peat is granulated through high pressure extrusion and extended drying, resulting in bioAPT, which is advertised as an inoculating

media (American Peat Technology, 2017c; Appendix III). APTsorb is derived from bioAPT, which takes bioAPT through an additional heat treatment step (American Peat Technology, 2017c). Metals removal in peat are attributed to surface and chemical adsorption, ion exchange, complexation, and chelation (Eger et al., 2015a).

A case study used APTsorb to treat mine water at the abandoned Soudan Mine in northeastern Minnesota (Eger et al., 2015a). Water treatment consisted of pumping mine water through a pressurized tank containing APTsorb media (Eger et al., 2015a). Using APTsorb, total Cu was decreased from a range of 30 to 50 micrograms per liter ($\mu\text{g/L}$) to a range of four to 13 $\mu\text{g/L}$ (Eger et al., 2015a). The effluent concentrations fell below local permit limits of 17 $\mu\text{g/L}$ (Eger et al., 2015a).

At a second site, an unnamed active mine in North America, APTsorb was able to decrease total Pb from 128 to one $\mu\text{g/L}$ and soluble Pb from 83 to one $\mu\text{g/L}$ after a preceding sand filter step (Eger et al., 2015b). The system also decreased total Zn from 40 to 8 $\mu\text{g/L}$ and soluble Zn from 45 to 17 $\mu\text{g/L}$ after the preceding sand filter step (Eger et al., 2015b). However, Eger et al. (2015b) made note of an anomaly involving soluble Zn being greater than total Zn. Shiller (2003) noted common water sample filtering materials and apparatuses can contribute to metals export in filtered samples due to the manufacturing processes of rubbers and plastics. At the same site, a gravity-flow system, also using a preceding sand filter step, produced similar results and decreased total Pb and Zn below permit limits (Eger et al., 2015b). The local permit limits for total Pb and Zn at the time were 12 and 137 $\mu\text{g/L}$, respectively (Eger et al., 2015b). In the early

investigation stages, American Peat Technology have not published data for nutrient removal performance (American Peat Technology, 2017b).

Although peat reserves in northern Minnesota still maintain over 90% of pre-settlement supply, it is a slow-renewable resource whose harvesting is scrutinized (Eger et al., 2015a). American Peat Technology is attempting to develop methods of increased peat accumulation rate and sustainable harvest (Eger et al., 2015a).

1.2.5 Other Reactive Media

Several other media have been studied for use in BRCs, many of which have been used in wastewater or agricultural drainage treatment applications. Though not an exhaustive list, several media that have been studied include biochar, granulated activated carbon (GAC), aluminum-based water treatment residuals, and iron shavings. Many of these media have been studied primarily with the focus of nutrient removal.

Biochar has become a low-cost medium for wastewater treatment for the removal of various organic, inorganic, and microbial pollutants (Hanandeh et al., 2017). Hanandeh et al. (2017) showed that amending sand with coarse biochar (CBC) or fine biochar (FBC), prepared from olive mill solid waste, can effectively precipitate and adsorb phosphorus. They used two sand mixtures with 8% CBC and 8% FBC to remove TP, in secondary treated wastewater, at efficiencies of 77.4% to 82.5% and 56.3% to 82.5%, respectively. The lower removal from FBC was attributed to greater negative surface charge from the smaller particle sizes, which decreased adsorption (Hanandeh et al.,

2017). The CBC also had a greater number of macro-pores, which allowed for microorganism growth for biological removal (Hanandeh et al., 2017).

The most common process used to remove N in wastewater is denitrification, but it typically requires longer residence time and water storage than is provided by stormwater treatment practices (Erickson et al., 2016). GAC has been suggested for potential abiotic treatment of NO_3^- in stormwater due to generally high sorption and ion exchange capacities of the material (Erickson et al., 2016). Erickson et al. (2016) demonstrated limited NO_3^- removal of 100% for 10 pore volumes (PV) in laboratory columns, packed with 100% GAC. They suggested capture of NO_3^- was attributed to ion exchange on the GAC, though limited by competition from bicarbonate (HCO_3^-).

O'Neill and Davis (2012) used columns packed with a loamy sand mixture composed of 5% aluminum-based water treatment residuals (WTR) and 3% triple-shredded hardwood bark mulch by mass to improve P removal in BRCs. The mixture was able to remove 88.5% of P. P removal was attributed to adsorption by amorphous aluminum hydroxide ($\text{Al}(\text{OH})_3$) from the water treatment residuals (O'Neill and Davis, 2012).

Erickson et al. (2012) introduced the "Minnesota Filter," which is a sand filter amended with iron shavings to focus on the removal of dissolved phosphorus species. Sand amended with 5% iron by mass removed an average of 88% phosphate in gravity-flow columns (Erickson et al., 2012). Systems that used iron amendments up to 10.7% operated for over one year without comprising hydraulic conductivity (Erickson et al., 2012).

In addition to the specifically mentioned media, Allred (2017) investigated 58 industrial byproducts of various material compositions for use in potential future studies in agricultural applications. Allred (2017) evaluated NO_3^- and PO_4^{3-} removal performance of the materials in batch experiments. Using 90-percent removal criteria for NO_3^- and PO_4^{3-} , two met standards for NO_3^- and 37 for PO_4^{3-} (Allred, 2017). Additionally, eight of the materials showed at least 50-percent removal for both NO_3^- and PO_4^{3-} (Allred, 2017). The results from this study do not only provide data for various materials to be used in future research, but they also illustrate the potential for even more materials to be introduced as BRC media or amendments.

1.2.6 Nutrient Analyses Reporting

NO_3^- was selected as the primary N species of concern for this study. NO_3^- removal is problematic because it is highly mobile in water and is difficult to remove abiotically. Although NO_2^- consumption can be toxic to humans and fish, it is often found at very low concentrations in runoff (Herrera Environmental Consultants, 2007). NO_2^- is very unstable, especially in aerobic waters, because it rapidly transforms into NO_3^- in the presence of oxygen (Wolff et al., 1998). NO_2^- is often reported with the combination of $\text{NO}_3^- + \text{NO}_2^-$ (Herrera Environmental Consultants, 2007).

Planktonic algae and bacteria mainly uptake orthophosphate (H_2PO_4^- , HPO_4^{2-} , or PO_4^{3-}), which is considered bioaccessible P (Boström et al., 1988). Dissolved reactive P (DRP) is often reported as the equivalent to orthophosphate, but the amount of available P can

be variable depending on concentration (Boström, et al., 1988). Twinch and Breen (1982) found that the concentrations of available P in DRP measurements were underestimated at concentrations less than 0.01 mg/L, overestimated at concentrations more than 0.1 mg/L, and variable between 0.01 to 0.1 mg/L. Dissolved unreactive P (DUP) can interfere with DRP measurements because DUP can be made available from a small amount of organically bound fractions (Bradford and Peters, 1987).

1.3 Hypotheses and Objectives

This study aims to address the removal of the dissolved fraction of pollutants and nutrient leaching issues present in BRCs by evaluating the pollutant removal performance of FA, MDR, APT, and BIO. Each reactive media will be evaluated by flowing SS upward through laboratory treatment columns. This study will focus on the removal of Cu^{2+} , Pb^{2+} , Zn^{2+} , NO_3^- , and PO_4^{3-} . Pollutant removal performance will be based on the net changes in pollutant concentrations from column effluents. Ideal reactive materials should not increase pollutant concentrations in infiltrating runoff. Provided the materials are inexpensive, they can also make BRCs even more cost-effective alternatives to traditional stormwater management. Basic cost analyses will be performed to evaluate the advantages and disadvantages of each reactive media against their costs. If the proposed reactive media have evidence of both improved water quality over typical sandy materials and cost effectiveness, they may be recommended for more widespread use in BRC designs.

1.3.1 Hypotheses

1. Effluents from laboratory treatment columns of all proposed reactive media will result in net decreases in Cu^{2+} , Pb^{2+} , and Zn^{2+} . Additionally, FA5.0 and MDR7.5 columns will result in net decreases in P.
2. Effluents from APT and BIO laboratory treatment columns will result in net decreases in NO_3^- .
3. Effluents from laboratory treatment columns of APTsorb and bioAPT will result in net increases in P concentrations. Due to the high composition of OM of peat, these media may be internal sources of nutrients (Liu et al., 2014; LeFevre et al., 2015).

1.3.2 Objectives

1. Preliminarily evaluate proposed reactive media for adequate infiltration to proceed into the primary study. Media should exhibit hydraulic conductivities of at least 2.54 centimeters per hour, per recommendations by Hunt and White (2001). This objective will also achieve optimum amendment ratios for FA and MDR.
2. Evaluate each of the proposed reactive media for pollutant removal performance of Cu^{2+} , Pb^{2+} , Zn^{2+} , NO_3^- , and PO_4^{3-} by flowing SS upward through laboratory treatment columns. Media performance comparisons will be evaluated and compared by normalizing column effluent concentrations with influent concentrations.

3. Characterize chemical and geotechnical properties of the reactive media to suggest possible removal mechanisms.
4. Perform cost analyses on each proposed reactive media to determine the cost-effectiveness in BRC design context.

CHAPTER 2: METHODS AND MATERIALS

Sand was locally purchased under the brand-name Quikrete® and classified as ASTM C33 sand, which is a specification for use as concrete aggregate (ASTM, 2016). The sand was sieved to pass the US Sieve Series No. 10 (two-millimeter (mm) openings). The FA used in this study was provided by the Grand River Dam Authority (GRDA) from the Grand River Energy Center coal-fired power plant in Chouteau, Oklahoma. It was formerly known as the GRDA Coal Fired Complex. Prior to collection, the FA was treated via quicklime FGD scrubbers, a process by which the material gets its quicklime, or calcium oxide (CaO) content (DEQ, 2014). MDRs were harvested from the oxidation pond at the Mayer Ranch Passive Treatment System in Commerce, Oklahoma. FA and MDRs were sieved to pass the US Sieve Series No. 200 (0.075-mm openings). American Peat Technologies provided samples of APT and BIO in granular and minus 30-mesh (0.60 mm) particle sizes. APT and BIO are reed-sedge peat materials sourced and processed in Aitkin, Minnesota.

Because FA and MDRs are comprised of particles like silt or clay, they were expected to have hydraulic conductivities less than 2.54 centimeters per hour, a minimum criterion by Hunt and Lord (2006). Therefore, a preliminary hydraulic conductivity study was conducted to screen the materials for adequate infiltration, prior to conducting the pollutant removal performance study. Materials were also characterized for various geotechnical and chemical properties to provide understanding of pollutant removal performance and overall appropriateness as media for bioretention systems.

100% sand (SAND) was used as the control group. Descriptions of the proposed reactive materials and their sources are summarized in Table 2. Many of the reactive materials have been previously used in the treatment of highly concentrated waters, such as wastewater or mine drainage (Nairn et al., 2009; Eger et al., 2015a; Eger et al., 2015b). However, this study proposed these reactive media for use in BRCs to remove relatively minute pollutant concentrations.

Table 2: Summary of reactive media, sources, and descriptions.

Material	Source	General Geochemical Components
Sand ¹	Quikrete® Commercial Product	Silica
Fly Ash ²	Grand River Energy Center, Chouteau, OK	Silica, Aluminum Oxide, Ferric Oxide, Calcium Oxide
Mine Drainage Residuals ³	Mayer Ranch Passive Treatment System Oxidation Pond, Commerce, OK	Ferrihydrite, Goethite, Hematite
APT _{sorb} ⁴	APT Peat Reserves, Aitkin, MN	Reed-sedge Peat
bioAPT ⁵	APT Peat Reserves, Aitkin, MN	Reed-sedge Peat

1. Appendix I
2. Appendix II
3. Neely and Nairn, 2010
4. Appendix III
5. Appendix III

2.1 Preliminary Hydraulic Conductivity Screening

Ratios for FA-sand and MDR-sand mixtures were selected based on the methods used in Zhang et al. (2006) for the FA used in that study. Zhang et al. (2006) selected various ratios of FA-sand mixtures of up to 10% FA by mass. Based on their findings, they concluded that amending sand using FA up to 5% by mass was appropriate for BRCs based on this range of mixtures meeting the minimum hydraulic conductivity criterion.

MDR-sand mixtures used in the hydraulic conductivity screening included MDR amendments at 2.5%, 5.0%, 7.5%, and 10.0% by mass. Despite recommendations by Zhang et al. (2006), FA-sand mixtures were evaluated again because different sand and FA sources were used. The media and amendment mixtures selected for this screening are summarized in Table 3.

Table 3: Material composition of media used in hydraulic conductivity screening percentages by mass.

Media	Material Composition
SAND	100% sand
APT	100% APT (granular) 100% APT (-30 mesh)
BIO	100% APT (granular) 100% APT (-30 mesh)
FA	97.5% sand + 2.5% FA 95.0% sand + 5.0% FA 92.5% sand + 7.5% FA 90.0% sand + 10.0% FA
MDR	97.5% sand + 2.5% MDRs 95.0% sand + 5.0% MDRs 92.5% sand + 7.5% MDRs 90.0% sand + 10.0% MDRs

Falling-head tests (Klute 1986), were conducted on the proposed materials to measure hydraulic conductivity. The falling-head test consisted of using a permeameter to measure the change in standing water level as the water infiltrated through the media, over an elapsed time. From these data, hydraulic conductivity was calculated using the following equation provided by Klute (1986):

$$K = \frac{aL}{At} \ln\left(\frac{H_1}{H_2}\right) \quad (3)$$

K = hydraulic conductivity (cm/hr)

a = cross-sectional area of the permeameter (cm²)

L = length of media (cm)

A = cross-sectional area of the media (cm²)

t = time elapsed (hr)

H₁ = initial head (cm)

H₂ = final head (cm)

A schematic of the permeameter to be used this study apparatus is shown in Figure 2. The permeameter was packed with a 10.2-centimeter pea gravel drainage layer, a 15.2-centimeter layer of media above it, then topped with a 5.1-centimeter layer of pea gravel to limit disturbance of pouring water. Non-woven geotextile (US 425NWE), provided by US Fabrics, Inc., was placed in between each layer to limit particle migration. The permeameter used for these falling-head tests is shown in Figure 3, with packing schematic also shown in Figure 2.

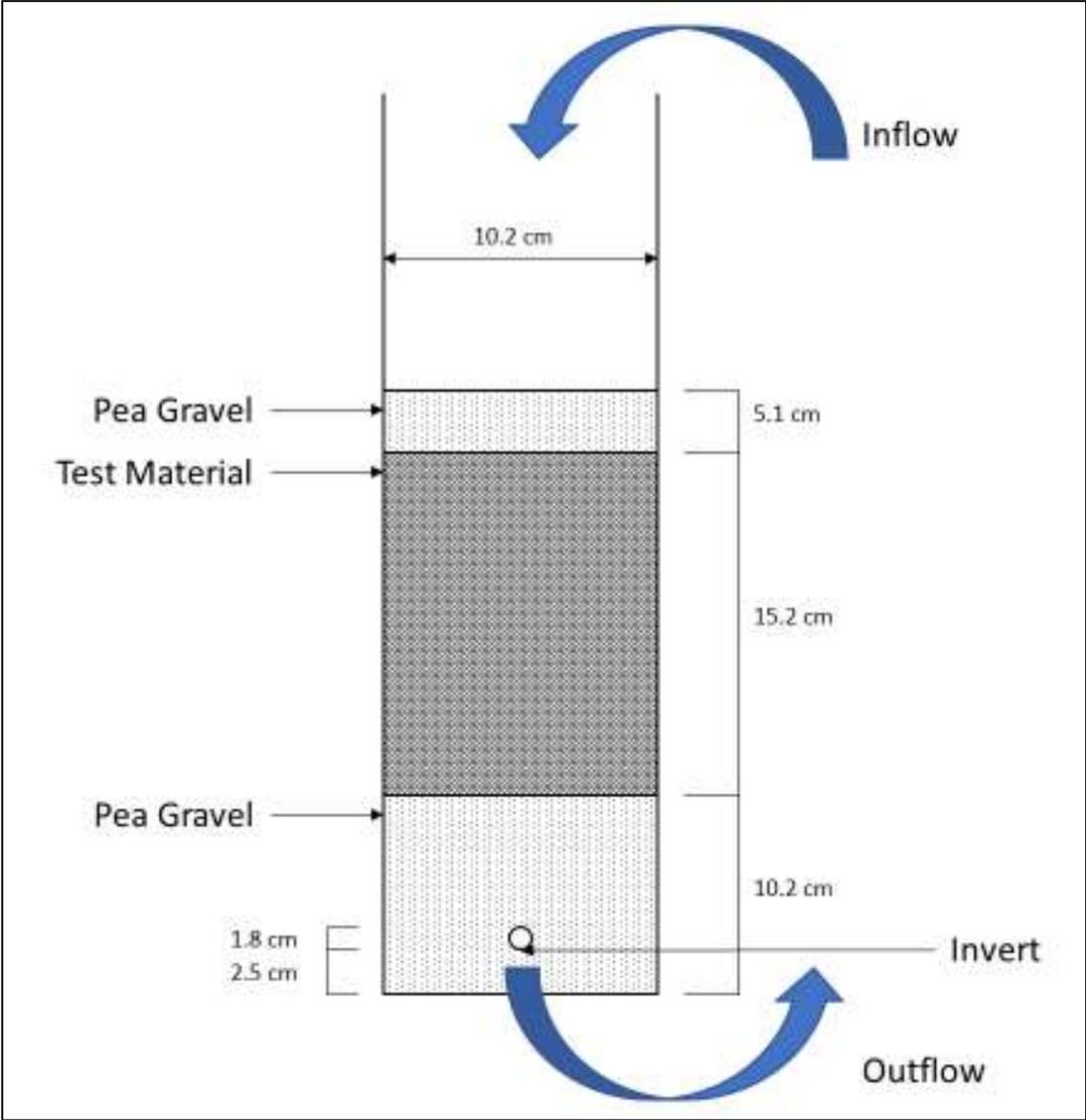


Figure 2: Falling-head permeameter packing schematic.

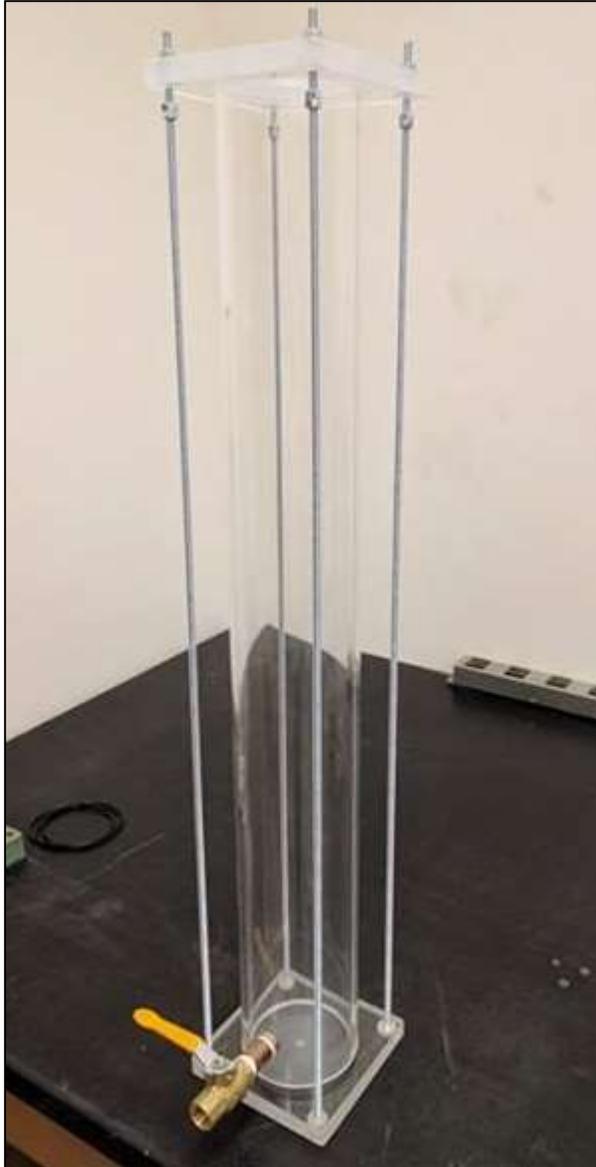


Figure 3: Falling-head permeameter for measuring hydraulic conductivity.

2.2 Laboratory Column Experiments

Based on the hydraulic conductivity screening (Section 3.1), the media selected for the laboratory column experiments included SAND, five-percent FA and 95-percent sand (FA5.0), 7.5-percent MDRs and 92.5-percent sand (MDR7.5), APT, and BIO. Dr. Glenn Brown designed the acrylic laboratory treatment columns used in this study. They are

10.2 centimeters in inner-diameter and 15.2 centimeters in length, which is also the minimum BRC media depth recommended by Hunt and White (2001). They consist of two end caps with O-rings. Additionally, nonwoven geotextile was placed at the ends to prevent material loss. Figure 4 shows a laboratory column used in this experiment with all its pieces.

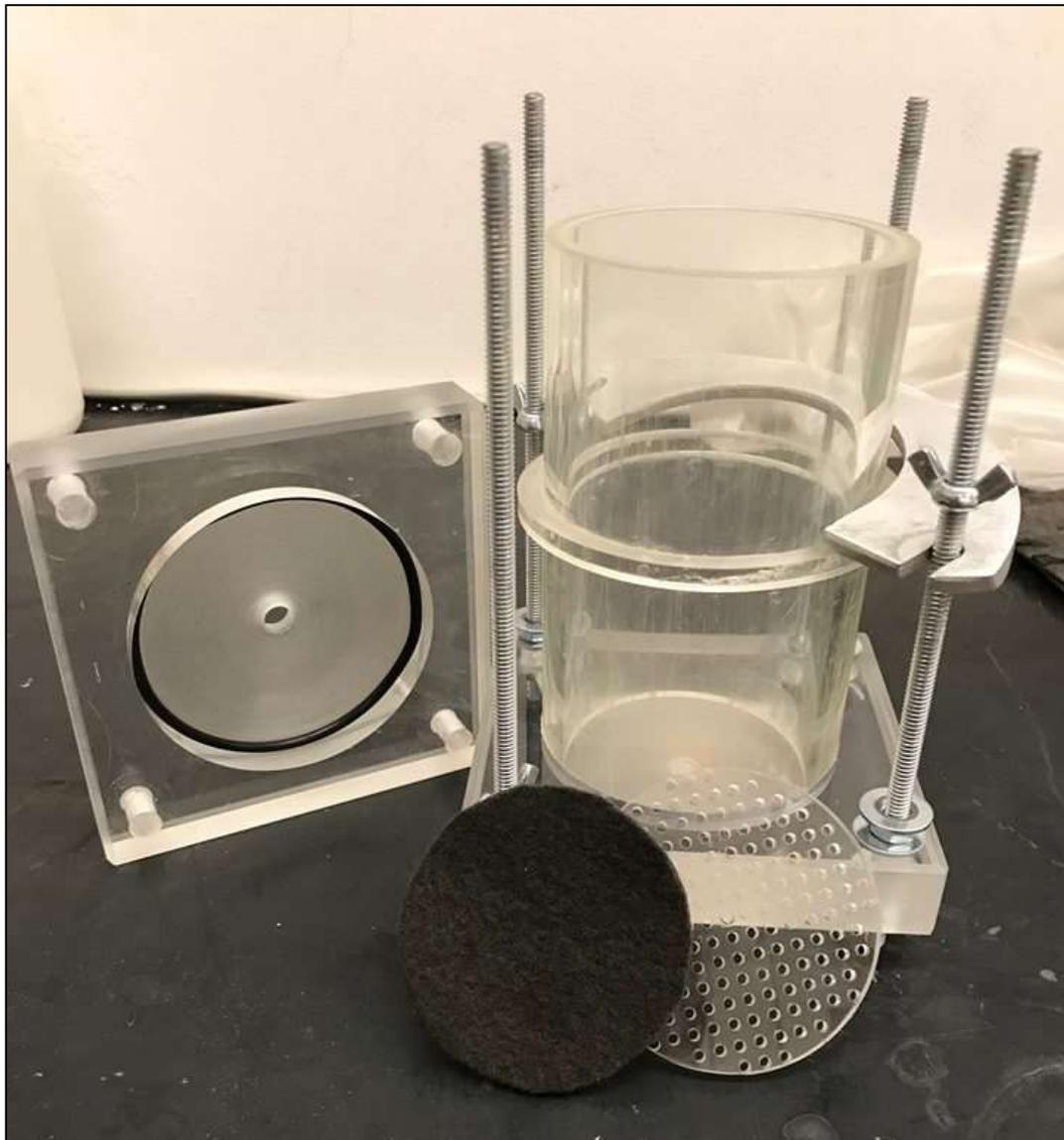


Figure 4: An acrylic column used in the pollutant removal experiments, designed by Dr. Glenn Brown.

SS was peristaltically pumped through clear, acrylic, up-flow columns packed with amendment mixtures or layered media. Water effluent samples were collected and analyzed to evaluate pollutant removal performance by normalizing effluent concentrations with influent concentrations. Normalized effluent values show net increases or decreases in pollutant concentrations to indicate media retention or export. Three replicate experiments were completed for each media for a total of 15 columns. The set-up for the column experiments is pictured in Figure 5.



Figure 5: Set-up of laboratory column experiments with synthetic stormwater sources in 20-L carboys, peristaltically pumped from bottom of packed columns (left: two FA5.0 columns; right: two MDR7.5 columns).

2.2.1 Column Packing and Flow Rates

Media were wet-packed in the columns in two-inch lifts. Each lift layer was added dry, saturated with deionized (DI) water, and hand-tamped. The surface of each preceding layer was scraped in a cross-hatch pattern to achieve better packing with the succeeding layer. The hydraulic conductivities of APT and BIO were found to be greater than that of SAND. To decrease the amount of material used and to maintain appropriate hydraulic conductivity, APT and BIO columns were each packed into two layers consisting of APT or BIO and sand at 1:3 ratios. The sand was placed at the outflow-end of the column to augment the hydraulic retention time (HRT) of APT or BIO to be approximately the same as columns that would have been packed with 100% APT or BIO. Flow rates were calculated using the equations for Darcy's velocity and seepage velocity, which is multiplied by the cross-sectional area of the laboratory column.

$$v_s = \frac{v}{\eta} \quad (5)$$

v_s = seepage velocity (cm/hr)

v = Darcy's velocity (cm/hr)

η = porosity

$$v = K \frac{dh}{dL} \quad (6)$$

v = Darcy's velocity (cm/hr)

K = hydraulic conductivity (cm/hr)

dh/dL = hydraulic gradient (1 for vertical flow)

SS was pumped at flow rates that matched the seepage flow through the media, based on the results from the hydraulic conductivity screening. Corresponding masses, flow rates, and PVs for each media are shown in Table 4.

Table 4: Column flow rates and pore volumes.

Column	Media Mass (g)	Flow Rate (mL/min)	Pore Volume (mL)
SAND1	1086	75	
SAND2	1100	75	230
SAND3	1070	75	
FA5.01	1130	6	
FA5.02	1132	7.5	270
FA5.03	1078	8	
MDR7.51	1001	6	
MDR7.52	1000	6	300
MDR7.53	998	8	
APT1	APTsorb: 72 sand: 678	75	
APT2	APTsorb: 82 sand: 688	75	APTsorb: 140 sand: 150
APT3	APTsorb: 74 sand: 688	75	
BIO1	bioAPT: 88 sand: 664	75	
BIO2	bioAPT: 80 sand: 754	75	bioAPT: 140 sand: 150
BIO3	bioAPT: 84 sand: 714	75	

2.2.2 Synthetic Stormwater

SS was created in the laboratory in several 20-liter (L) batches. DI water was spiked with KNO_3 , KH_2PO_4 , CuCl_2 , PbCl_2 , and ZnCl_2 laboratory salts. Target concentrations for Cu^{2+} , Pb^{2+} , Zn^{2+} , NO_3^- , and PO_4^{3-} , are summarized in Table 5. Solutions were adjusted using one normality (N) HCl and KOH to approximately pH 7, which is typical of residential stormwater runoff (BMP Database, 2015). Because BRCs are already effective

at removing TSS and particulates via physical filtration, only soluble pollutant species were included in the SS (Liu et al., 2014; LeFevre et al., 2015).

Table 5: Target synthetic stormwater constituent concentrations, based on typical residential runoff (BMP Database, 2015).

Constituent	Units	Concentration	Salt
Cu ²⁺	µg/L	25	CuCl ₂
Pb ²⁺	µg/L	30	PbCl ₂
Zn ²⁺	µg/L	100	ZnCl ₂
NO ₃ ⁻	mg/L as N	1.5	KNO ₃
PO ₄ ³⁻	mg/L as P	0.5	KH ₂ PO ₄

2.2.3 Water Sample Collection and Preservation

Influent source water was collected at the beginning of each experiment for the same analyses as the effluent samples. Effluent water samples were collected at four different points for each column experiment: after one, three, 10, and 30 PVs had passed through. Times for these collection points were determined by a medium's respective flow rate and PV. Water samples were collected for the analyses of nutrients (TP, TDP, TN, NO₃⁻, and NH₃), total and filtered metals, and carbon content. Carbon content includes total carbon (TC), total inorganic carbon (TIC), and total organic carbon (TOC).

Water samples for filtered metals and TDP were filtered through a 0.45-micron filter upon collection prior to any acidification. Nutrient samples were analyzed within 48 hours or acidified with concentrated H₂SO₄, at two milliliters (mL) of acid to one L of sample, if timely analyses were not likely. Water samples for total and filtered metals were acidified with concentrated HNO₃ at two mL of acid to one L of sample. Carbon samples were

preserved by acidification with concentrated hydrochloric acid (HCl) at two mL per one L of sample. Nutrient and TC/TIC samples were placed in refrigerated storage.

2.2.4 Water Quality Analyses

Water samples collected for nutrients were analyzed for TP, TDP, TN, NO_3^- , and NH_3 . TP and TDP were measured via EPA Method 365.3 using a Cole and Parmer UV/VIS SQ-2800 spectrophotometer (EPA, 1978). NO_3^- was measured via EPA Method 352.1 using the same spectrophotometer (EPA, 1971). NH_3 was measured immediately upon water sample collection using Hach TNTplus 830 analysis kits and Hach DR 3800 Spectrophotometer, which followed Hach Method 10205 (Hach, 2016). TN was measured using the AnalytikJena multi-N/C 2100S. Water samples collected for total and filtered metals analyses were digested via EPA Method 3015A (EPA, 2007a). Digested metals samples were analyzed via inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Varian Vista-PRO simultaneous axial ICP-OES, following EPA Method 6010C (EPA, 2000b). Water samples for carbon content were also analyzed using the AnalytikJena multi-N/C 2100S. TC concentrations were calculated by difference of TC and TIC.

In addition to analyses of collected water samples, column effluents were immediately measured for pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), temperature (T), and specific conductance (SC). Measurements were performed using Fisher Scientific Accumet XL600 instrumentation with appropriate electrodes. Influent

source water was measured at the beginning of each experiment for the same parameters. The methods of water quality analyses and instruments used are summarized in Table 6.

Table 6: Water quality analytical methods and instrumentation.

Analyte	Method/Instrumentation
pH, ORP, DO, T, SC	Accumet XL600
TP	EPA Method 365.3
TDP	EPA Method 365.3
TN	AnalytikJena multi-N/C 2100S
NO ₃ ⁻	EPA Method 352.1
NH ₃	Hach Method 10205
Total Metals, Filtered Metals	EPA 6010C*
TC, TIC, TOC	AnalytikJena multi-NC 2100S

*Although measured, the following metals do not have fully developed laboratory methods: Ag, Hg, Se

2.2.5 Statistical Tests

Normalized effluent concentrations, effluent concentrations (C_e) divided by influent concentrations (C_i), of the reactive media were compared to the SAND control group using the Mann-Whitney U test for nonparametric data. A significance level (α) of 0.10 was used to determine statistical significances based on the p-values from the comparison tests.

2.3 Chemical Characterization of Media

Reactive media underwent various chemical characterization procedures. Chemical characterization helped determine material composition, identify hazardous materials, and suggest possible pollutant removal mechanisms. The points of zero charge (PZC) of the media were determined to deduce potential sorption based on material surface charge. The pore water pH in a medium directly impacts the material's surface charge due to H⁺ or hydroxide ion (OH⁻) displacement. A solution pH greater than the material's PZC will

yield a net negative surface charge and vice versa for pH less than the PZC. The PZC was determined by the “pH drift method.” Media also underwent the EPA Toxicity Characteristic Leaching Procedure (TCLP), described in EPA Method 1311 (EPA, 1992). The TCLP is a chemical extraction method to simulate landfill leaching to determine proper waste disposal protocol. Pollutants from TCLP leachate that exceed EPA’s list of “D” wastes determine if the material is considered hazardous. Metals from the media were also extracted using EPA Method 3051A and analyzed via EPA Method 6010C (EPA, 2000b; EPA, 2007b). EPA Method 3051A partially decomposes the media and does not completely reflect the composition of the materials.

PZCs of column experiment media were determined using the pH drift method. This method measures compares the initial and final pH of a salt solution with the addition of material of interest. Six centrifuge tubes were filled with 50 mL of 0.1 molar KNO_3 solution and purged of carbon dioxide (CO_2) by bubbling pure nitrogen gas (N_2) for 10 minutes. The solutions were then adjusted to approximately pH 2, 4, 6, 8, 10, and 12 by 0.1 molar nitric acid (HNO_3) or 0.1 molar potassium hydroxide (KOH). The acid and base were chosen to limit the interference of other ion species. To each pH solution, 0.2 grams (g) of material were added and agitated on a shaker for 24 hours. This procedure was done on SAND, FA, FA5.0, MDR, MDR7.5, APT, and BIO for a total of 42 samples. After 24 hours, the final pH reading was taken from each sample and plotted against initial pH readings. The PZC was determined where pH curve intersected the 1:1 sloped line of equal initial and final pH. PZC determinations were repeated with 0.01 M KNO_3 for verification of PZC at different electrolyte concentrations.

2.4 Geotechnical Characterization of Media

Materials that passed the preliminary hydraulic conductivity screening underwent a series of geotechnical analyses for characterization. Media were measured for OM as loss-on-ignition (LOI) by ASTM D7348 (ASTM, 2013). Air dried materials were analyzed for moisture content by ASTM D2216 (ASTM, 2010). Sieve analyses by ASTM D6913 were performed on air dried samples to obtain particle-size distributions for each material (ASTM, 2017b). Modified sieve analyses were performed on APT and BIO to obtain particle-size distributions for expanded materials upon water saturation. APT and BIO were submerged in DI water for at least six hours and wet sieved. The fractions remaining on each sized sieve were oven dried and weighed. Additionally, the particle-size distribution of MDR was characterized using the ASTM D7928 sedimentation method (ASTM, 2017c). Particle-size distribution of FA was not characterized because the sedimentation method was not applicable to pozzolanic materials. Bulk densities of packed media were measured by ASTM D7263 (ASTM, 2009). Finally, particle densities were measured by pycnometer, following Klute (1986). A summary of geotechnical analytical methods is shown in Table 7.

Table 7: Geotechnical parameters and associated analytical methods.

<u>Analysis</u>	<u>Method</u>
Loss-on-Ignition	ASTM D7348
Moisture Content	ASTM D2216
Particle-Size Distribution	ASTM D6913
Particle-Size Distribution (Fine-Grain)	ASTM D7928
Bulk Density	ASTM D7263
Particle Density	Klute (1986)

PVs were estimated by measuring the bulk densities, moisture contents, and estimated porosities of packed and saturated media. Porosity was estimated by the following equation with the assumption of a particle density of 2.65 gram per cubic centimeter (g/cm^3).

$$\eta = \frac{1 - \rho_{b,d}}{\rho_p} \quad (7)$$

η = porosity

$\rho_{b,d}$ = dry bulk density (g/cm^3)

ρ_p = particle density (g/cm^3)

2.5 Cost Analyses

A cost analysis with pricing per ft^2 were calculated for each of the proposed BRC media. Cited costs from various sources were normalized for the year 2018 and regionalized for Oklahoma. The costs of the BRCs were compared to the general pricing model, EPA Opti-Tool, the cost of the systems at the Trailwoods residential neighborhood site in Norman, Oklahoma (Coffman, 2014; EPA, 2016b). Opti-Tool estimates the general pricing of BRCs to be \$15.46 per cubic feet (ft^3) (in 2016 dollars) of water quality volume (WQV), which is the quantity of water storage required to treat 90% of the runoff of a given area (EPA, 2016b). This pricing was converted from ft^3 to ft^2 based on an area similar to Trailwoods. The WQV is calculated using the following equation:

$$WQV = \frac{1.5R_vA}{12} \quad (8)$$

WQV = water quality volume (acre-feet)

A = total drainage area (acres)

$R_v = 0.05 + 0.009I$ (I = % of impervious cover; assumed 90%)

The pricing rate also includes a 35% add-on for engineering and contingency fees. A set of assumptions were made regarding BRC construction practices, pricing, and constraints to make fair comparisons between each media. Listed pricings include bare material, equipment, and labor costs. Additionally, Norman, OK was chosen as the location for the cost estimate to be able to compare with Trailwoods. For estimates in other locations, costs can easily be adjusted by applying the appropriate regional cost adjustment factor and transportation mileages (Weiss et al., 2005). These assumptions are presented in Table 8. Costs of various BRCs using FA in Grove, Oklahoma were also presented to provide a relative cost range for systems using fly ash (Chavez, 2015).

Table 8: Assumptions used in bioretention cell cost analysis (pricing not adjusted in this table).

Parameter	Assumption
Application	Residential
Geography	
Location	Norman, OK
Rainfall Zone	Zone 5
Size	
Area	3940 ft ²
Total Depth	1.5 ft
Media Depth	0.5 ft
Construction and Materials	
Excavation	\$9.38 per yd ³ (2016)
Fill and Spread	\$2.04 per yd ³ (2016)
6-Inch Layer of #57 Stone Aggregate	\$32.56 per yd ³ (2016)
3-Inch Layer of #89 Stone Aggregate	\$24.42 per yd ³ (2016)
6-Inch Perforated Pipe	\$12.00 per ft (2016)
Geotechnical Fabric Liner	\$1.25 per ft ² (2016)
Vegetation (65% coverage)	\$1.94 per ft ² (2008)
Media Cover	\$0.20 per ft ² (2008)
Landfill	120.21 per yd ³ (2016)
Trucking Transportation	\$0.17 per ton per mile (2007)
Maintenance Costs	
Annual Maintenance Cost	6% of construction cost per year
Annual Maintenance Hours	20.7 hours
BRC Operation Time	20 years
Cost Adjustment Factors	
Average Annual Inflation	2.00% per year (1997-2017)
Developed Area Cost Adjustment Factor	2
Cost of Required Land Area	5%
Zone 5 Regional Cost Adjustment Factor	0.67
Engineering Fees & Contingencies	35%

Sources: (EPA, 1999; Hunt and White, 2001; Weiss et al., 2005; Chavez et al., 2008; Barr Engineering Company, 2011; Coffman, 2014; EPA 2016; 2016; BTS, 2017 McLemore et al., 2017; BLS, 2018; Gordian, 2018)

It is important to note that BRC lifetime and media replacement frequencies were discounted because pollutant removal capacities were studied. The variable components, which primarily consisted of material costs and transportation are summarized in Table 9. Proportions of reactive media materials were taken from the amounts used in the laboratory columns.

Table 9: Variable costs of materials and hauling distances used in bioretention cell cost analysis.

Material	\$ per ton	Miles to Norman, OK	Source Location
#57 Stone	See Table 8	28	Quikrete, Oklahoma City, OK
#89 Stone	See Table 8	28	Quikrete, Oklahoma City, OK
Sand (2018)	80	28	Quikrete, Oklahoma City, OK
Fly Ash (2010)	70	161	Grand River Energy Center, Chouteau, OK
Mine Drainage Residuals (2016)	158	214	Mayer Ranch, Commerce, OK
APT sorb (2017)	3200	931	American Peat Technology, Aitkin, MN
bioAPT (2017)	3200	931	American Peat Technology, Aitkin, MN

Sources: (SHRP2, 2012; Hedin, 2016; Local purchase, 2017; Jones and Eger, 2017)

CHAPTER 3: RESULTS, DISCUSSION, AND CONCLUSIONS

3.1 Preliminary Hydraulic Conductivity Screening

A summary of all measured hydraulic conductivities is shown in Table 10. The hydraulic conductivity of SAND was 45.1 centimeters per hour. Increasing the amount of FA decreased hydraulic conductivity of sand dramatically. The trend of decreasing hydraulic conductivity with increasing FA content is shown in Figure 6. Hydraulic conductivities of 7.5 and 10.0-percent additions could not be measured using the falling-head test due no flow being observed after one day.

Increasing the amount of MDRs also decreased hydraulic conductivity of sand. However, flow through the falling-head permeameter was still observed up to 10.0%, unlike FA. The trend of decreasing hydraulic conductivity with increasing MDRs content is shown in Figure 7. The 5.0-percent FA and 7.5-percent MDR mixtures were selected to pass the screening because they met the minimum hydraulic conductivity criterion of 2.54 centimeters per hour.

Granular APT and BIO had hydraulic conductivities greater than SAND by an order of magnitude. Even the smaller -30 mesh size fractions of APT and BIO had hydraulic conductivities greater than SAND. Therefore, the -30 mesh size fractions of APT and BIO were selected to pass the screening. A comparison of hydraulic conductivities of all media is shown in Figure 8.

Table 10: Summary of measured hydraulic conductivities of various media.

Media	K (cm/hr)
Sand	45.1
Fly Ash, 2.5%	12.2
Fly Ash, 5.0%	3.6
Fly Ash, 7.5%	<1 cm/day
Fly Ash, 10.0%	<1 cm/day
Mine Drainage Residuals, 2.5%	19.1
Mine Drainage Residuals, 5.0%	9.3
Mine Drainage Residuals, 7.5%	3.5
Mine Drainage Residuals, 10.0%	2.1
APT sorb, granular	988.7
APT sorb, -30 mesh	170.2
bioAPT, granular	740.4
bioAPT, -30 mesh	50.1

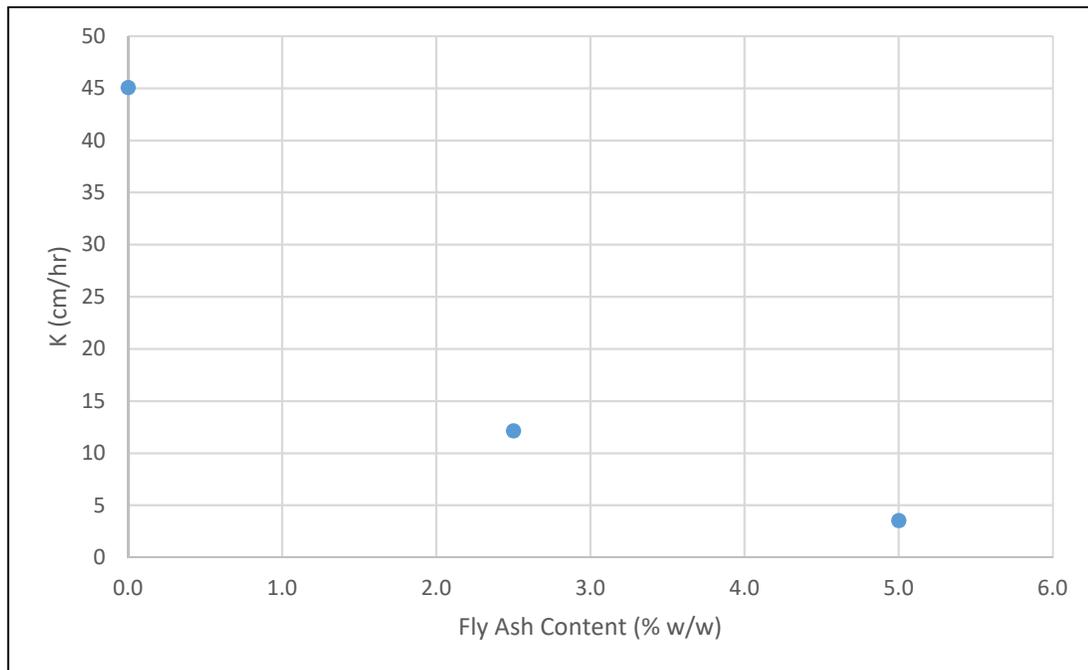


Figure 6: Effect of increasing fly ash content on hydraulic conductivity of sand.

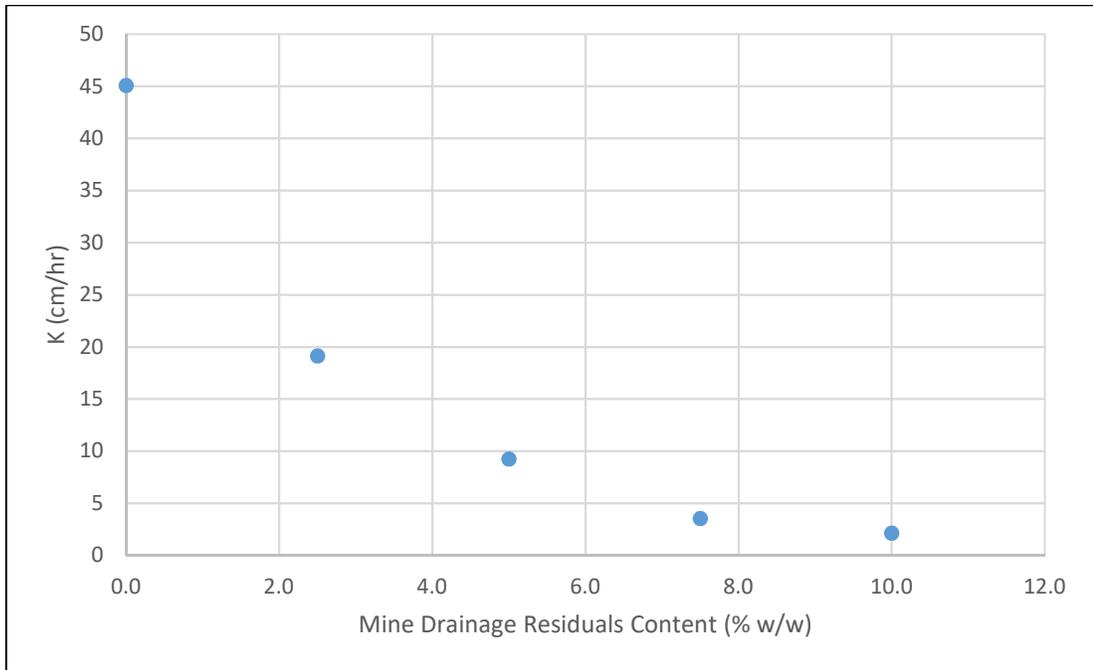


Figure 7: Effect of increasing mine drainage residuals content on hydraulic conductivity of sand.

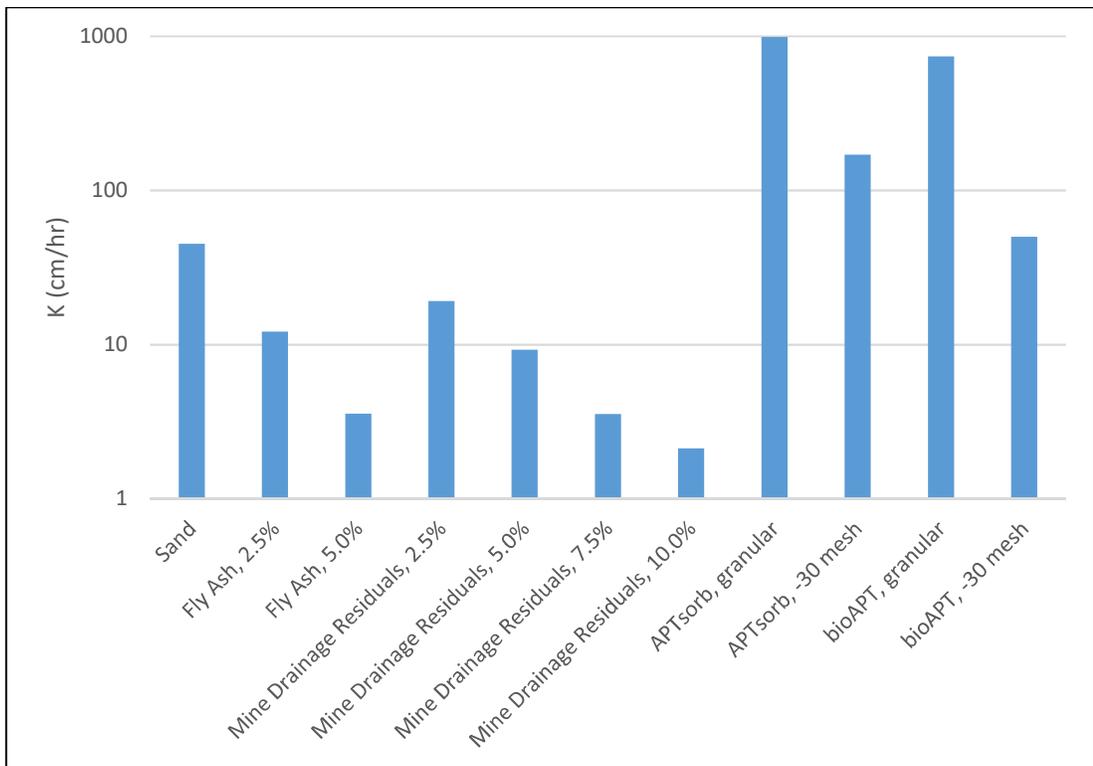


Figure 8: Comparison of hydraulic conductivities among all measured media.

3.2 Media Characterization

3.2.1 Toxicity Characteristic Leaching Procedure

The metals analyses of the TCLP extracts of each solids sample show that none of the materials used in this study exceeded the EPA maximum contaminant levels (MCL) of the RCRA-8 metals, which include silver (Ag), As, barium (Ba), Cd, Cr, Pb, mercury, and selenium (Se). The metals concentrations in the TCLP extracts are summarized in Table 11, as well as available instrument detection limits (IDL). Several constituents fell below detection limits (BDL) with those data listed as ‘BDL.’ Based on these results, none of the media are considered hazardous materials.

Table 11: EPA RCRA-8 metals concentrations in media and material Toxicity Characteristic Leaching Procedure extracts.

	Ag (µg/L)	As (µg/L)	Ba (mg/L)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	Se (µg/L)
IDL	-	2.86	-	0.18	0.31	3.98	-	-
MCL	5000	5000	100	1000	5000	5000	200	1000
SAND	8	BDL	0.79	1	BDL	15	BDL	BDL
FA	214	BDL	1.07	8	0.20	BDL	BDL	BDL
FA5.0	32	BDL	2.26	1	0.02	25	BDL	BDL
MDR	18	BDL	0.05	0.3	BDL	52	BDL	BDL
MDR7.5	10	BDL	0.16	5	BDL	15	BDL	BDL
APT	15	BDL	0.34	1	BDL	48	BDL	BDL
BIO	14	BDL	0.37	1	BDL	46	BDL	BDL

3.2.2 Solids Digestion Extraction

Table 12 summarizes the results of the ICP-OES analyses of the solids-digestion extract. The incorporation of sand in the FA5.0 and MDR7.5 mixtures showed a common decrease in concentrations, by an order of magnitude. Materials, other than Si, were found in substantial quantities, especially Ca, which was measured at 23,600 mg/kg. Extractable Ca from FA was at least an order of magnitude greater than all other materials, which was

expected. However, Ca concentrations in FA5.0 were less than that of SAND. This may suggest possible heterogeneity of Ca distributed in the sand or incomplete dissolution of CaO in FA. APT and BIO also measured similar amounts of Ca, which may be naturally occurring from the peat source.

Table 12: Results of solids digestion extraction.

	SAND	FA	FA5.0	MDR	MDR7.5	APT	BIO
Ag (mg/kg)	2.7	12	3.2	4.0	BDL	3.1	2.8
Al (mg/kg)	620	9,100	550	1,500	660	2,800	2,500
As (mg/kg)	BDL	14	BDL	320	22	BDL	BDL
Ba (mg/kg)	63	730	430	39	36	110	110
Ca (mg/kg)	23,600	235,400	16,800	25,500	5,700	27,900	28,700
Cd (mg/kg)	0.4	3.6	0.4	25	2.7	0.8	0.4
Co (mg/kg)	0.8	15	0.8	7.6	90	0.8	0.8
Cr (mg/kg)	2.3	70	4.7	3.6	1.9	4.6	4.3
Cu (mg/kg)	1.5	158	9.9	11	1.6	7.0	7.1
Fe (mg/kg)	890	48,600	3,300	514,000	44,000	6,300	6,200
Hg (mg/kg)	BDL	BDL	BDL	BDL	BDL	BDL	BDL
K (mg/kg)	460	4,400	630	558	460	970	900
Li (mg/kg)	14	63	12	9.6	4.6	14	15
Mg (mg/kg)	850	38,700	2,400	1,100	500	2,500	2,400
Mn (mg/kg)	56	280	35	100	27	230	227
Na (mg/kg)	BDL	8,900	510	BDL	BDL	BDL	BDL
Ni (mg/kg)	BDL	57	BDL	390	32	5.0	BDL
Pb (mg/kg)	7.3	47	4.7	10	3.5	8.9	6.7
S (mg/kg)	11,800	6,700	750	16,000	1,400	2,800	2,700
Si (mg/kg)	160	1,100	1,900	680	160	250	290
Zn (mg/kg)	3.9	180	14	10,200	810	20	19

3.2.3 Points of Zero Charge

Media and material PZC solutions are summarized in Table 13. Measurements were done in 0.1 M and 0.01 M KNO₃ to verify the PZC at different electrolyte concentrations. The PZC measurements were fairly consistent between both electrolyte solutions, except where the greatest discrepancies were observed in SAND and MDR7.5, with differences

of 0.5 and 0.6, respectively. The PZC of SAND was greater than expected as pure SiO₂ sand would have typically measured less than four (Kosmulski, 2009). Table 12 shows extractable Ca from SAND, which confirms that the sand was not entirely SiO₂ and CaCO₃ or CaO may be present. The presence of these Ca materials would increase the pH of a solution and measure PZC between eight to 11. The PZC of FA5.0 was nearly the same as FA, suggesting that FA may be the primary adsorptive surface. The PZC of MDR7.5 was elevated compared to MDR alone, which is likely caused by the mixing with sand.

Table 13: Point of zero charge results in 0.01 M and 0.1 M KNO₃ electrolyte solutions.

	PZC in 0.01M KNO ₃	PZC in 0.1M KNO ₃
SAND	10.3	10.8
FA	12.1	12.1
FA5.0	12.2	12.2
MDR	6.8	6.8
MDR7.5	8.3	8.9
APT	6.5	6.4
BIO	6.5	6.5

3.3 Geotechnical Characterization

A summary of geotechnical characteristics of media and materials is shown in Table 14. Saturated bulk densities (ρ_b) were used to estimate porosity (η) and PVs of column media. The FA material analysis report, by Analytical Testing Service Laboratories, Inc. (2017), lists the particle density of FA to be 2.75 g/cm³ (Appendix II). The greatest amount of OM was observed in APT and BIO, which showed similar LOI results. The substantial amount of OM likely contributes to the 65% expansion when saturated, as well as greater porosity compared to the other materials (Appendix III). Various measurements like LOI,

air-dried moisture content, and particle density were the only measurements for FA and MDR because they were not used in column experiments, therefore column parameters were not needed.

Table 14: Summary of geotechnical characteristics of media and materials.

	SAND	FA	FA5.0	MDR	MDR7.5	APT	BIO
LOI (%)	0.2	0.1	0.2	11.4	0.5	82.6	84.8
$\theta_{\text{air-dried}}$ (%)	0.12	0.07		14.88		12.25	12.26
$\theta_{\text{saturated}}$ (%)	14.20		12.86		16.09	64.28	70.50
$\rho_{\text{bulk, sat}}$ (g/cm ³)	2.03		1.85		1.73	0.96	1.02
$\rho_{\text{bulk, dry}}$ (g/cm ³)	1.78		1.64		1.49	0.58	0.60
η (%)	32.61		38.04		43.54	61.31	57.72
Pore Volume (mL)	230		270		300	430	400
ρ_{particle} (g/cm ³)	2.64	2.75	2.64	2.59	2.64	1.51	1.48

3.3.1 Particle-size Distribution

Particle-size distributions are shown in Table 15 for air-dried SAND and saturated APT and BIO. Approximately 41% of the particles were larger than 0.3 microns in diameter. Approximately 98% of the particles were at least 0.0002 microns in diameter. A particle-size distribution of FA was not obtained because the methods were deemed inappropriate due to pozzolanic characteristics. However, Analytical Testing Service Laboratories, Inc. (2017) lists material fineness where 10.20% of the particles are larger than a 325 mesh, or 0.044 mm (Appendix II). The particle sizes of SAND showed a well-graded distribution, while APT and BIO showed more uniform particle sizes with over 30% more particles larger than 0.425 mm. This may explain why the hydraulic conductivities of the APT and BIO were greater than SAND.

Table 15: Particle-size distributions by sieve analysis of course materials.

Diameter (mm)	SAND (% _{passing})	APT (% _{passing})	BIO (% _{passing})
9.53	99.62	100	100
2.00	96.10	100	100
0.85	86.77	100	94.61
0.425	67.16	35.30	33.89
0.250	34.98	15.78	16.35
0.150	11.17	8.79	5.83
0.105	4.87	6.69	3.76
0.075	0.00	4.29	1.68

The particle-size distribution of MDR by hydrometer analysis is shown in Table 16. Over 58% of particles were smaller than 0.024 microns. This would suggest MDR to have clayey characteristics (also because MDRs behave “putty-like” when wetted), which explains the large decrease in hydraulic conductivity when blended with sand.

Table 16: Particle-size distribution by hydrometer analysis of mine drainage residuals.

Diameter (µm)	MDR (% _{passing})
0.31878	58.84
0.15939	58.84
0.04782	58.84
0.02391	58.84
0.01194	58.68
0.00600	58.68
0.00318	57.69
0.00159	49.85
0.00080	32.36
0.00020	1.15
0.00003	0.34

3.4 Pollutant Removal Performance

3.4.1 Observations of Data Below Detection Limits

The primary constituents for which analytical data fell below detection limits (BDL) include NH₃, total and filtered Cu, total and filtered Pb, and total and filtered Zn.

Although these data do not have numeric values and are not detected they are not necessarily zero. These data could range from zero to the detection limit and should be treated as such. Information was extracted from BDL data by assigning all points the value of half the detection limit (EPA, 2000a). This method is one of the most widely used methods to address BDL data for statistical tests and estimates for data sets with less than 15% BDL data (Cohen and Ryan, 1989; EPA, 2000a). Statistical comparisons were not performed on data sets with over 15% BDL data. Table 17 shows the percentage of BDL data for each analyte.

Table 17: Percentage of below-detection-limit data for ammonia, copper, lead, and zinc samples.

Analyte (n=68)	% of data BDL	BDL Treatment
NH ₃	26.47	None
Total Cu	8.82	DL/2
Filtered Cu	19.12	None
Total Pb	11.76	DL/2
Filtered Pb	45.56	None
Total Zn	55.88	None
Filtered Zn	57.35	None

3.4.2 Laboratory Column Physical Characteristics

Table 18 summarizes the physical characteristics of the laboratory columns. The table includes the names of the influent SS associated with each column, mass of sand used in each column, mass of reactive media (m_{rm}), flow rate (Q), and hydraulic retention time (HRT). Overall, APT and BIO used much less sand than FA5.0 and MDR7.5. FA5.0 and MDR7.5 had the longest HRT, while APT and BIO were similar to SAND.

Table 18: Summary of laboratory column physical characteristics.

	Influent Synthetic Stormwater	m _{sand} (g)	m _{rm} (g)	Flow Rate (mL/min)	Hydraulic Retention Time (hr)
SAND1	SS1.03	1086	0	75	0.05
SAND2	SS1.03	1100	0	75	0.05
SAND3	SS2.04	1070	0	75	0.05
FA5.01	SS1.01	1073	57	6	0.75
FA5.02	SS1.01	1075	57	7.5	0.60
FA5.03	SS1.05	1024	54	8	0.56
MDR7.51	SS2.01	929	75	6	0.83
MDR7.52	SS2.01	925	75	6	0.83
MDR7.53	SS1.05	923	75	8	0.63
APT1	SS2.03	678	72	75	0.06
APT2	SS2.02	688	82	75	0.06
APT3	SS2.03	688	74	75	0.06
BIO1	SS1.04	664	88	75	0.07
BIO2	SS2.02	754	80	75	0.07
BIO3	SS1.04	714	84	75	0.07

3.4.3 Influent Synthetic Stormwater Characteristics

The pH of the influent SS ranged from 6.27 to 7.71, which is a range typical to urban runoff (BMP Database, 2015). SC ranged from 20.73 to 39.44 microSiemens per centimeter (mS/cm). ORP ranged from 103 to 207 millivolts. DO ranged from 5.72 to 8.74 mg/L and T ranged from 19.7 to 21.5 degrees Celsius (°C). Table 19 shows a summary of in-situ measurements of all SS batches used in this study as well as the columns into which each batch was fed.

Table 19: In-situ measurements of influent synthetic stormwater.

	pH	SC ($\mu\text{S}/\text{cm}$)	ORP (mV)	DO (mg/L)	T ($^{\circ}\text{C}$)
SS1.01	7.14	31.22	198	7.42	20.1
SS1.03	6.27	39.44	157	6.98	21.2
SS1.04	7.14	22.46	162	7.72	19.7
SS1.05	6.40	22.42	130	8.04	21.4
SS2.01	6.60	20.73	207	7.56	20.2
SS2.02	7.12	21.71	135	5.72	21.1
SS2.03	7.71	22.09	103	7.77	21.4
SS2.04	6.35	23.81	130	8.74	21.5

The TP and TDP concentrations were slightly elevated compared to mean concentrations in typical urban runoff, but still fell within observed ranges. Similarly, NO_3^- was slightly elevated compared to mean concentrations in typical urban runoff. NH_3 was observed in one batch of SS, while most showed NH_3 concentrations BDL. Although other forms of N were not dosed in the SS, all batches showed slightly greater TN concentrations than NO_3^- . One possible explanation for these observations may be the calibration of the TN analysis instrument. Calibration of 1.0 mg/L of TN resulted in a measurement that was approximately 9% greater than the standard. Therefore, the TN measurements between 1.0 and 2.5 mg/L may report as slightly greater than what is represented. A summary of N and P nutrients from the influent SS is shown in Table 20.

Table 20: Nitrogen and phosphorus concentrations of influent synthetic stormwater.

	NO_3^- (mg/L as N)	NH_3 ($\mu\text{g}/\text{L}$ as N)	TN (mg/L as N)	TP (mg/L as P)	TDP (mg/L as P)
SS1.01	1.6	98	1.91	0.52	0.51
SS1.03	1.4	BDL	1.56	0.56	0.55
SS1.04	1.5	BDL	1.82	0.54	0.54
SS1.05	1.4	BDL	1.69	0.55	0.55
SS2.01	1.5	BDL	1.80	0.53	0.53
SS2.02	1.6	BDL	1.78	0.63	0.63
SS2.03	1.3	BDL	1.74	0.57	0.57
SS2.04	1.6	BDL	1.78	0.54	0.54

Metals were dosed with chloride salts for Cu, Pb, and Zn, in which all metals would be expected to be associated with the dissolved fraction, e.g., total metals equal to filtered metals. However, measurements of filtered metals showed that this was not the case, where many filtered Cu and Pb samples did not equal total metals. Additionally, some filtered Zn samples, a fraction of total Zn, resulted in greater concentrations than the total. Shiller (2003) provides a possible explanation for these phenomena, suggesting possible issues with laboratory filtration techniques. Some adsorption of metals can affect the first 10-mL of filtered sample, where initial flushing with sample may address this issue (Shiller, 2003). Shiller (2003) also notes common plastic syringes used for filtering can be contaminated with metal oxides, especially zinc oxide (ZnO) from the manufacturing of the rubber gaskets in the syringe plunger. Overall, these filtered Pb measurements did not affect the discussion and conclusions because the SS was made with PbCl₂, which would yield only dissolved Pb. Therefore, total lead data was sufficient to draw conclusions. Table 21 represents a summary of total and filtered metals concentrations in influent SS.

Table 21: Total and filtered metals concentrations of influent synthetic stormwater.

	Total Metals			Filtered Metals		
	Cu (µg/L)	Pb (µg/L)	Zn (µg/L)	Cu (µg/L)	Pb (µg/L)	Zn (µg/L)
SS1.03	25	30	100	23	19	104
SS2.04	21	25	85	20	19	97
SS1.01	27	24	98	24	8	96
SS1.05	23	29	96	25	BDL	95
SS2.01	31	30	101	24	BDL	102
SS2.03	23	25	93	22	19	95
SS2.02	23	29	99	23	20	101
SS1.04	24	23	104	23	23	98

Table 22 is a summary of additional measured parameters, TOC, TIC, TC, and hardness, to show ‘background’ levels in the influent SS. These data were shown to illustrate the minimization of impurities in the influent SS. None of the SS had preexisting hardness and all showed similar concentrations in TOC, TIC, and TC.

Table 22: Total organic carbon, total inorganic carbon, total carbon, and hardness concentrations of influent synthetic stormwater.

	TOC (mg/L)	TIC (mg/L)	TC (mg/L)	Hardness (mg/L as CaCO ₃)
SS1.03	0.89	0.45	0.95	0
SS2.04	0.88	0.06	0.94	0
SS1.01	1.85	0.20	2.05	0
SS1.05	0.99	0.04	1.03	0
SS2.01	1.41	0.09	1.50	0
SS2.03	0.97	0.11	1.08	0
SS2.02	1.28	0.23	1.51	0
SS1.04	1.01	0.10	1.11	0

3.4.4 General Effluent Characteristics

Table 23 shows a summary of average measurements and standard deviations of various in-situ parameters for PV sampling points of each column. Overall, all columns consistently showed pH values greater than 7. Elevated pH, especially in SAND and FA5.0, are important in metal hydroxide precipitation processes (Banerjee et al., 2003; Erol et al., 2005; Zhang et al., 2008a). All columns exhibited conditions that favored oxidative reactions with positive ORP measurements and abundant DO.

Table 23: Averaged results and standard deviations for in-situ characteristics of column effluents.

	PV #	pH	Conductivity ($\mu\text{S}/\text{cm}$)	ORP (mV)	DO (mg/L)	T ($^{\circ}\text{C}$)
SAND	01	9.67 ± 0.03	54 ± 3	127 ± 17	7.27 ± 1.21	21.4 ± 0.7
	03	9.78 ± 0.03	56 ± 2	121 ± 7	7.74 ± 0.67	21.2 ± 0.6
	10	9.75 ± 0.03	56 ± 2	120 ± 7	7.41 ± 0.31	21.3 ± 0.7
	30	9.83 ± 0.06	57 ± 1	122 ± 6	7.29 ± 1.07	21.2 ± 0.5
FA5.0	01	11.38 ± 0.13	749 ± 212	122 ± 2	7.59 ± 0.43	19.9 ± 1.5
	03	11.42 ± 0.18	681 ± 196	99 ± 11	7.65 ± 0.20	20.0 ± 1.4
	10	11.24 ± 0.13	465 ± 87	91 ± 43	7.37 ± 0.43	20.1 ± 1.5
	30	11.06 ± 0.10	363 ± 82	76 ± 30	7.68 ± 0.47	20.4 ± 1.1
MDR7.5	01	7.89 ± 0.15	278 ± 16	185 ± 24	4.63 ± 1.78	18.7 ± 2.5
	03	7.84 ± 0.31	229 ± 5	180 ± 2	5.90 ± 0.95	19.8 ± 1.5
	10	8.19 ± 0.15	168 ± 10	141 ± 34	6.09 ± 0.60	20.0 ± 1.4
	30	7.96 ± 0.36	107 ± 4	132 ± 18	6.40 ± 0.80	20.4 ± 1.1
APT	01	8.09 ± 0.95	65 ± 5	90 ± 7	6.80 ± 1.30	21.2 ± 0.2
	03	8.33 ± 0.88	56 ± 5	84 ± 14	6.90 ± 1.64	21.1 ± 0.2
	10	8.28 ± 0.87	53 ± 6	96 ± 14	7.59 ± 0.34	21.0 ± 0.3
	30	8.27 ± 1.11	52 ± 3	92 ± 5	7.18 ± 0.77	19.8 ± 0.1
BIO	01	8.98 ± 0.20	68 ± 8	116 ± 7	6.36 ± 1.60	20.1 ± 0.7
	03	9.26 ± 0.10	62 ± 11	101 ± 6	6.48 ± 1.40	20.5 ± 0.5
	10	9.27 ± 0.12	60 ± 6	106 ± 7	7.36 ± 0.31	20.4 ± 0.1
	30	9.45 ± 0.11	59 ± 4	103 ± 6	6.92 ± 0.78	19.8 ± 0.3

Table 24 summarizes average residual Ca concentrations at each PV sampling point of each media with standard deviations. FA5.0 showed the greatest concentrations in residual Ca compared to the other columns, with MDR7.5 showing slightly lesser concentrations. SAND, APT, and BIO had similar residual Ca concentrations in the effluent. These were data were reported because the presence of Ca-materials is important in P and metals precipitation processes (Banerjee et al., 2003; Erol et al., 2005; Zhang et al., 2006; Uwamariya et al., 2016)

Table 24: Averaged results and standard deviations for calcium concentrations of column effluents.

	PV01 (mg/L)	PV03 (mg/L)	PV10 (mg/L)	PV30 (mg/L)
SAND	12 ± 2	9 ± 1	8 ± 0.3	7 ± 0.3
FA5.0	90 ± 20	76 ± 11	51 ± 7	40 ± 12
MDR7.5	66 ± 7	53 ± 6	34 ± 2	21 ± 1
APT	16 ± 7	11 ± 2	9 ± 0.5	8 ± 0.7
BIO	16 ± 4	14 ± 3	12 ± 2	10 ± 2

Tables Table 25, Table 26, and Table 27 summarize average TOC, TIC, and TC concentrations, respectively, at each PV sampling point of each media with standard deviations. These values are important because N and P are often associated with TOC (Schnitzer et al., 1983; Du et al., 2013). APT and BIO measured the greatest concentrations of TOC and TC, which was expected due to the large percentage of OM that comprised the materials (Table 14). Additionally, TOC made up much of the TC measured in APT and BIO effluent samples, while SAND, FA5.0, and MDR7.5 had little TOC. TIC concentrations were fairly similar among all effluent samples from all columns.

Table 25: Averaged results and standard deviations for total organic carbon concentrations of column effluents.

	PV01 (mg/L)	PV03 (mg/L)	PV10 (mg/L)	PV30 (mg/L)
SAND	1.32 ± 0.15	1.26 ± 0.03	1.19 ± 0.08	1.17 ± 0.03
FA5.0	1.94 ± 0.67	1.77 ± 0.55	1.65 ± 0.53	1.58 ± 0.48
MDR7.5	2.59 ± 0.47	2.50 ± 0.21	2.19 ± 0.09	1.99 ± 0.11
APT	8.98 ± 3.49	6.80 ± 2.40	4.98 ± 1.54	3.65 ± 0.84
BIO	19.04 ± 5.82	16.12 ± 4.89	12.32 ± 3.47	8.70 ± 1.77

Table 26: Averaged results and standard deviations for total inorganic carbon concentrations of column effluents.

	PV01 (mg/L)	PV03 (mg/L)	PV10 (mg/L)	PV30 (mg/L)
SAND	0.12 ± 0.04	0.08 ± 0.03	0.08 ± 0.02	0.07 ± 0.02
FA5.0	0.21 ± 0.12	0.14 ± 0.08	0.11 ± 0.03	0.14 ± 0.06
MDR7.5	1.30 ± 0.89	1.28 ± 0.40	0.67 ± 0.54	0.34 ± 0.24
APT	1.00 ± 0.85	0.61 ± 0.42	0.36 ± 0.24	0.23 ± 0.21
BIO	0.48 ± 0.57	0.31 ± 0.32	0.25 ± 0.23	0.16 ± 0.10

Table 27: Averaged results and standard deviations for total carbon concentrations of column effluents.

	PV01 (mg/L)	PV03 (mg/L)	PV10 (mg/L)	PV30 (mg/L)
SAND	1.45 ± 0.17	1.29 ± 0.11	1.27 ± 0.10	1.24 ± 0.04
FA5.0	2.14 ± 0.78	1.91 ± 0.63	1.76 ± 0.55	1.71 ± 0.53
MDR7.5	3.89 ± 1.33	3.53 ± 1.02	2.86 ± 0.57	2.33 ± 0.36
APT	9.98 ± 2.64	7.41 ± 2.00	5.34 ± 1.30	3.87 ± 0.63
BIO	19.52 ± 5.26	16.44 ± 4.57	12.57 ± 3.25	8.86 ± 1.67

3.4.5 Phosphorus

The averaged normalized effluent concentrations from each column are summarized in Table 28 for TP and in Table 29 for TDP. Additionally, mass balances of TP in Table 30 and TDP in Table 31 were estimated by assuming concentrations for water volumes that were not samples. The concentration at PV01 was assumed to be representative of the first PV. Water volumes from PV01 to PV03 assumed to have concentrations measured at PV03. Similarly, PV03 to PV10, the volumes assumed concentrations measured at PV10. Finally, volumes from PV10 to PV30 assumed concentrations measured at PV30. These mass balances were presented to described pollutant removal in terms of mass. With regard to overall mass removal, SAND removed approximately 20% of TP and TDP. FA5.0 and MDR7.5 both removed

Table 28: Averaged results and standard deviations for normalized effluent total phosphorus concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.31 ± 0.11	0.25 ± 0.06	0.73 ± 0.21	0.91 ± 0.02
FA5.0	0.06 ± 0.03	0.07 ± 0.03	0.12 ± 0.10	0.14 ± 0.09
MDR7.5	0.08 ± 0.06	0.04 ± 0.00	0.17 ± 0.02	0.12 ± 0.04
APT	0.52 ± 0.25	0.69 ± 0.26	0.83 ± 0.05	0.99 ± 0.05
BIO	0.98 ± 0.31	1.31 ± 0.32	1.36 ± 0.23	1.30 ± 0.24

Table 29: Averaged results and standard deviations for normalized effluent total dissolved phosphorus concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.21 ± 0.04	0.24 ± 0.05	0.74 ± 0.22	0.91 ± 0.04
FA5.0	0.05 ± 0.04	0.06 ± 0.04	0.12 ± 0.10	0.12 ± 0.10
MDR7.5	0.07 ± 0.06	0.03 ± 0.00	0.15 ± 0.02	0.12 ± 0.04
APT	0.35 ± 0.25	0.60 ± 0.26	0.91 ± 0.05	0.88 ± 0.05
BIO	0.93 ± 0.31	1.21 ± 0.32	1.27 ± 0.23	1.24 ± 0.24

Table 30: Averaged results and standard deviations of estimated total phosphorus mass balances of each column.

	TP _{in} (mg)	TP _{out} (mg)	% Removed
SAND	3.82 ± 0.08	3.07 ± 0.31	20 ± 7
FA5.0	4.29 ± 0.14	0.51 ± 0.42	88 ± 9
MDR7.5	4.83 ± 0.10	0.58 ± 0.18	88 ± 3
APT	5.31 ± 0.31	4.66 ± 0.70	12 ± 13
BIO	5.13 ± 0.47	6.62 ± 0.66	-30 ± 24

Table 31: Averaged results and standard deviations of estimated total dissolved phosphorus mass balances of each column.

	TDP _{in} (mg)	TDP _{out} (mg)	% Removed
SAND	3.77 ± 0.04	3.02 ± 0.31	20 ± 7
FA5.0	4.24 ± 0.19	0.48 ± 0.45	89 ± 10
MDR7.5	4.83 ± 0.10	0.54 ± 0.24	89 ± 5
APT	5.31 ± 0.31	4.15 ± 0.62	22 ± 10
BIO	5.13 ± 0.47	6.27 ± 0.73	-24 ± 24

SAND columns showed limited ability to remove TP and TDP, with average concentration decreases ranging between approximately 69% to 75% for TP and 76% to 79% for TDP in the first three PVs. However, overall P removal dramatically decreases

after the PV03, reaching only 9% in concentration decrease after PV30. The decreasing trend in removal is shown in Figure 9 for TP and Figure 10 for TDP. The decreases in TP and TDP could be attributed to release of free Ca^{2+} , which would allow for coprecipitation as a removal mechanism for SAND. TP and TDP eventually reach concentrations near equal to the influent concentrations by PV30, but at PV10, removal rates have drastically decreased. Relatively small Ca concentrations in column effluents, compared to the other media, may explain the limited ability of SAND to remove TP and TDP (Table 24).

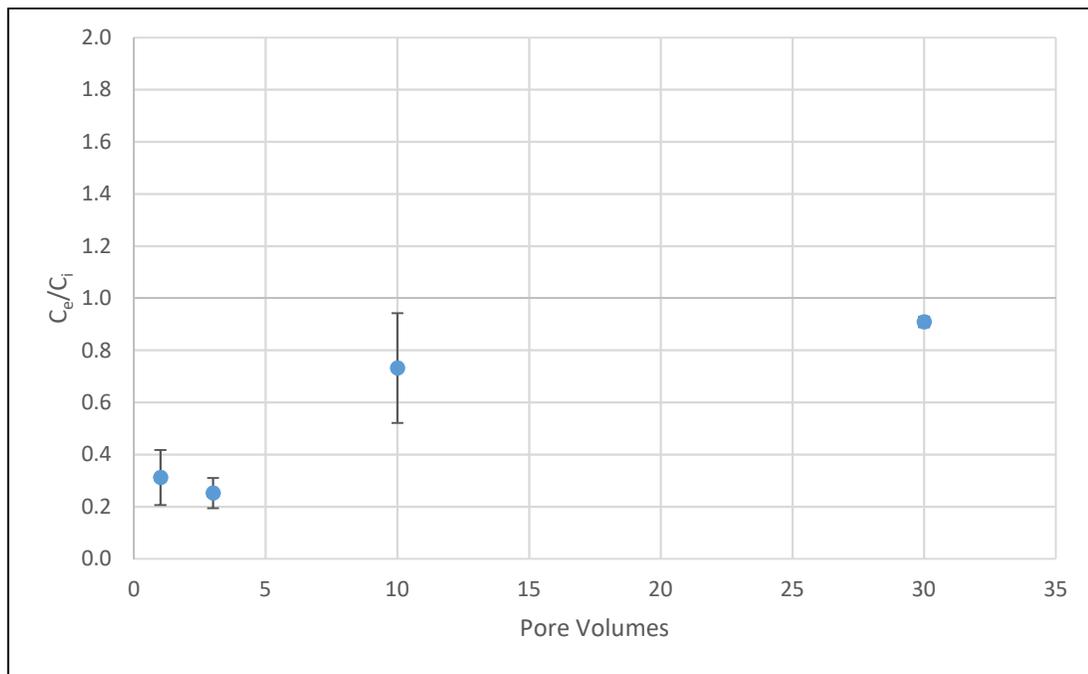


Figure 9: Normalized effluent total phosphorus concentrations of SAND columns.

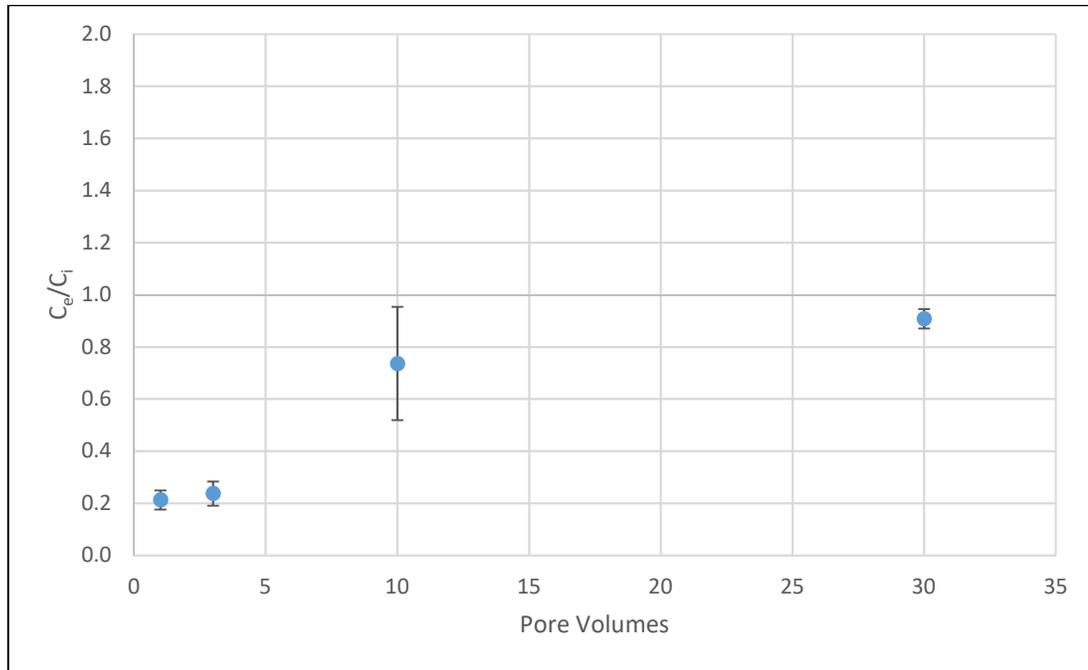


Figure 10: Normalized effluent total dissolved phosphorus concentrations of SAND columns.

FA5.0 columns decreased TP concentrations at average between 86% to 94% across all PVs. TDP decreased between 88% to 95% across all PVs. These trends can be seen in Figure 11 for TP and Figure 12 for TDP. The primary P removal mechanism in FA5.0 columns is likely coprecipitation as hydroxyapatite due to elevated CaO content and elevated pH (Zhang et al., 2006). P removal shows correlation with residual Ca in the effluent. Figure 13 displays a correlation scatter plot between the log of Ca concentration and log of normalized effluent TP concentration, showing a strong negative correlation, with a coefficient of -0.83. Figure 14 displays a correlation scatter plot between the log of Ca concentration and log of normalized TDP concentration, similarly showing a strong negative correlation, with a coefficient of -0.83.

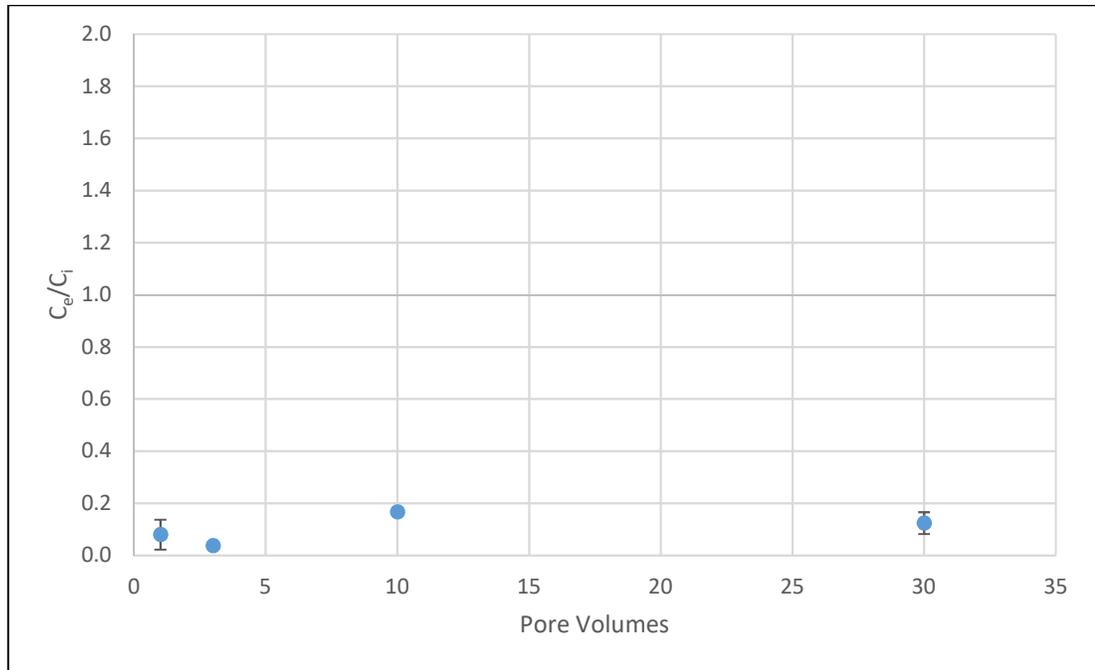


Figure 11: Normalized effluent total phosphorus concentrations of FA5.0 columns.

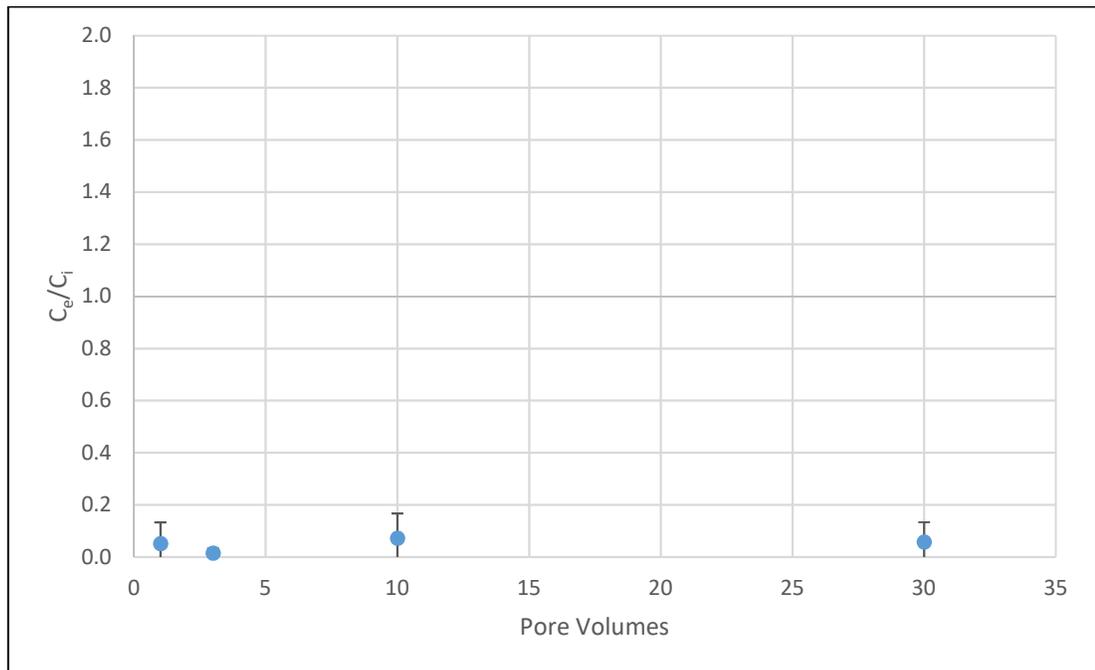


Figure 12: Normalized effluent total dissolved phosphorus concentrations of FA5.0 columns.

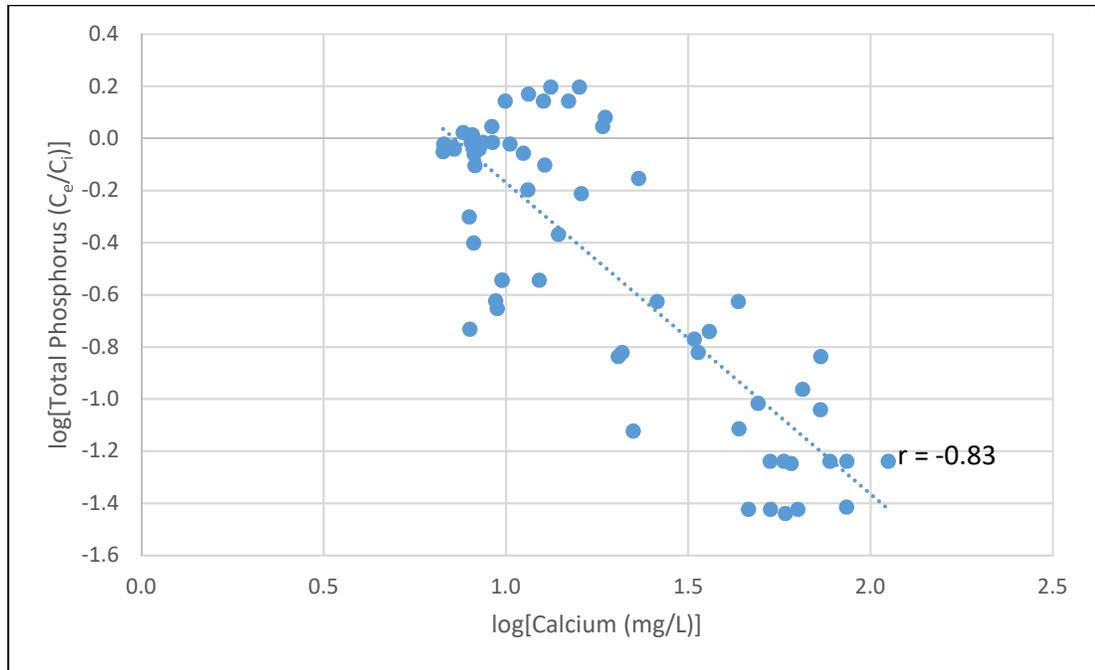


Figure 13: Correlation scatter plot of log of calcium concentration and log of normalized effluent total phosphorus concentration.

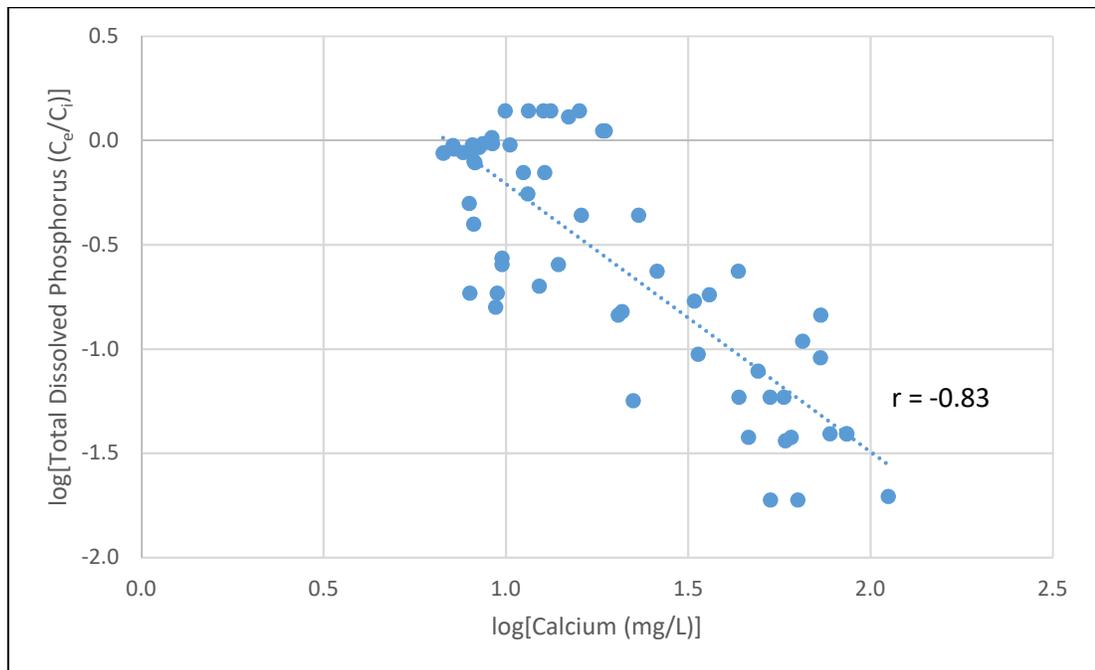


Figure 14: Correlation scatter plot of log of calcium concentration and log of normalized effluent total dissolved phosphorus concentration.

MDR7.5 columns decreased TP concentrations by average between 92% to 96% in the first three PVs. In PV10 and PV30, removal was between 83% to 88%. Changes in TP can be seen in Figure 15. TDP was decreased by averages between 93% to 97% in the first three PVs and between 85% to 88% in PV10 and PV30 (Figure 16). Because of limited P removal in SAND columns by coprecipitation, the dominant removal mechanism in MDR7.5 is most likely adsorption to the hydroxyl groups on the iron oxides. Although, MDR7.5 produces increased residual Ca compared to SAND (Table 24) and close to that of FA5.0, P removal performance is not substantially greater than FA5.0. This may suggest that FA5.0 produces a greater amount of free Ca^{2+} as compared to MDR7.5, from CaO, resulting in similar removal performance outside of adsorption.

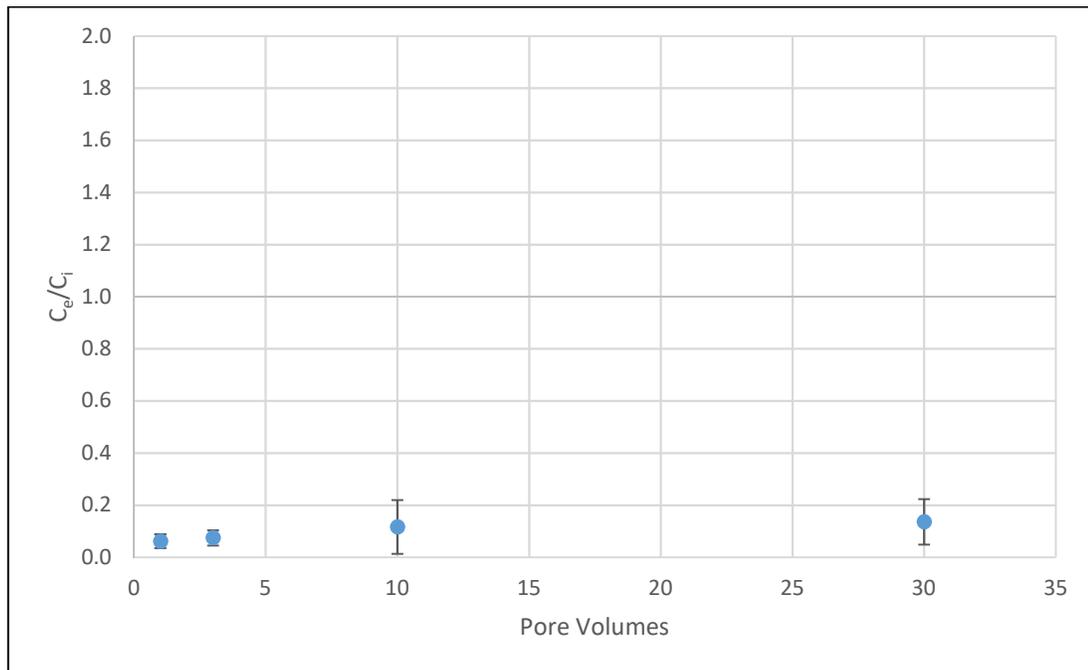


Figure 15: Normalized effluent total phosphorus concentrations of MDR7.5 columns.

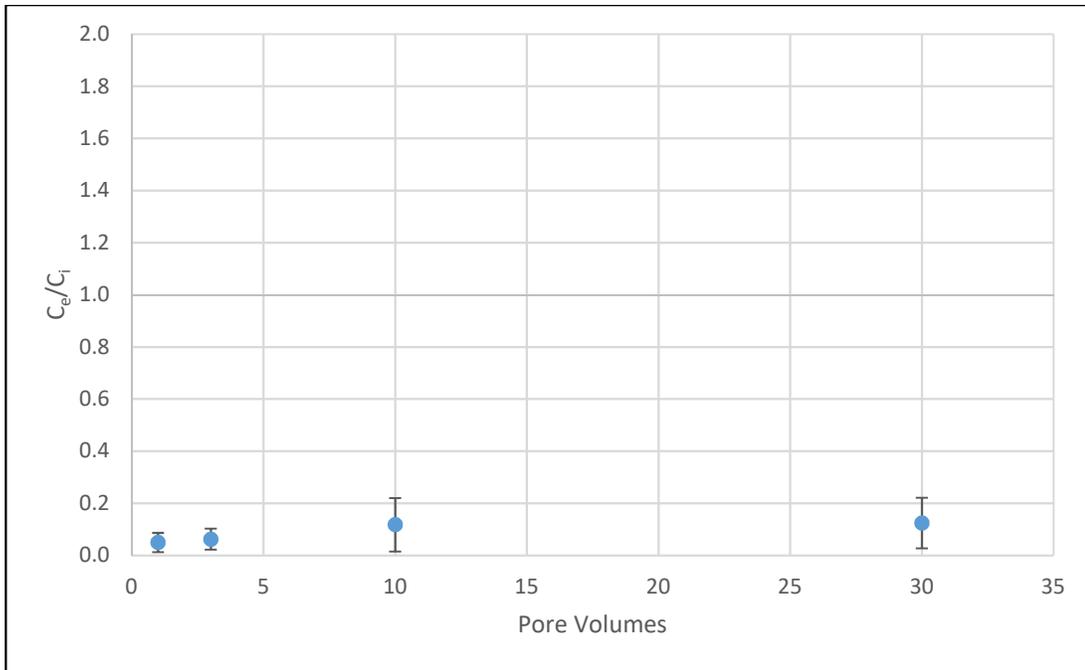


Figure 16: Normalized effluent total dissolved phosphorus concentrations of MDR7.5 columns.

APT columns showed limited decreases in TP and TDP concentrations in the first three PVs, TP and TDP reached near influent levels by PV10. Slight export of TP was observed in one replicate column, APT1, at PV30 with a normalized concentration of 1.05. However, TDP concentrations from all APT columns were shown to be near influent levels. Although, overall removal was limited, APT columns showed some ability to retain P, especially TDP, with only one effluent sample showing in slight export. Figure 17 and Figure 18 show the average normalized effluent concentrations for TP and TDP, respectively. Decreases in both TP and TDP concentrations are seen in PV01 and PV03 with more variable concentrations than PV10 and PV30.

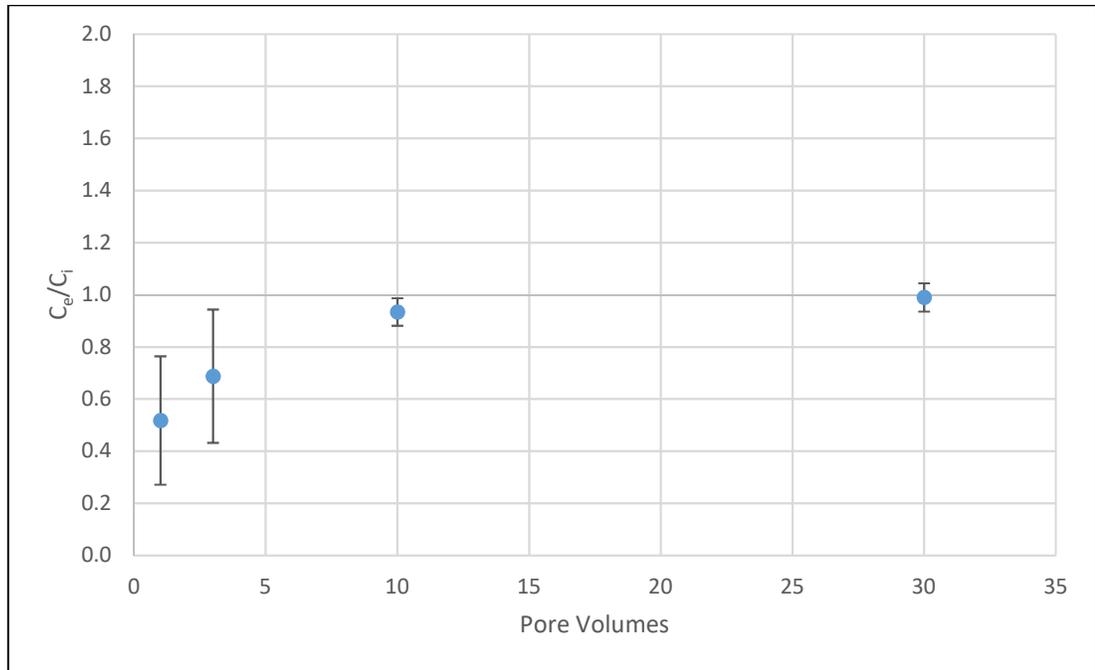


Figure 17: Normalized effluent total phosphorus concentrations of APT columns.

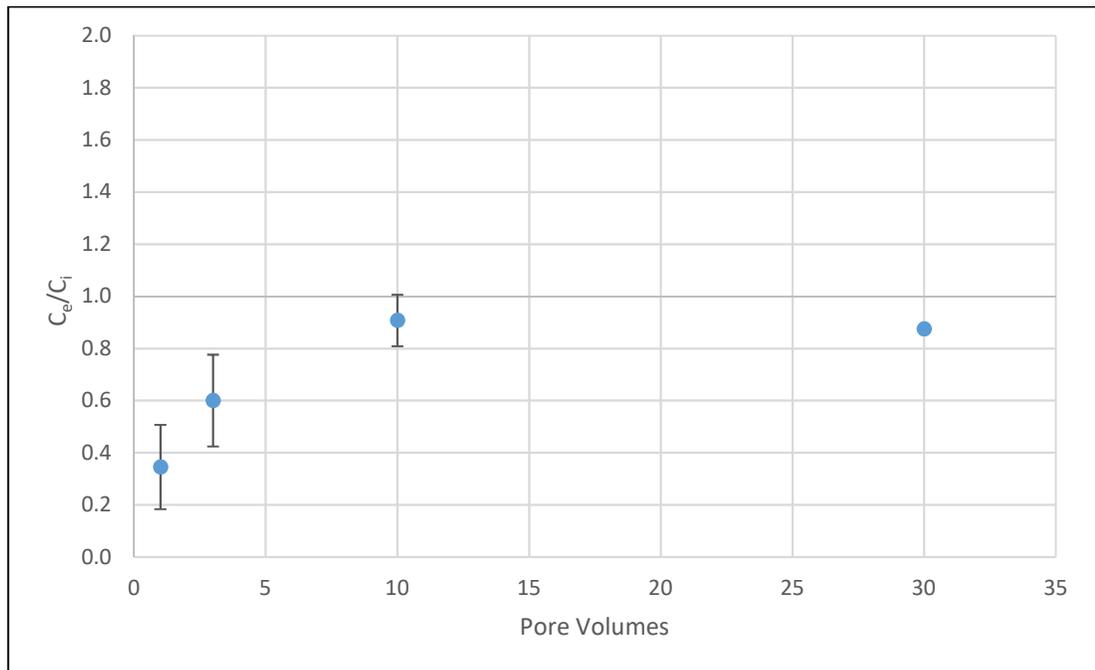


Figure 18: Normalized effluent total dissolved phosphorus concentrations of APT columns.

BIO columns resulted in overall net export of P. TP increased over 30% across PV03, PV10, and PV30 (Figure 19). TDP also increased over the same PVs at over 20% (Figure 20). Because APT is manufactured from BIO with an additional heating process to improve granular strength of the product, this might suggest that some degradation of the BIO material could contribute to P export. Additionally, BIO was found to export more TOC than APT and the rest of the media. Figure 21 and Figure 22 show TOC concentration correlations with normalized effluent TP and TDP concentrations. With an r-value of 0.71, a strong positive correlation is shown for TOC concentration and normalized effluent TP concentration. Similarly, TOC concentration and normalized effluent TDP concentration show a strong positive correlation with an r-value of 0.68. Humic and fulvic acid, common organic acids found in soil and especially peat, have been used in agricultural applications to improve nutrient uptake in crops (Du et al., 2013). The applications of P fertilizers in combination with humic and fulvic acids have been shown increase the amount of soluble P in soil, by inhibiting Ca and P coprecipitation by chelating with metals, including Ca (Wang et al., 1995; Yang et al., 2013, Du et al., 2013).

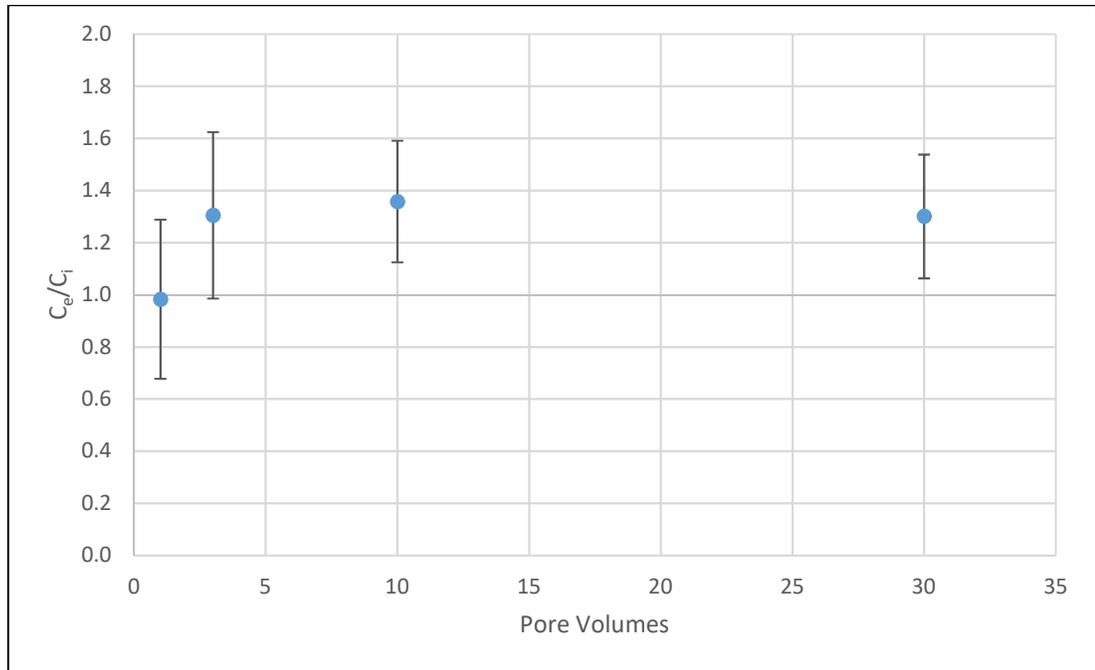


Figure 19: Normalized effluent total phosphorus concentrations of BIO columns.

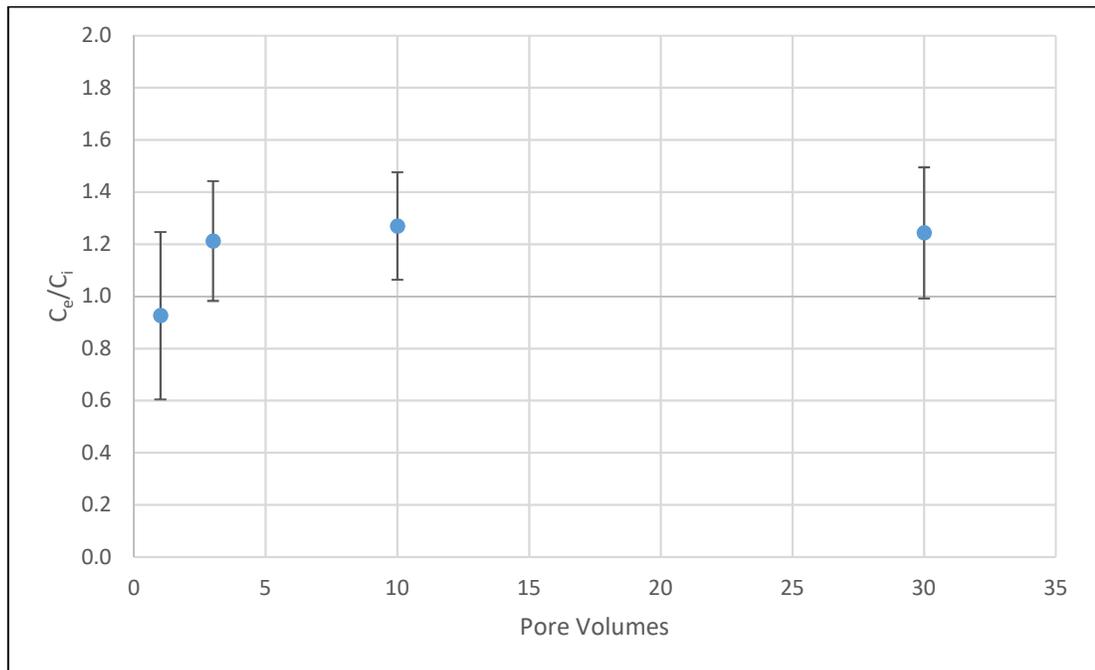


Figure 20: Normalized effluent total dissolved phosphorus concentrations of BIO columns.

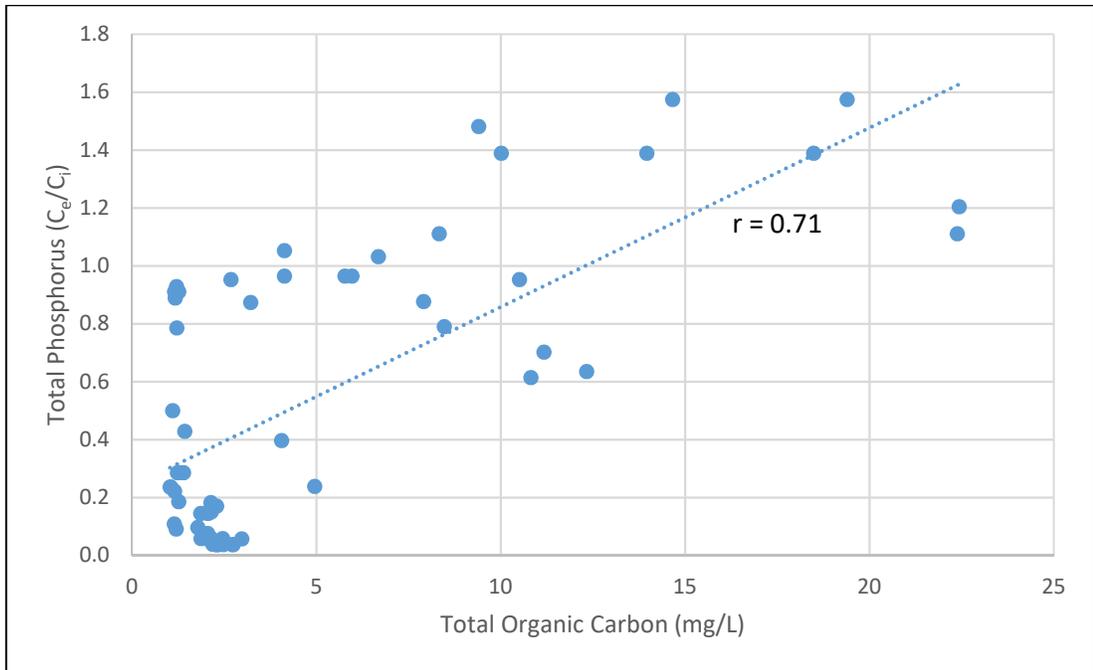


Figure 21: Correlation scatter plot of total organic carbon concentration and normalized effluent total phosphorus concentration.

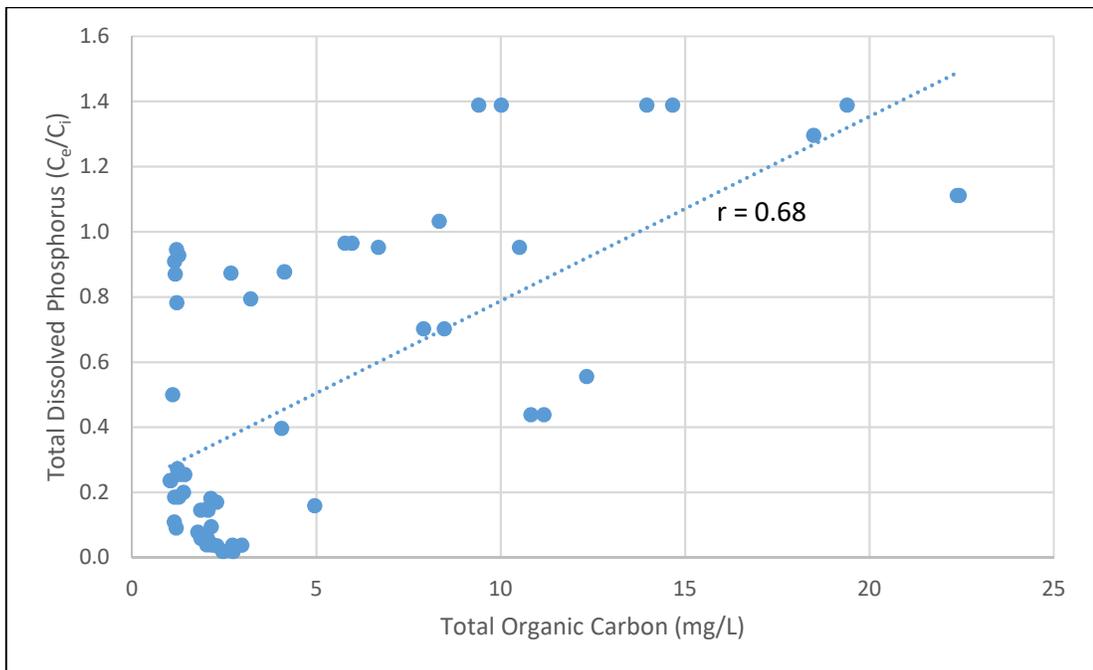


Figure 22: Correlation scatter plot of total organic carbon concentration and normalized effluent total dissolved phosphorus concentration.

Table 32 shows the results of the Mann-Whitney U test for the TP normalized effluent concentrations, which compared FA5.0, MDR7.5, APT, and BIO to SAND with an α -value of 0.10. In PV01 and PV10, FA5.0, MDR7.5, and BIO were significantly different from SAND. In the PV03 and PV30, all media were significantly different from SAND. This means that FA5.0 and MDR7.5 showed statistically significant improvement in TP removal, while BIO showed net export.

Table 32: Results of Mann-Whitney U test comparing normalized effluent total phosphorus concentrations of reactive media with SAND ($\alpha = 0.10$).

Sample	n	Mean	Median	Std. Dev.	Min	Max	p-Value
SANDPV01	3	0.21	0.20	0.04	0.18	0.26	
FA5.0PV01	3	0.05	0.04	0.04	0.02	0.09	0.0495
MDR7.5PV01	3	0.07	0.04	0.07	0.02	0.15	0.0495
APTPV01	3	0.35	0.44	0.16	0.16	0.44	0.2752
BIOPV01	3	0.93	1.11	0.32	0.56	1.11	0.0495
SANDPV03	3	0.24	0.26	0.05	0.19	0.27	
FA5.0PV03	3	0.06	0.04	0.04	0.04	0.11	0.0431
MDR7.5PV03	3	0.03	0.04	0.01	0.02	0.04	0.0431
APTPV03	3	0.60	0.70	0.18	0.40	0.70	0.0463
BIOPV03	3	1.21	1.30	0.23	0.95	1.39	0.0463
SANDPV10	3	0.74	0.78	0.22	0.50	0.93	
FA5.0PV10	3	0.12	0.06	0.10	0.06	0.24	0.0463
MDR7.5PV10	3	0.15	0.17	0.05	0.09	0.18	0.0495
APTPV10	3	0.91	0.97	0.10	0.79	0.97	0.1212
BIOPV10	3	1.27	1.39	0.21	1.03	1.39	0.0495
SANDPV30	3	0.91	0.91	0.04	0.87	0.95	
FA5.0PV30	3	0.13	0.08	0.10	0.06	0.24	0.0495
MDR7.5PV30	3	0.12	0.15	0.05	0.06	0.15	0.0495
APTPV30	3	0.88	0.88	0.002	0.87	0.88	0.0495
BIOPV30	3	1.24	1.39	0.25	0.95	1.39	0.0495

Table 33 shows the results of the Mann-Whitney U test for the TDP normalized effluent concentrations, which compared FA5.0, MDR7.5, APT, and BIO to SAND with an α -value of 0.10. In PV01, PV10, and PV30, FA5.0, MDR7.5, and BIO were statistically different from SAND. In PV03, all media were statistically different from SAND. Like

their TP performance, FA5.0 and MDR7.5 showed statistically significant improvements in TDP removal, while BIO showed net export.

Table 33: Results of Mann-Whitney U test comparing normalized effluent total dissolved phosphorus concentrations of reactive media with SAND ($\alpha = 0.10$).

Sample	n	Mean	Median	Std. Dev.	Min	Max	p-Value
SANDPV01	3	0.21	0.20	0.04	0.19	0.26	
FA5.0PV01	3	0.05	0.04	0.04	0.02	0.09	0.0495
MDR7.5PV01	3	0.07	0.04	0.07	0.02	0.15	0.0495
APTPV01	3	0.35	0.44	0.16	0.16	0.44	0.5066
BIOPV01	3	0.93	1.11	0.32	0.56	1.11	0.0463
SANDPV03	3	0.24	0.26	0.05	0.19	0.27	
FA5.0PV03	3	0.06	0.04	0.04	0.04	0.11	0.0463
MDR7.5PV03	3	0.03	0.04	0.01	0.02	0.04	0.0495
APTPV03	3	0.60	0.70	0.18	0.40	0.70	0.0463
BIOPV03	3	1.21	1.30	0.23	0.95	1.39	0.0495
SANDPV10	3	0.74	0.78	0.22	0.50	0.93	
FA5.0PV10	3	0.12	0.06	0.10	0.06	0.24	0.0463
MDR7.5PV10	3	0.15	0.17	0.05	0.09	0.18	0.0495
APTPV10	3	0.91	0.97	0.10	0.79	0.97	0.1212
BIOPV10	3	1.27	1.39	0.21	1.03	1.39	0.0463
SANDPV30	3	0.91	0.91	0.04	0.87	0.95	
FA5.0PV30	3	0.13	0.08	0.10	0.06	0.24	0.0495
MDR7.5PV30	3	0.12	0.15	0.05	0.06	0.15	0.0495
APTPV30	3	0.88	0.88	0.002	0.87	0.88	0.5066
BIOPV30	3	1.24	1.39	0.25	0.95	1.39	0.0463

3.4.6 Nitrogen

3.4.6.1 Nitrate

The averaged normalized effluent concentrations from each column are summarized in Table 34 for NO_3^- . Additionally, mass balances of NO_3^- (Table 35) were estimated using the same calculations as the previous mass balances.

Table 34: Averaged results and standard deviations for normalized effluent nitrate concentrations from each column.

	PV01 (C_e/C_i)	PV03 (C_e/C_i)	PV10 (C_e/C_i)	PV30 (C_e/C_i)
SAND	0.78 ± 0.15	0.83 ± 0.23	0.93 ± 0.07	0.98 ± 0.04
FA5.0	0.85 ± 0.03	0.82 ± 0.18	0.89 ± 0.04	0.89 ± 0.03
MDR7.5	1.00 ± 0.00	0.95 ± 0.08	1.05 ± 0.16	0.96 ± 0.08
APT	0.68 ± 0.26	0.76 ± 0.37	1.06 ± 0.16	0.93 ± 0.20
BIO	0.88 ± 0.23	1.13 ± 0.11	1.05 ± 0.16	0.91 ± 0.10

Table 35: Averaged results and standard deviations of estimated nitrate mass balances of each column.

	NO_3^- in (mg)	NO_3^- out (mg)	% Removed
SAND	10.12 ± 0.80	9.61 ± 0.35	5 ± 5
FA5.0	12.42 ± 0.94	9.87 ± 0.20	20 ± 8
MDR7.5	13.20 ± 0.52	12.04 ± 1.18	9 ± 12
APT	12.60 ± 1.56	12.06 ± 1.40	4 ± 12
BIO	13.80 ± 1.11	13.20 ± 1.11	4 ± 6

All columns showed limited ability to remove NO_3^- . Except for FA5.0 columns, none of the columns showed appreciable and consistent decreases in NO_3^- concentrations after the PV10. The formation of hydroxyapatite in all columns in the presence of Ca and effluent pH above 6, where hydroxyapatite was found to be stable, may contribute to some NO_3^- removal, if any (Islam et al., 2010). The limited NO_3^- removal may be from adsorptive competition with Cl^- , which would have come from the dissolution of Cu, Pb, and Zn salts during SS preparation and possibly preexisting in the media. When using hydroxyapatite as the adsorbent for NO_3^- removal, Cl^- was found to decrease removal by 25% by competing for adsorption sites (Islam et al., 2010). Microbial influence in NO_3^- removal was unlikely in all columns because measured DO in all columns showed oxic conditions, in addition to oxidation conditions with regard to ORP (Table 23).

SAND displayed some ability to remove NO_3^- in the first 10 PVs, shown in Figure 23. A similar trend was observed by Erickson et al. (2016) where removal of NO_3^- by SAND only occurred in the first 10 PVs in upflow column experiments. NO_3^- removal could possibly be attributed to hydroxyapatite formation in the first 10 PVs, where similar trends were observed with P removal (Figure 9 and Figure 10), likely by Ca-coprecipitation. Additionally, the pH in all SAND column effluent samples (Table 23) fell below the PZC of range of 10.3 to 10.8 (Table 13), suggesting possible removal via adsorption to positive surface charges.

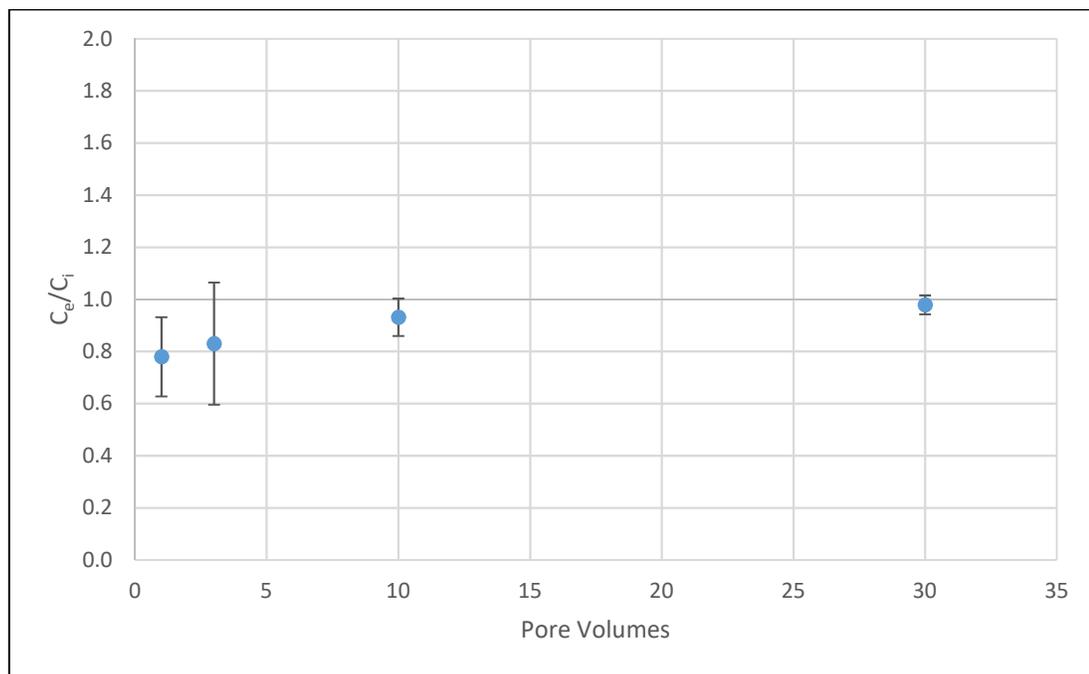


Figure 23: Normalized effluent nitrate concentrations from SAND columns.

FA5.0 columns showed the greatest ability of all media to remove NO_3^- by decreasing concentrations by approximately 10% after PV10 and PV30, which is shown in Figure 24. The primary P removal mechanism in FA5.0 is likely Ca-coprecipitation as

hydroxyapatite, which would form sites for NO_3^- to be adsorbed. This would also suggest FA5.0 columns may produce the greatest amounts of hydroxyapatite among all column media. However, the presence of other anions such as Cl^- and PO_4^{3-} from SS preparation salts may decrease NO_3^- removal via this mechanism, by competing for adsorption sites (Islam et al., 2010).

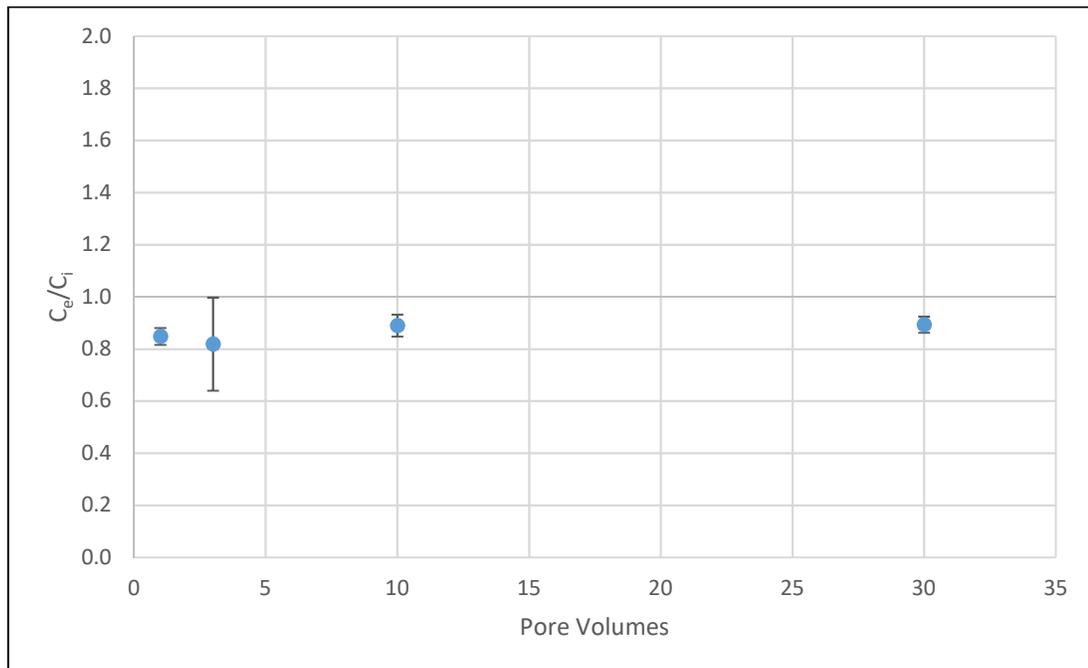


Figure 24: Normalized effluent nitrate concentrations from FA5.0 columns.

MDR7.5 showed almost no NO_3^- in all effluent sampling points, which is seen in Figure 25. Since a P removal mechanism in MDR7.5 likely included adsorption to hydroxyl groups on MDR particles, this may suggest that little to no hydroxyapatite formation occurred and that P removal was dominated by adsorption. The pH of MDR7.5 column effluent samples (Table 23) fell below the media PZC (Table 13) but did not show appreciable NO_3^- removal. This may suggest surface charges have a very small impact

toward NO_3^- removal compared to other processes or that Cl^- and PO_4^{3-} may be competing for positively charged adsorption sites.

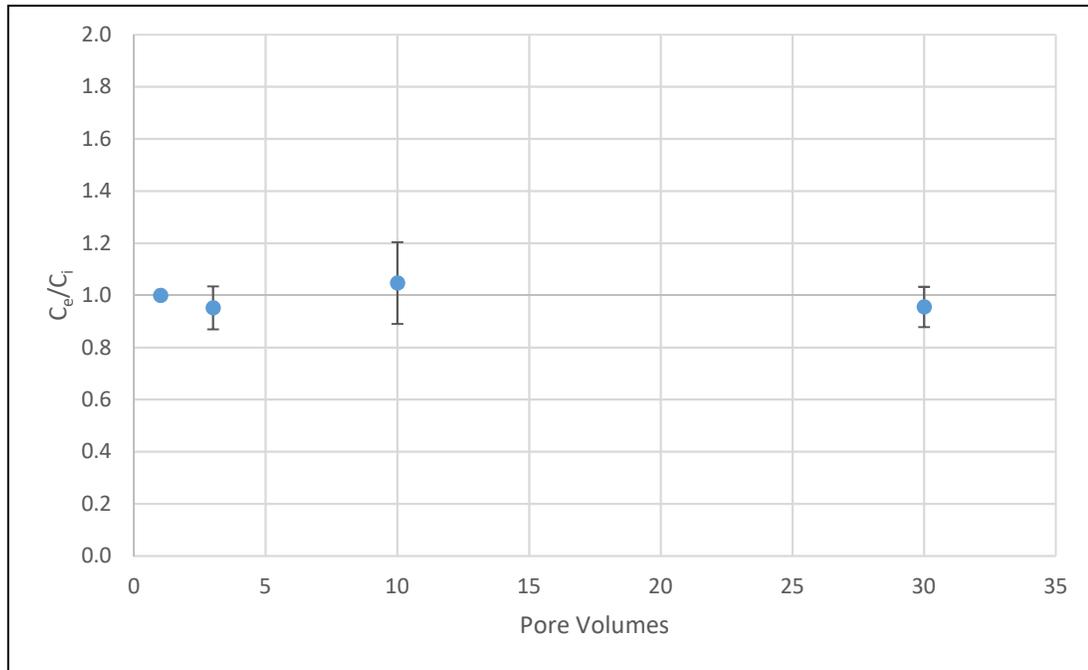


Figure 25: Normalized effluent nitrate concentrations from MDR7.5 columns.

Both APT and BIO columns showed some NO_3^- removal, though highly variable, in the first three PVs. However, NO_3^- showed net export on average after PV10 in both columns. However, NO_3^- seemed to have been flushed by PV30, with concentrations nearly equal to the influent. These trends can be seen in Figure 26 for APT and Figure 27 for BIO. The complexity and dynamic structure of peat may explain some NO_3^- removal as well as export at certain sampling points in the column experiments. Kleimeier et al. (2014) describes the pore structure of peat soils to have “dual-porosity,” which means they contain two porous domains with regard to solute transport: the “mobile” macropores and “immobile” micropores. The macropores are responsible for much of the hydraulic and

solute transport, while some solutes diffuse into micropores. Rezanezhad et al. (2017) examined solute transport in a peat profile, showing that at the beginning of rewetting the peat, preferential flow and solute diffusion into micropores was observed. This may explain the initial NO_3^- removal observed in APT and BIO columns. Additionally, Kleimeier et al. (2014) observed NO_3^- export for the first 3.8 PVs in a flushing study. They noted the NO_3^- came from mineralization of N in drying activities during peat harvesting. This would explain the some NO_3^- export before PV30.

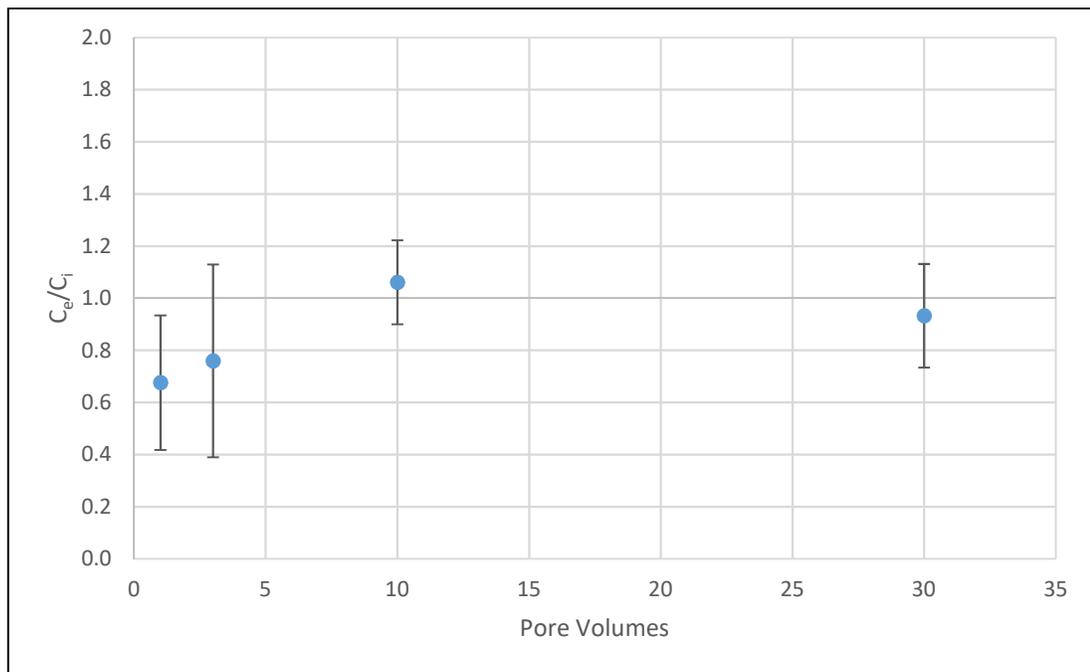


Figure 26: Normalized effluent nitrate concentrations from APT columns.

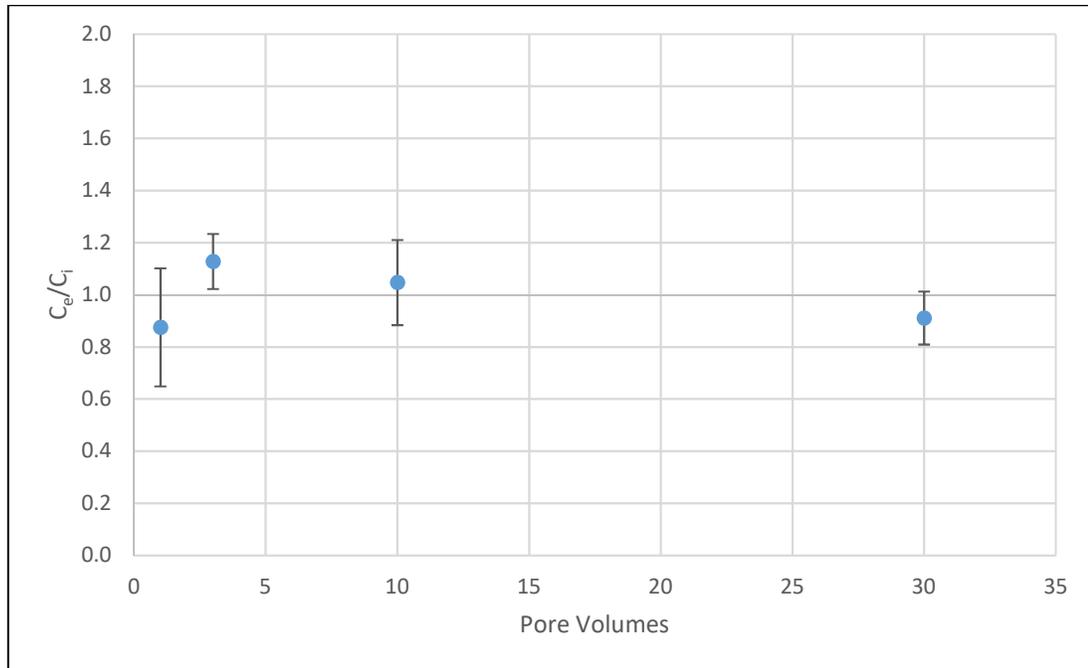


Figure 27: Normalized effluent nitrate concentrations from BIO columns.

Table 36 shows the results of the Mann-Whitney U test for the NO_3^- normalized effluent concentrations, which compared FA5.0, MDR7.5, APT, and BIO to SAND with an α -value of 0.10. Only MDR7.5 showed statistical differences with SAND PV01. In PV03, only BIO showed statistical differences with SAND. None of the media were statistically different from SAND in PV03, but FA5.0 was statistically different in PV30. This shows that none of the media showed consistent improvements to NO_3^- removal, compared to SAND.

Table 36: Results of Mann-Whitney U test comparing normalized effluent nitrate concentrations of reactive media with SAND ($\alpha = 0.10$).

Sample	n	Mean	Median	Std. Dev.	Min	Max	p-Value
SANDPV01	3	0.78	0.79	0.15	0.63	0.93	
FA5.0PV01	3	0.85	0.86	0.03	0.81	0.88	0.5127
MDR7.5PV01	3	1.00	1.00		1.00	1.00	0.0369
APTPV01	3	0.68	0.77	0.26	0.39	0.88	0.5127
BIOPV01	3	0.88	0.93	0.23	0.63	1.07	0.3758
SANDPV03	3	0.83	0.93	0.24	0.56	1.00	
FA5.0PV03	3	0.82	0.81	0.18	0.64	1.00	1.0000
MDR7.5PV03	3	0.95	1.00	0.08	0.86	1.00	0.4867
APTPV03	3	0.76	0.77	0.37	0.39	1.13	0.8273
BIOPV03	3	1.13	1.07	0.11	1.07	1.25	0.0463
SANDPV10	3	0.93	0.94	0.07	0.87	1.00	
FA5.0PV10	3	0.89	0.88	0.04	0.87	0.94	0.5002
MDR7.5PV10	3	1.05	1.13	0.16	0.87	1.14	0.2752
APTPV10	3	1.06	1.15	0.16	0.88	1.15	0.2683
BIOPV10	3	1.05	1.07	0.16	0.88	1.20	0.2752
SANDPV30	3	0.98	1.00	0.04	0.94	1.00	
FA5.0PV30	3	0.89	0.88	0.03	0.88	0.93	0.0431
MDR7.5PV30	3	0.96	1.00	0.08	0.87	1.00	0.7963
APTPV30	3	0.93	0.88	0.20	0.77	1.15	0.5066
BIOPV30	3	0.91	0.93	0.10	0.80	1.00	0.2463

3.4.6.2 Ammonia Leaching

Even after being flushed for 10 PVs with DI water, NH_3 initially leached from all columns. However, the influent SS seemingly continued to flush the NH_3 leachate as concentrations quickly tapered off. NH_3 concentrations of column effluents at PV01, PV03, PV10, and PV30 are shown in Table 37. The source of NH_3 from SAND, FA5.0, and MDR7.5 columns, may be preexisting NH_3 in the media. The MDRs used in the MDR7.5 media were air-dried without any additional treatment. Sediments and clay from the bottom of the oxidation pond source may have preexisting NH_3 , which would explain leaching from the columns. NH_3 is commonly found in sediments, form complexes with metal ions, and be associated with colloidal particles (Jermakka et al., 2015). NH_3 seems

to be flushed out as leaching decreases as more water is passed through the columns. Additionally, APT and BIO columns initially leach large amounts of NH₃ but get flushed out by considerable amounts with each following sample. NH₃ from APT and BIO might be associated with organic compounds in peat. Figure 28 shows a correlation scatter plot of TOC and NH₃ concentrations, indicating strong positive correlations. When plotted separately, APT had a coefficient of 0.95, BIO had a coefficient of 0.97, and SAND, FA5.0, and MDR7.5 had a coefficient of 0.74.

Table 37: Summary of average ammonia concentrations and standard deviations in column effluents.

	PV01 (µg/L as N)	PV03 (µg/L as N)	PV10 (µg/L as N)	PV30 (µg/L as N)
SAND	51 ± 16	38 ± 8	25 ± 5	2 ± 2
FA5.0	11 ± 9	9 ± 13	1 ± 0	1 ± 0
MDR7.5	170 ± 110	120 ± 49	150 ± 71	40 ± 21
APT	820 ± 340	600 ± 230	260 ± 77	49 ± 28
BIO	610 ± 400	500 ± 350	230 ± 110	80 ± 78

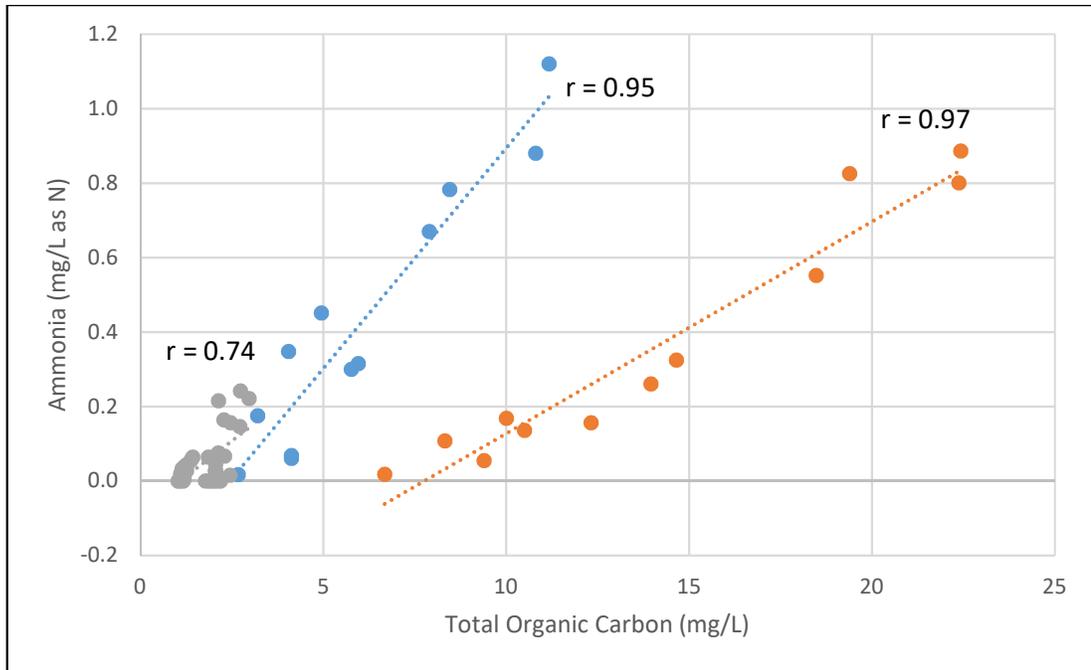


Figure 28: Correlation scatter plot of total organic carbon concentration and ammonia concentration.

3.4.6.3 Total Nitrogen Balance

The averaged normalized effluent concentrations from each column are summarized in Table 38 for TN. Additionally, mass balances of TN in Table 39 were estimated using the same calculations as the previous mass balances. TN concentrations from SAND, FA5.0, and MDR7.5 columns did not change appreciably from the influent to each of the effluent sampling points (Table 38 and Table 39). APT and BIO showed substantial net export of TN in both concentration changes and mass differences (Table 38 and Table 39).

Table 38: Averaged results and standard deviations for normalized effluent total nitrogen concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	1.04 ± 0.02	0.99 ± 0.02	1.01 ± 0.03	1.03 ± 0.00
FA5.0	0.91 ± 0.02	0.93 ± 0.00	0.92 ± 0.01	0.95 ± 0.01
MDR7.5	0.99 ± 0.07	0.96 ± 0.02	0.97 ± 0.04	0.95 ± 0.02
APT	1.52 ± 0.20	1.42 ± 0.17	1.21 ± 0.10	1.05 ± 0.03
BIO	1.77 ± 0.35	1.55 ± 0.24	1.33 ± 0.11	1.12 ± 0.01

Table 39: Averaged results and standard deviations of estimated total nitrogen mass balances of each column.

	TN _{in} (mg)	TN _{out} (mg)	% Removed
SAND	11.27 ± 0.88	11.56 ± 0.80	-3 ± 1
FA5.0	14.88 ± 1.03	12.52 ± 0.39	15 ± 9
MDR7.5	15.87 ± 0.57	14.16 ± 0.13	11 ± 4
APT	15.78 ± 0.21	18.55 ± 1.76	-18 ± 12
BIO	16.26 ± 0.21	19.81 ± 1.24	-22 ± 6

Because TKN was not measured, organic N cannot be assumed to be absent. NO₃⁻ and NH₃ were summed to quantify the amount of N accounted for in this study, as a part of TN. The difference between TN and the sum of NO₃⁻ and NH₃ were considered other N species, which may include organic N. Percentages of NO₃⁻ and NH₃ of TN for SAND, FA5.0, and MDR7.5 are shown in Figures Figure 29, Figure 30, and Figure 31, respectively. The absence of appreciable changes in TN concentrations may suggest poor N removal abilities overall, from SAND, FA5.0, and MDR7.5.

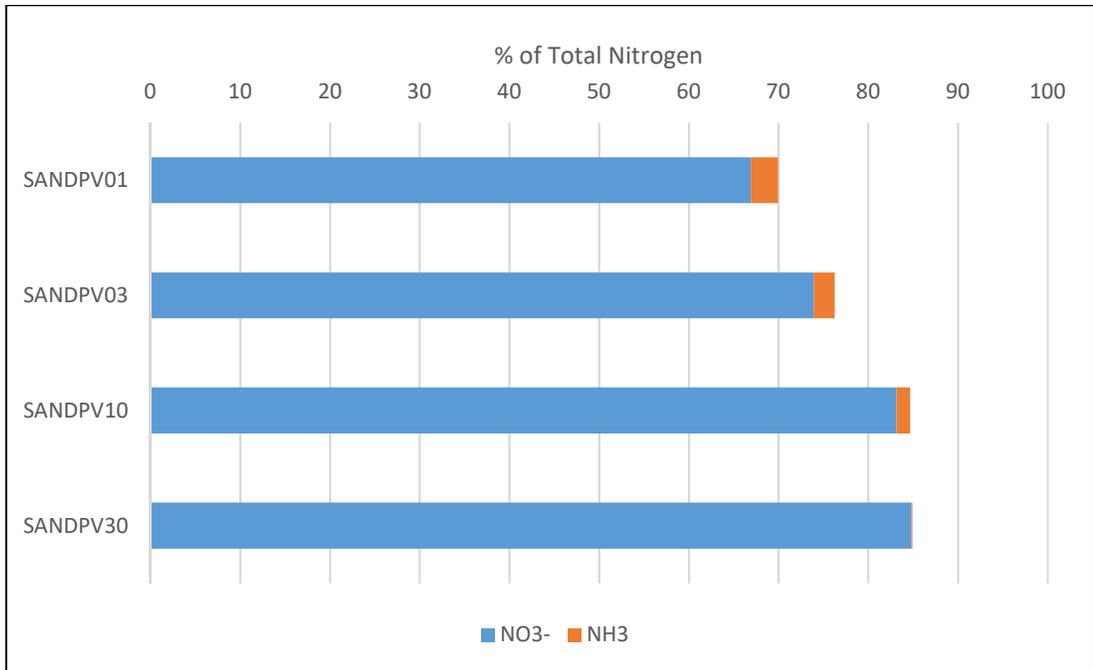


Figure 29: Percentages of nitrate and ammonia of total nitrogen in SAND column water samples.

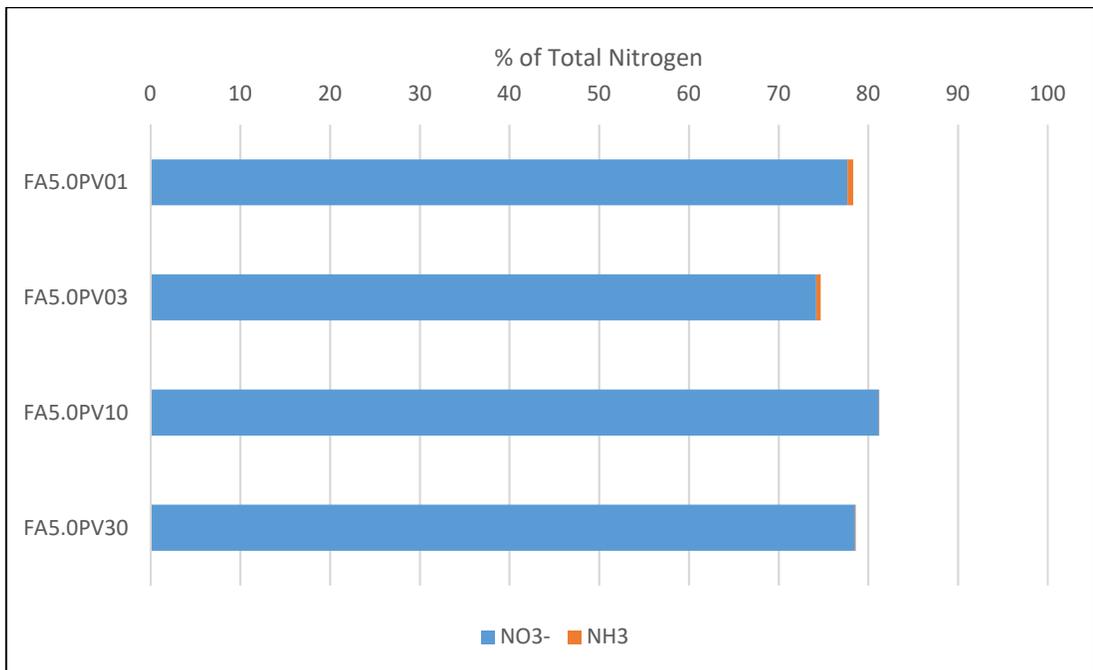


Figure 30: Percentages of nitrate and ammonia of total nitrogen in FA5.0 column water samples.

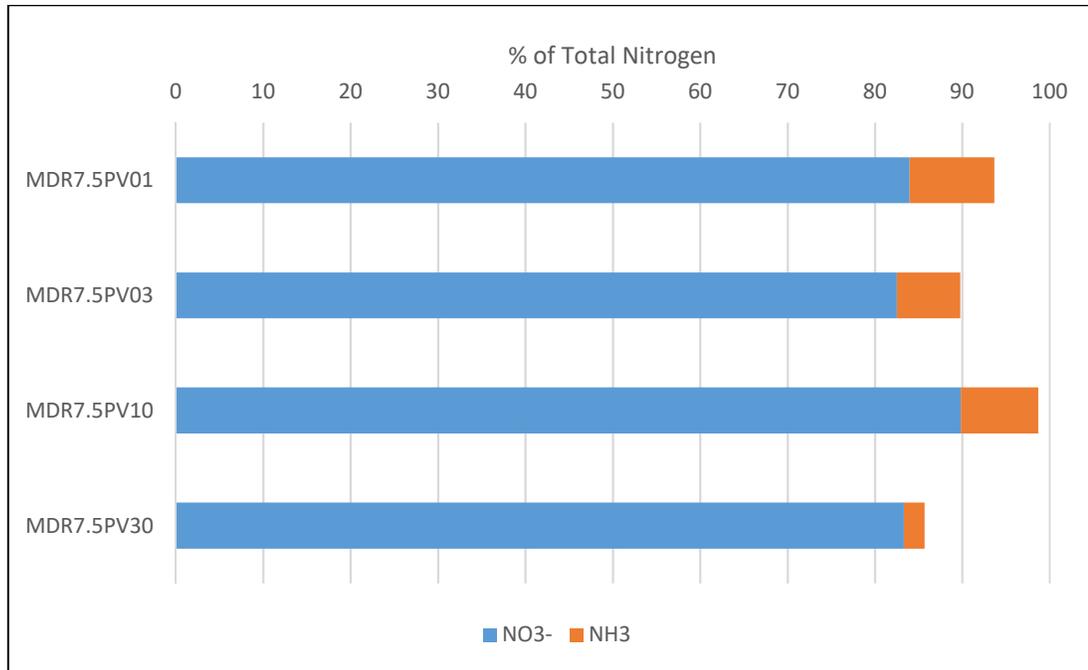


Figure 31: Percentages of nitrate and ammonia of total nitrogen in MDR7.5 column water samples.

APT (Figure 32) and BIO (Figure 33) show clear changes in N fractions of TN. These changes primarily show production of NH_3 and other N species. These other N species are most likely associated with organic forms, with the addition of NH_3 export. Schnitzer et al. (1983) attempted to quantify the amount of “unknown N” that are associated with the organic fraction of N. They found that approximately 98% of the TN associated with humic and fluvic acids was comprised of unknown N. This may suggest organic N to be the primary form associated with any TN export observed in APT and BIO columns. Figure 34 displays a correlation scatter plot of TOC concentration and normalized effluent TN concentration, showing positive correlations. When plotted separately, APT had a coefficient of 0.95, BIO had a coefficient of 0.98, and SAND, FA5.0, and MDR7.5 had a coefficient of 0.50.

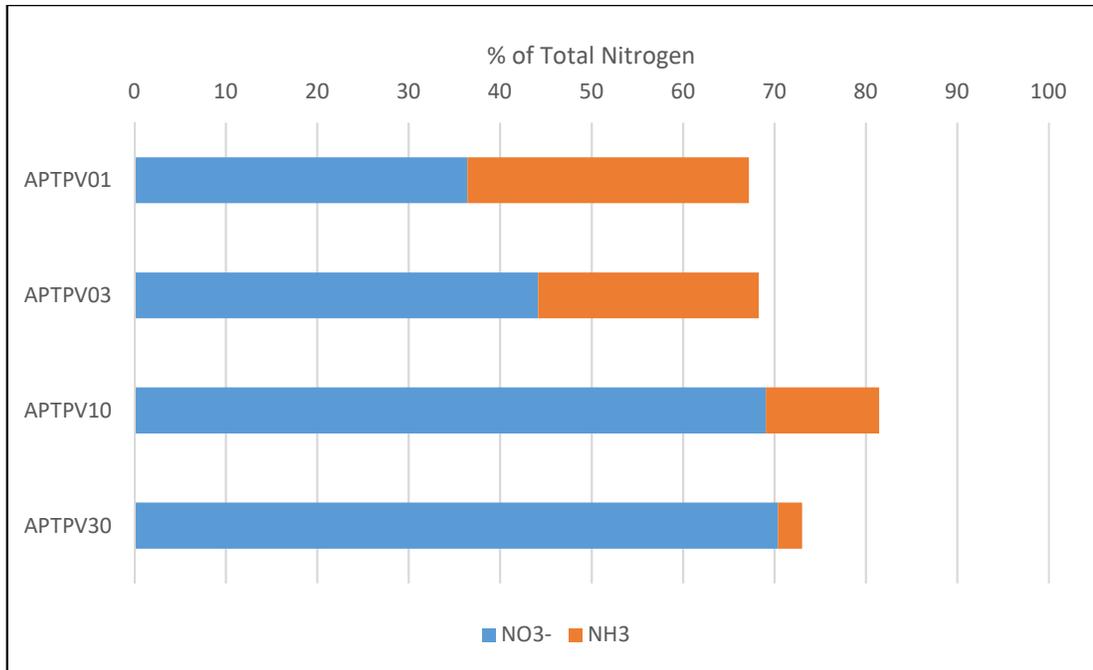


Figure 32: Percentages of nitrate and ammonia of total nitrogen in APT column water samples.

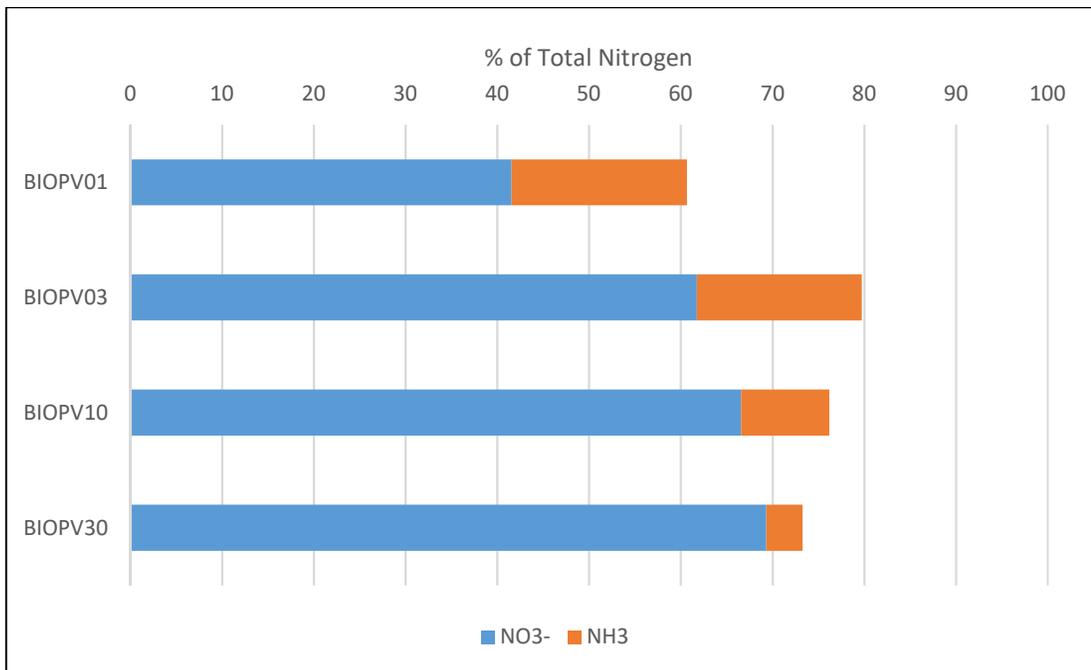


Figure 33: Percentages of nitrate and ammonia of total nitrogen in BIO column water samples.

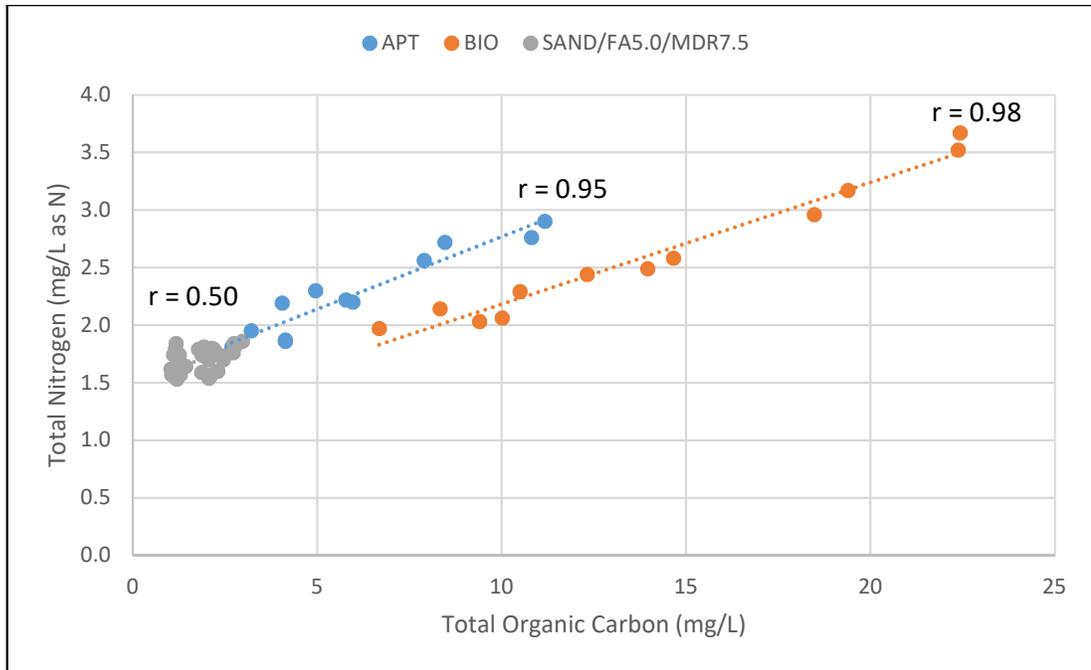


Figure 34: Correlation scatter plot of total organic carbon concentration and normalized effluent total nitrogen concentration.

3.4.7 Metals

3.4.7.1 Copper

The averaged normalized effluent concentrations from each column are summarized in Table 40 for total Cu and Table 41 for filtered Cu. Values were omitted for those sample concentrations that all measured BDL. Additionally, mass balances of total Cu in Table 42 and filtered Cu in Table 43 were estimated using the same calculations as the previous mass balances.

Table 40: Averaged results and standard deviations for normalized effluent total copper concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.08 ± 0.04	0.08 ± 0.04	0.07 ± 0.02	0.03 ± 0.02
FA5.0	0.17 ± 0.15	0.17 ± 0.16	0.12 ± 0.10	0.46 ± 0.47
MDR7.5	0.10 ± 0.08	0.17 ± 0.01	0.16 ± 0.05	0.10 ± 0.08
APT	0.13 ± 0.04	0.09	0.16 ± 0.07	0.06 ± 0.03
BIO	0.13	0.13	0.08	0.10 ± 0.07

Table 41: Averaged results and standard deviations for normalized effluent filtered copper concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.05	0.06 ± 0.02	0.08 ± 0.12	
FA5.0	0.14 ± 0.03	0.08 ± 0.07	0.08 ± 0.04	0.03 ± 0.02
MDR7.5	0.09 ± 0.09	0.08 ± 0.07		0.04 ± 0.07
APT	0.12 ± 0.02	0.07 ± 0.03	0.07 ± 0.03	0.05 ± 0.04
BIO	0.12 ± 0.03	0.12 ± 0.03	0.09	0.09 ± 0.04

Table 42: Averaged results and standard deviations of estimated total copper mass balances of each column.

	Cu _{in} (mg)	Cu _{out} (mg)	% Removed
SAND	0.163 ± 0.016	0.007 ± 0.002	96 ± 1
FA5.0	0.208 ± 0.019	0.065 ± 0.051	67 ± 29
MDR7.5	0.255 ± 0.042	0.028 ± 0.013	89 ± 4
APT	0.207	0.022 ± 0.003	90 ± 1
BIO	0.213 ± 0.005	0.021 ± 0.009	90 ± 5

Table 43: Averaged results and standard deviations of estimated filtered copper mass balances of each column.

	Cu _{in} (mg)	Cu _{out} (mg)	% Removed
SAND	0.152 ± 0.012	0.004 ± 0.005	97 ± 3
FA5.0	0.197 ± 0.005	0.009 ± 0.002	96 ± 1
MDR7.5	0.219 ± 0.005	0.008 ± 0.012	96 ± 5
APT	0.201 ± 0.005	0.018 ± 0.007	91 ± 4
BIO	0.207 ± 0.115	0.019 ± 0.006	91 ± 3

Except for FA5.0, all columns decreased total Cu concentrations by at least 85%. FA5.0 decreased total Cu by at least 83% in PV01, PV03, and PV10. However, one replicate column produced one sample at PV30 that measured total Cu that equaled the influent

concentration. All columns performed similarly with over 90% removal of filtered Cu. Overall, SAND columns showed the greatest decrease in both total and filtered Cu concentrations. Total and filtered Cu concentrations were decreased by averages of over 90%. These decreases in concentration seem to be consistent across all PVs, shown in Figure 35 for total Cu and Figure 36 for filtered Cu. The primary removal mechanism is most likely precipitation, which would be promoted by alkaline pH and presence of Ca in the effluent. Uwamariya et al. (2016) observed instability of Cu^{2+} in synthetic water, with increasing Ca^{2+} and increased pH, which both increase precipitation as $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$.

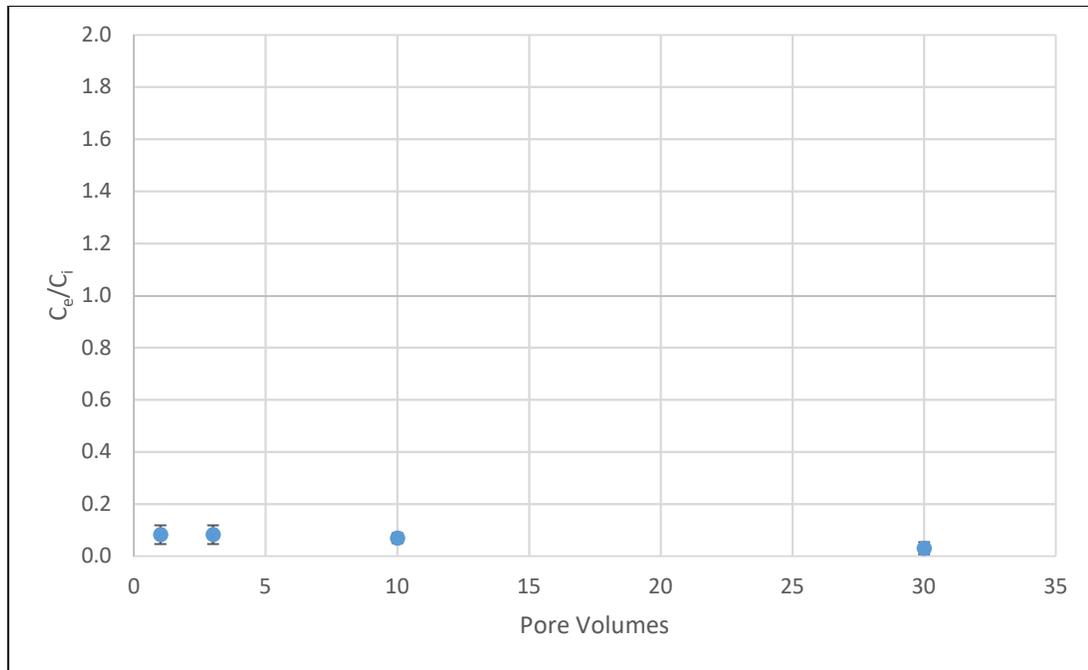


Figure 35: Normalized effluent total copper concentrations of SAND columns.

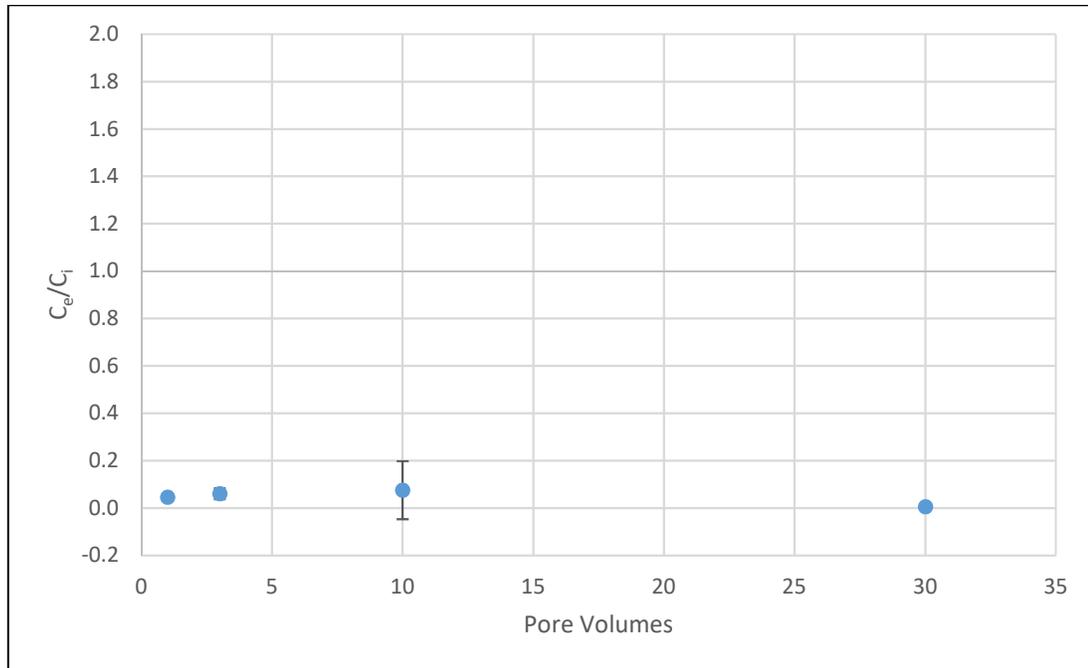


Figure 36: Normalized effluent filtered copper concentrations of SAND columns.

FA5.0 and MDR7.5 showed the smallest decreases in total Cu. The Cu removal mechanism in FA5.0 is likely precipitation, primarily due to the elevated CaO content in the FA and alkaline solution pH (Erol et al., 2005). Erol et al. (2005) observed maximum Cu removal rates of 90 to 100%, by FA in batch experiments, at pH values above 8 where Cu precipitates as hydroxides. This phenomenon is not observed for total Cu, seen in Figure 37, but is observed in Figure 38 where filtered Cu concentrations decrease by at least 92% after PV03, PV10, and PV30. This discrepancy may be explained by precipitation as Cu removal mechanism. Effluent water samples were slightly turbid, with very fine particulates seen suspended. This may suggest a combination of loss of FA particles from the columns, which may include precipitated Cu hydroxides.

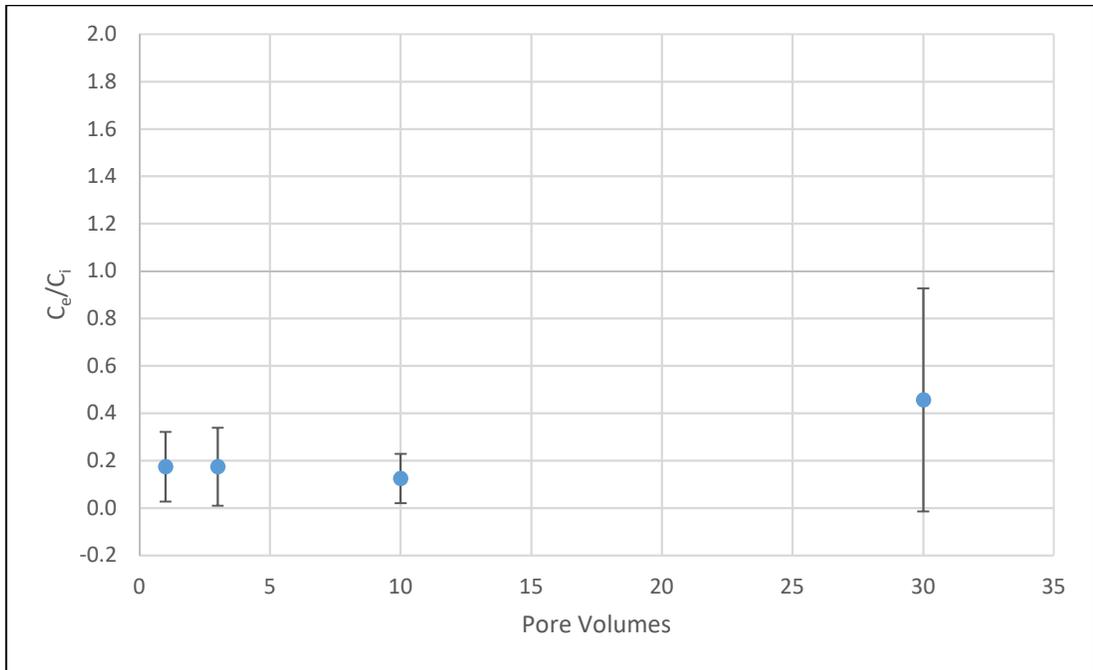


Figure 37: Normalized effluent total copper concentrations of FA5.0 columns.

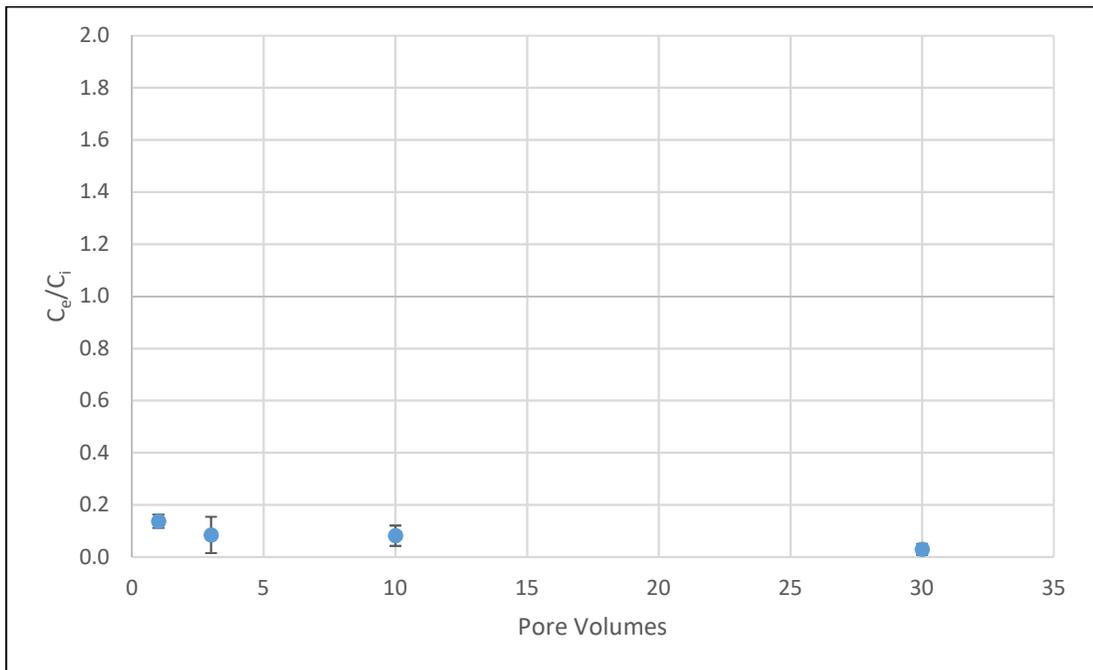


Figure 38: Normalized effluent filtered copper concentrations of FA5.0 columns.

MDR7.5 columns most likely remove Cu using a combination of precipitation and adsorption from the elevated Ca in the effluent, effluent pH above 8, and presence of hydroxyl groups as surface adsorption sites. Figure 39 shows average decreases in total Cu concentrations consistently ranging from 83 to 90 across all PVs. Figure 40 shows similar trends for filtered Cu with average concentration decreases ranging from 94 to 100%. Uwamariva et al. (2016) showed precipitation and adsorption to be the primary Cu^{2+} removal mechanisms by iron oxide-coated sand and granular ferric hydroxide. Ca^{2+} was found to compete with Cu^{2+} for surface adsorption sites, which decreased overall removal performance (Uwamariva et al., 2016). Even though MDR7.5 produced greater concentrations of Ca in the effluent than SAND (Table 24), adsorption inhibition may explain the lack of appreciable improvements in Cu removal.

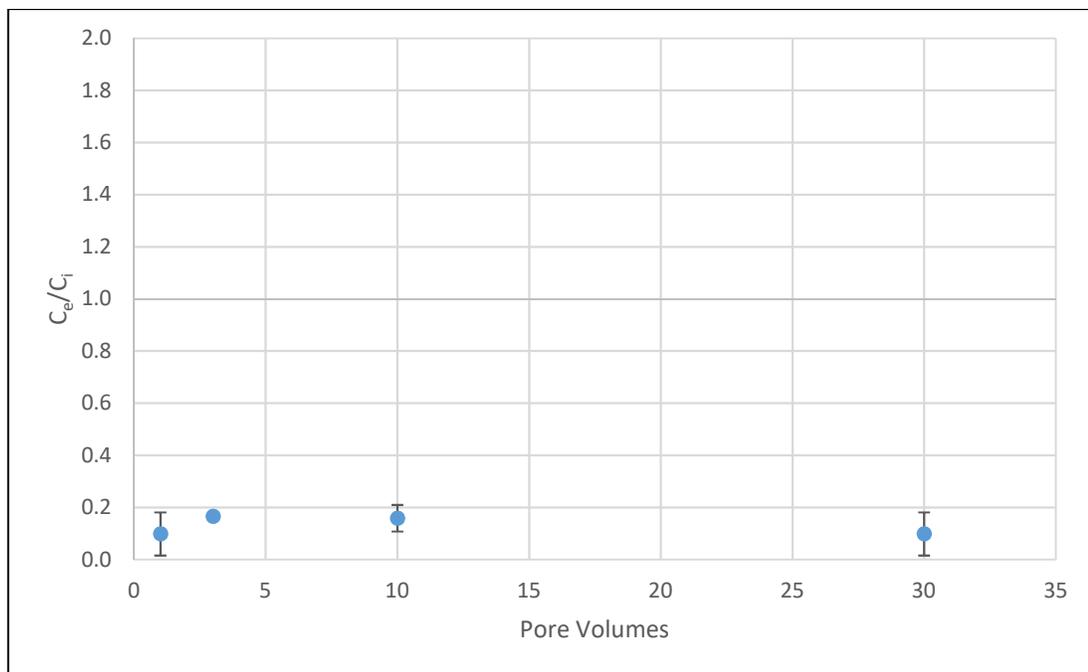


Figure 39: Normalized effluent total copper concentrations of MDR7.5 columns.

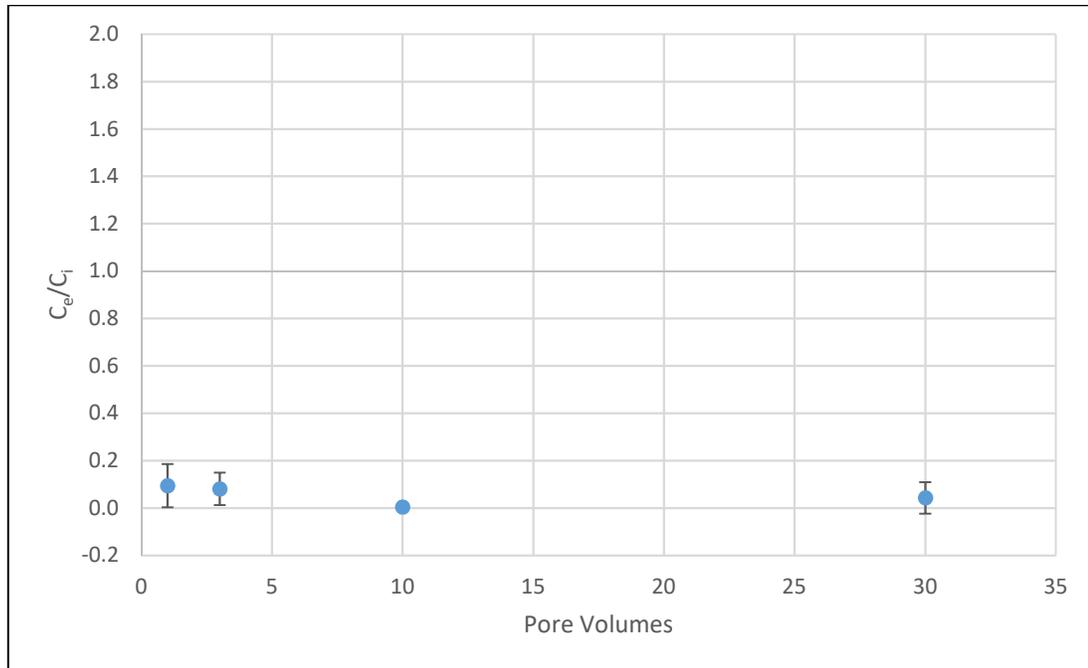


Figure 40: Normalized effluent filtered copper concentrations of MDR7.5 columns.

APT columns were able to decrease total Cu at averages of between 84 to 94%. However, removal performance seemed to fluctuate slightly at each PV, which is reflected in Figure 41. However, removal performance of filtered Cu after PV01 was consistently over 93% (Figure 42). Removal mechanisms are most likely precipitation due to the presence of Ca, pH near 8, and various interactions with organic functional groups due to elevated organic carbon in the effluent (refer to Table 25). Gondar et al. (2006) found adsorption to humic and fulvic acids preferred Cu^{2+} over Pb^{2+} , where metals binding was the greatest in humic acid.

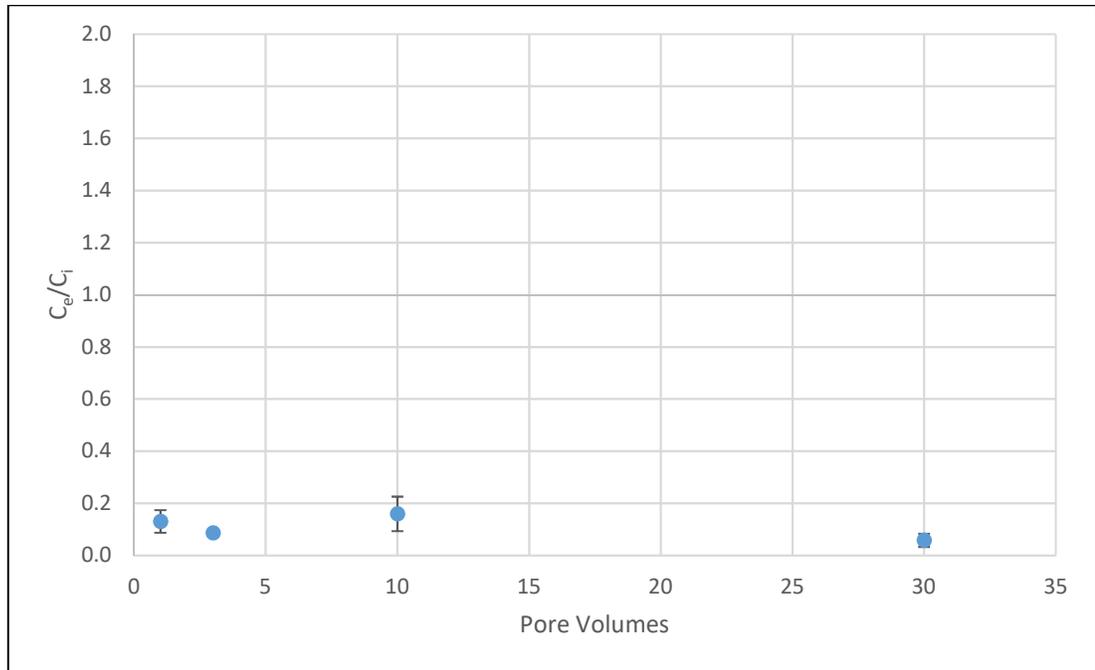


Figure 41: Normalized effluent total copper concentrations of APT columns.

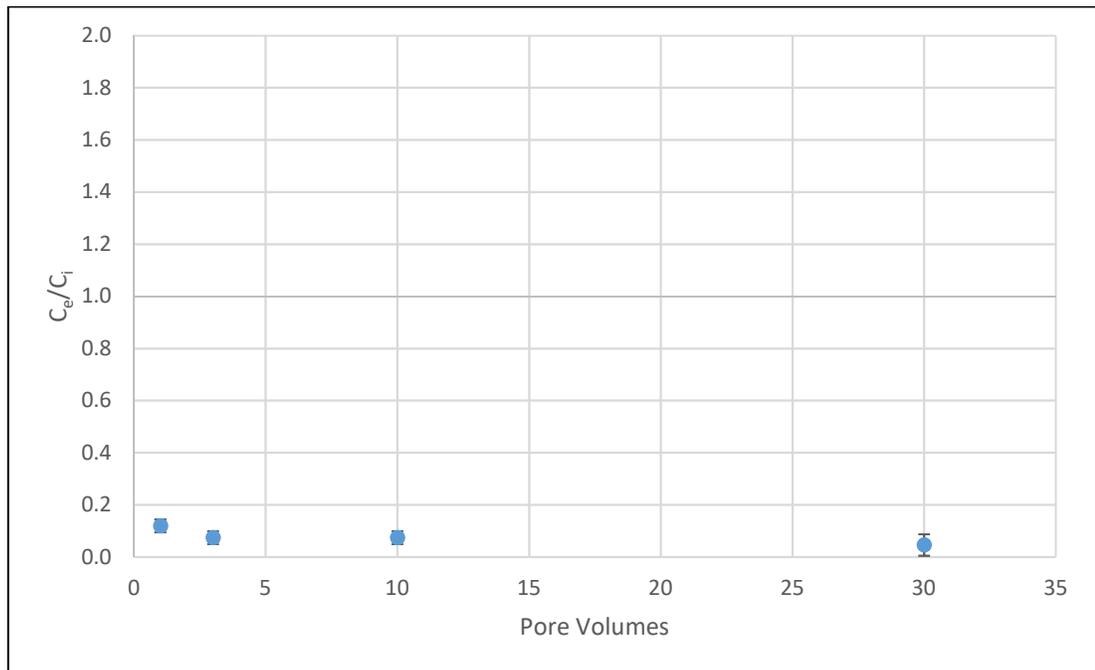


Figure 42: Normalized effluent filtered copper concentrations of APT columns.

BIO performed similarly to APT, but with slightly more consistent performance across all PVs. Total and filtered Cu concentrations decreased by 87% and 88%, respectively, in the first three PVs. After PV10 and PV30, total and filtered Cu concentrations decreased at averages of over 90%. These trends can be seen in Figure 43 for total Cu and Figure 44 for filtered Cu. The primary removal mechanisms are also suggested to be precipitation and interactions with organic functional groups.

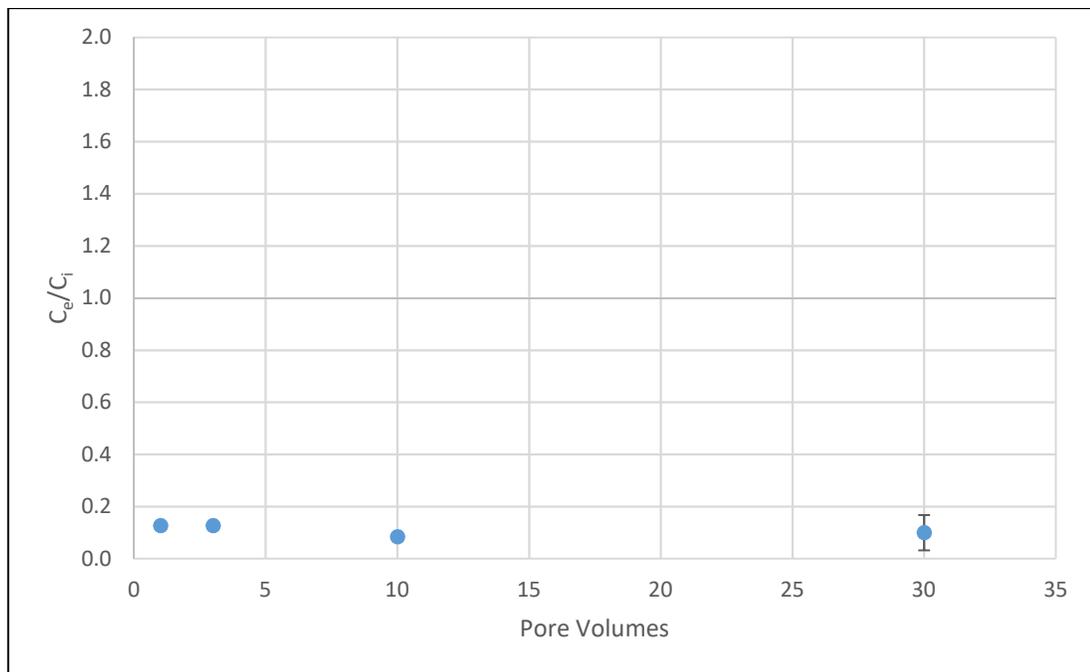


Figure 43: Normalized effluent total copper concentrations of BIO columns.

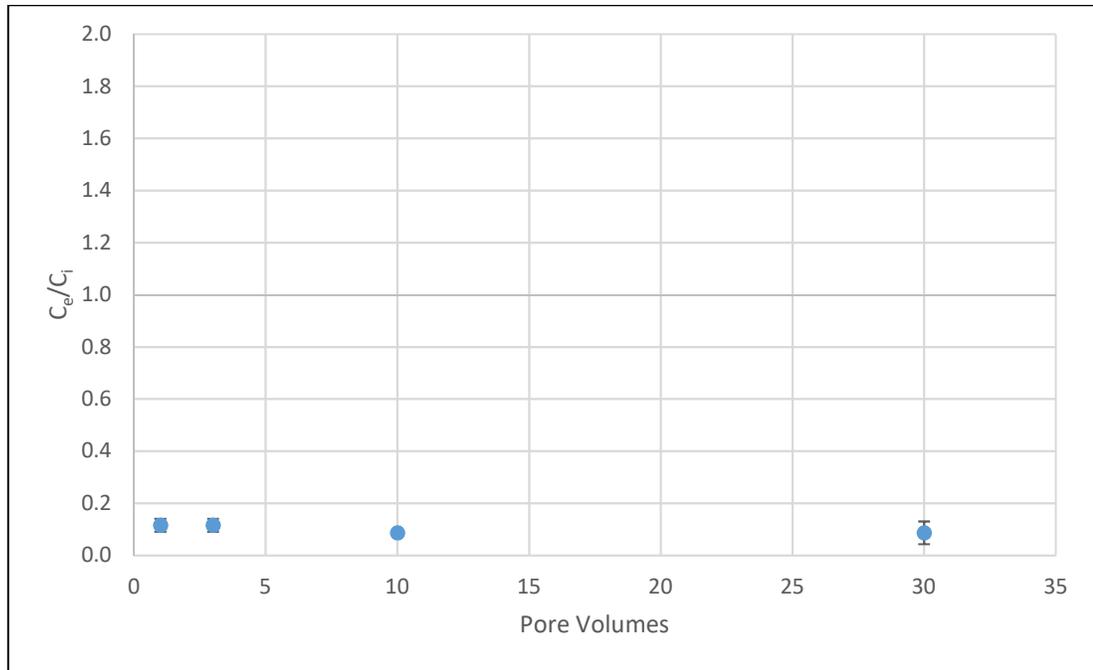


Figure 44: Normalized effluent filtered copper concentrations of BIO columns.

Table 44 shows the results of the Mann-Whitney U test for the total Cu normalized effluent concentrations, which compared FA5.0, MDR7.5, APT, and BIO to SAND with an α -value of 0.10. FA5.0 was only statistically different from SAND in PV30, suggesting similar performance in the first 10 PVs. BIO was statistically different in the first 10 PVs but was not in PV30. None of the media showed consistent significant differences with SAND across all PVs, suggesting similar performance overall.

Table 44: Results of Mann-Whitney U test comparing normalized effluent total copper concentrations of reactive media with SAND ($\alpha = 0.10$).

Sample	n	Mean	Median	Std. Dev.	Min	Max	p-Value
SANDPV01	3	0.08	0.08	0.04	0.05	0.12	
FA5.0PV01	3	0.17	0.26	0.15	0.01	0.26	0.5066
MDR7.5PV01	3	0.10	0.13	0.08	0.01	0.16	0.5127
APTPV01	3	0.13	0.13	0.04	0.09	0.17	0.1266
BIOPV01	3	0.13	0.13	0.00	0.13	0.13	0.0463
SANDPV03	3	0.08	0.08	0.04	0.05	0.12	
FA5.0PV03	3	0.17	0.19	0.17	0.005	0.33	0.5127
MDR7.5PV03	3	0.17	0.16	0.01	0.16	0.17	0.0463
APTPV03	3	0.09	0.09		0.09	0.09	0.4867
BIOPV03	3	0.13	0.13	0.003	0.13	0.13	0.0463
SANDPV10	3	0.07	0.08	0.02	0.05	0.08	
FA5.0PV10	3	0.13	0.19	0.10	0.005	0.19	0.5002
MDR7.5PV10	3	0.16	0.13	0.05	0.13	0.22	0.0431
APTPV10	3	0.16	0.17	0.07	0.09	0.22	0.0463
BIOPV10	3	0.09	0.08	0.002	0.08	0.09	0.0431
SANDPV30	3	0.03	0.04	0.02	0.004	0.05	
FA5.0PV30	3	0.46	0.19	0.47	0.19	1.00	0.0463
MDR7.5PV30	3	0.10	0.13	0.08	0.01	0.16	0.2752
APTPV30	3	0.06	0.04	0.03	0.04	0.09	0.2683
BIOPV30	3	0.10	0.08	0.07	0.04	0.17	0.1266

3.4.7.2 Lead

The averaged normalized effluent concentrations from each column are summarized in Table 45 for total Pb and Table 46 filtered Pb. Additionally, mass balances of total Pb in Table 47 and filtered Pb in Table 48 were estimated using the same calculations as the previous mass balances.

Table 45: Averaged results and standard deviations for normalized effluent total lead concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.78 ± 0.12	0.72 ± 0.05	0.65 ± 0.10	0.75 ± 0.02
FA5.0	0.88 ± 0.12	1.03 ± 0.25	0.76 ± 0.28	0.59 ± 0.45
MDR7.5	0.72 ± 0.07	0.55 ± 0.13	0.53 ± 0.09	0.29 ± 0.19
APT	0.18 ± 0.12	0.17 ± 0.08	0.12 ± 0.05	0.23 ± 0.10
BIO	0.44 ± 0.28	0.31 ± 0.39	0.50 ± 0.36	1.47 ± 1.30

Table 46: Averaged results and standard deviations for normalized effluent filtered lead concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND	0.98 ± 0.08	0.67 ± 0.48	0.56 ± 0.39	0.32 ± 0.36
FA5.0	5.94 ± 4.87	2.42 ± 1.25	2.08 ± 1.06	1.46 ± 0.59
MDR7.5	8.54 ± 2.51	7.03 ± 5.25	6.03 ± 4.47	4.02 ± 2.80
APT	0.30 ± 0.34	0.10	0.16 ± 0.09	0.16 ± 0.09
BIO	0.09 ± 0.01	0.09 ± 0.01	0.12 ± 0.05	0.13 ± 0.07

Table 47: Averaged results and standard deviations of estimated total lead mass balances of each column.

	Pb _{in} (mg)	Pb _{out} (mg)	% Removed
SAND	0.196 ± 0.020	0.143 ± 0.018	27 ± 3
FA5.0	0.208 ± 0.023	0.116 ± 0.055	42 ± 31
MDR7.5	0.267 ± 0.005	0.093 ± 0.022	65 ± 8
APT	0.237 ± 0.021	0.088 ± 0.062	63 ± 28
BIO	0.225 ± 0.031	0.274 ± 0.265	-13 ± 94

Table 48: Averaged results and standard deviations of estimated filtered lead mass balances of each column.

	Pb _{in} (mg)	Pb _{out} (mg)	% Removed
SAND	0.127 ± 0.004	0.054 ± 0.042	42 ± 32
FA5.0	0.049 ± 0.028	0.083 ± 0.057	-61 ± 40
MDR7.5	0.018	0.079 ± 0.051	-339 ± 282
APT	0.174 ± 0.005	0.026 ± 0.008	15 ± 5
BIO	0.198 ± 0.016	0.025 ± 0.013	13 ± 6

Figure 45 shows that SAND had some ability to remove Pb with total Pb concentrations decreasing between 22% to 35% across all PVs. Figure 46 shows filtered Pb concentrations decreasing between 44% to 68% after the first three PVs. The primary

removal mechanism for Pb is likely precipitation as lead hydroxide ($\text{Pb}(\text{OH})_2$) at elevated pH (Erol et al., 2005).

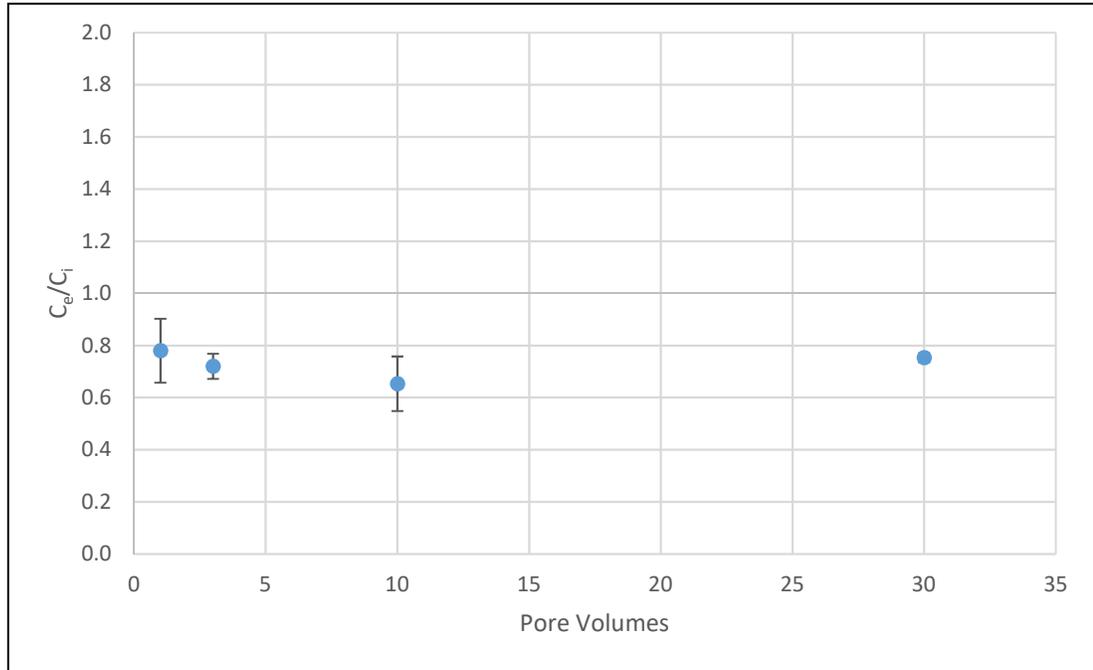


Figure 45: Normalized effluent total lead concentrations of SAND columns.

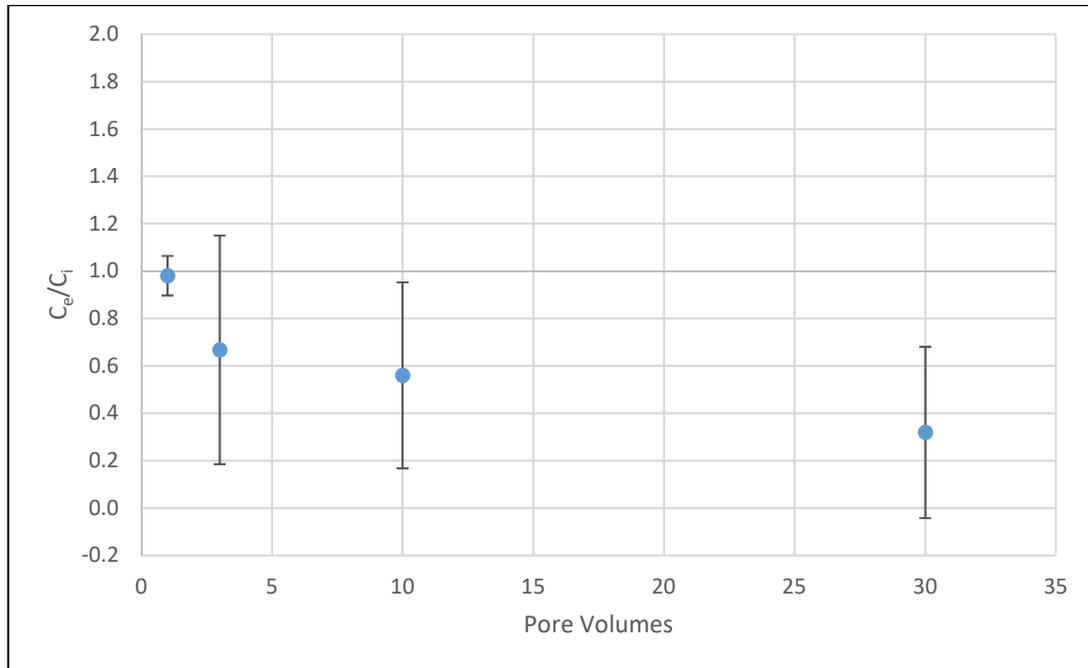


Figure 46: Normalized effluent filtered lead concentrations of SAND columns.

FA5.0 was able to remove between 24% to 41% of total Pb after PV03, seen in Figure 47. FA5.0 generally showed next export of filtered Pb, seen in Figure 48. The primary reason for this was that two of three FA5.0 columns showed filtered Pb concentrations as BDL in the influent water, therefore any detected Pb would show as greater than influent. The primary removal mechanism for Pb in FA5.0 was likely precipitation as $Pb(OH)_2$ (Erol et al., 2005). However, Erol et al. (2005) found that Pb^{2+} removal generally diminished when solution pH, in batch studies using various types of FA, was greater than 10.

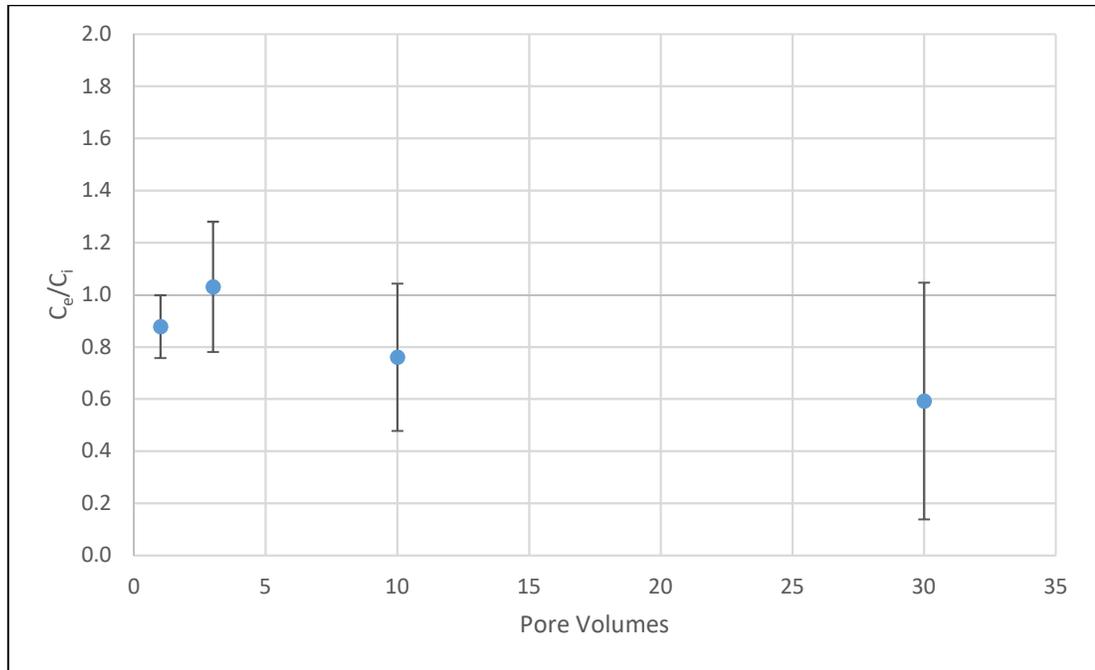


Figure 47: Normalized effluent total lead concentrations of FA5.0 columns.

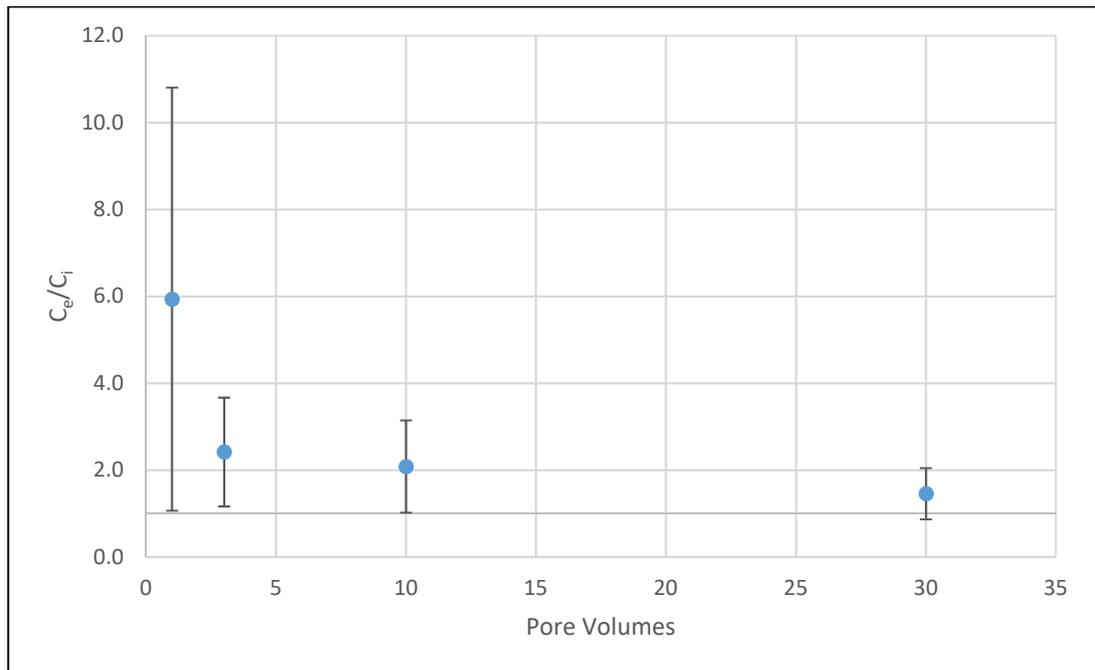


Figure 48: Normalized effluent filtered Pb concentrations of FA5.0 columns.

MDR7.5 was able to remove total Pb at 45% to 71% after the first PV (Figure 49). Figure 50 shows export of filtered Pb from MDR7.5 for the same reasons as FA5.0, where influent filtered Pb was BDL. The Pb removal mechanisms in MDR7.5 are likely precipitation and adsorption.

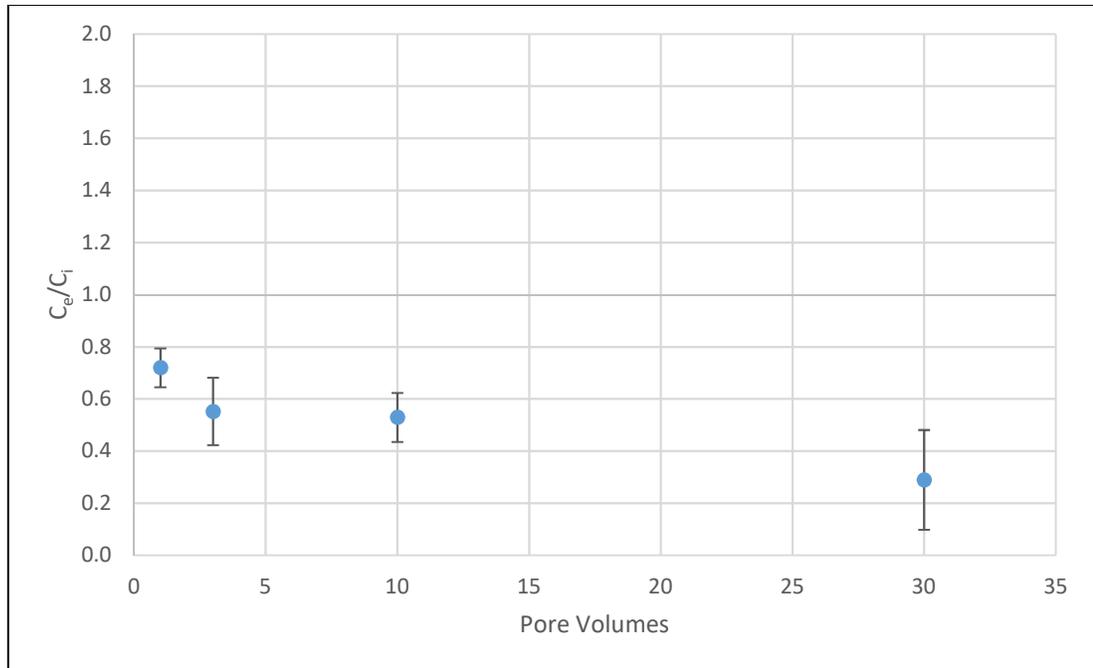


Figure 49: Normalized effluent total lead concentrations of MDR7.5 columns.

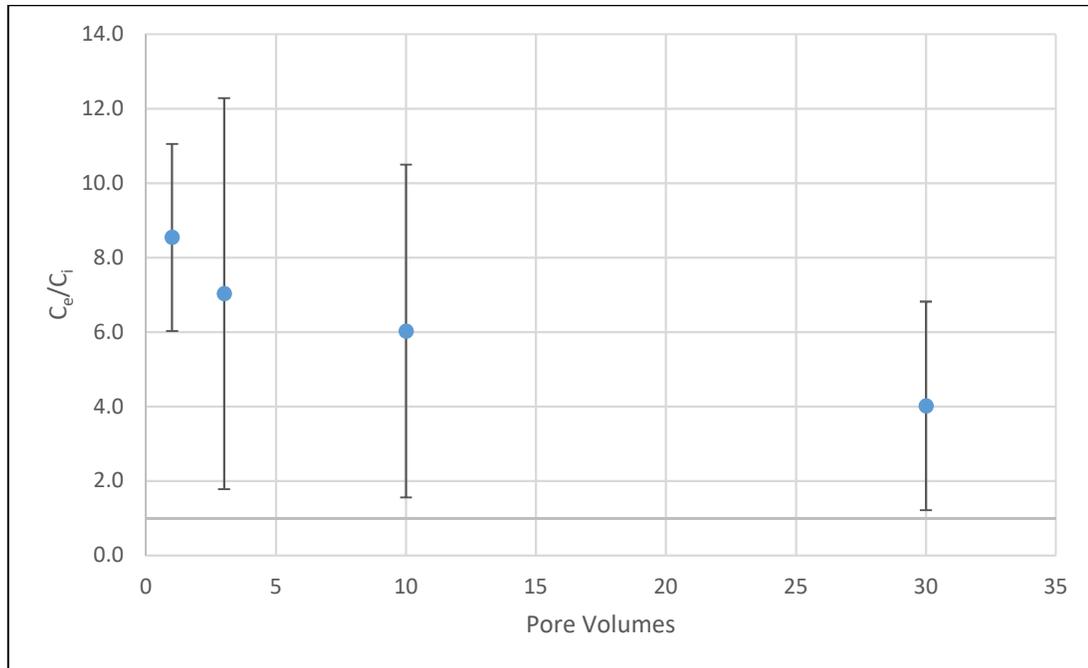


Figure 50: Normalized effluent filtered lead concentrations of MDR7.5 columns.

APT and BIO showed the greatest removal abilities for total and filtered Pb. APT was able to decrease total Pb concentrations by over 77% across all PVs (Figure 51) and over 84% for filtered Pb after the first PV (Figure 52). BIO showed at least 50% removal in the first 10 PVs but showed net export in PV30 (Figure 53). One sample showed a total Pb concentration of more than two times the influent concentration, which likely skewed the results at PV30. However, BIO was able to decrease filtered Pb concentrations between 87% to 91% across all PVs, as seen in Figure 54. The primary Pb removal mechanisms in APT and BIO are likely a variety of sorption processes with organic functional groups, such as surface adsorption, ion exchange, chelation, and complexation.

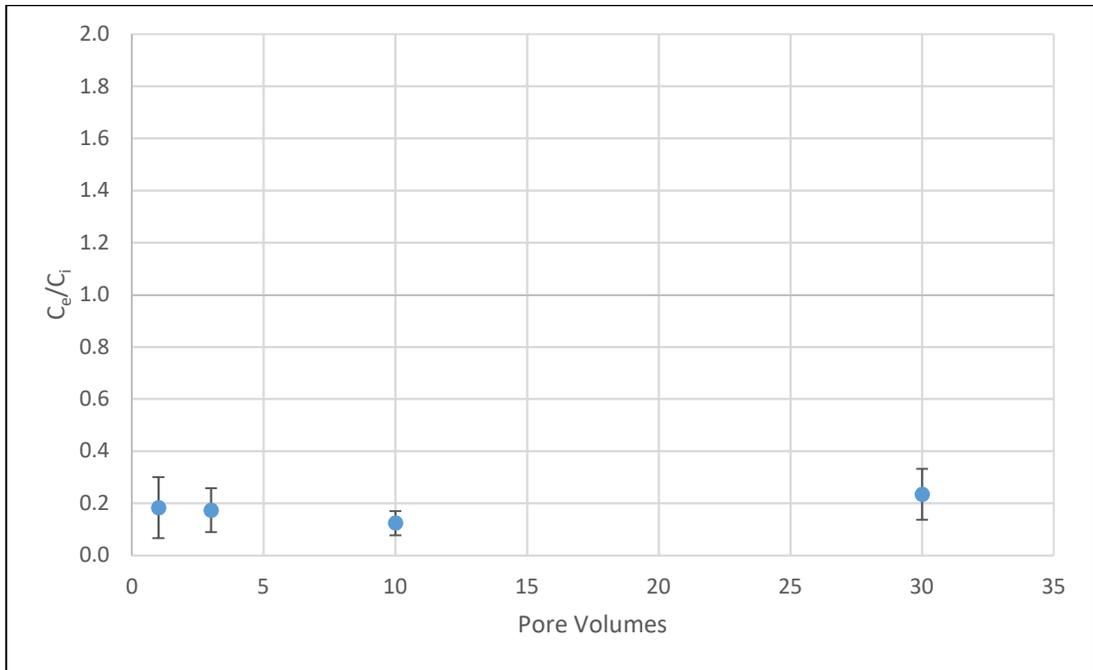


Figure 51: Normalized effluent total lead concentrations of APT columns.

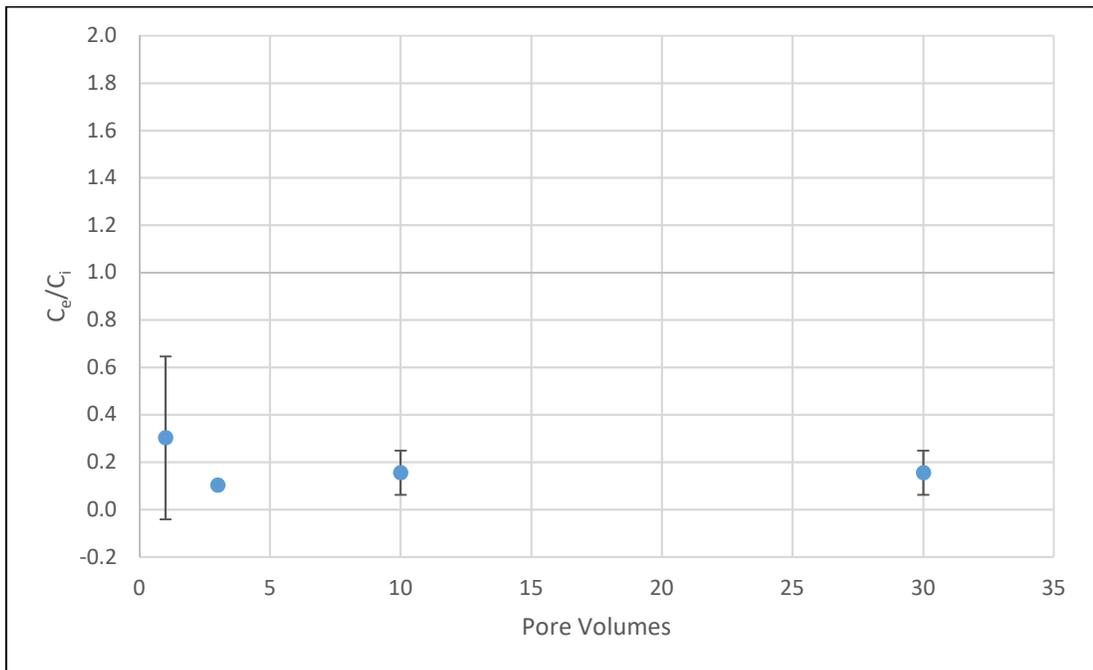


Figure 52: Normalized effluent filtered lead concentrations of APT columns.

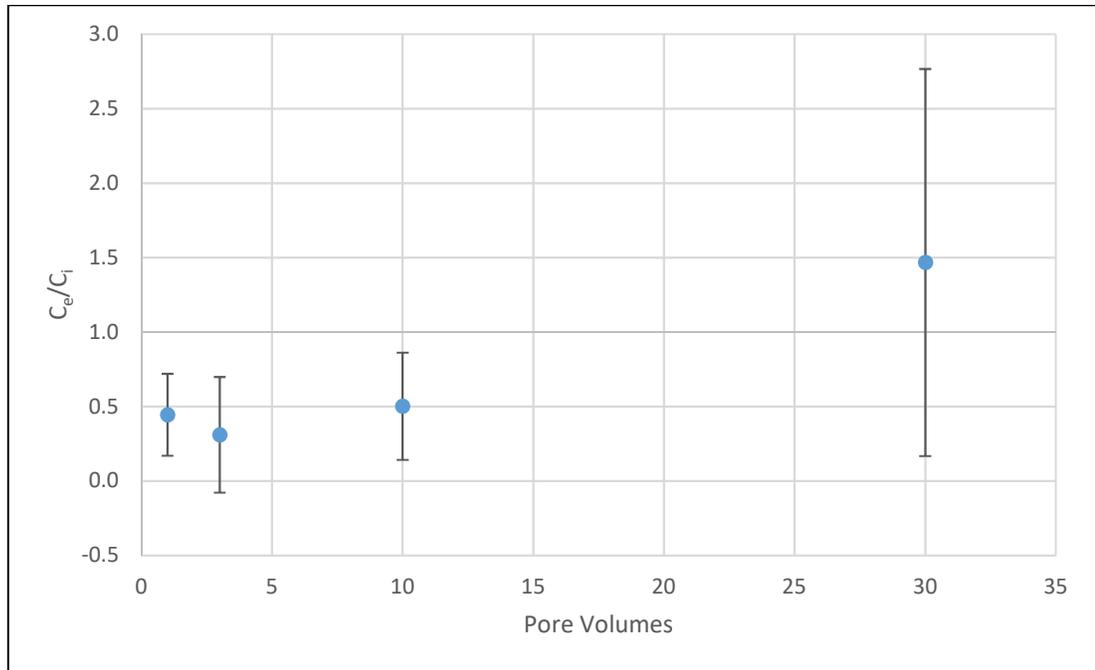


Figure 53: Normalized effluent total lead concentrations of BIO columns.

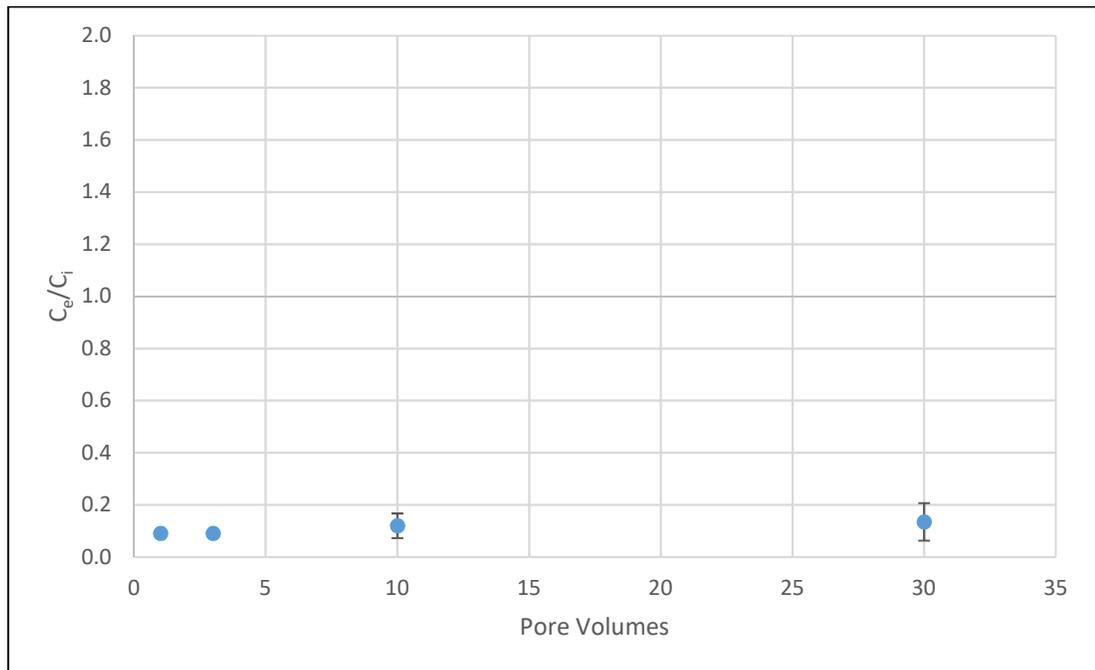


Figure 54: Normalized effluent filtered lead concentrations of BIO columns.

Table 49 shows the results of the Mann-Whitney U test for the total Pb normalized effluent concentrations, which compared FA5.0, MDR7.5, APT, and BIO to SAND with an α -value of 0.10. APT showed significant differences across all PVs, which would mean total Pb removal was improved from SAND. BIO showed no significant differences. FA5.0 and MDR7.5 did not have significant differences, except for PV30.

Table 49: Results of Mann-Whitney U test comparing normalized effluent total lead concentrations of reactive media with SAND ($\alpha = 0.10$).

Sample	n	Mean	Median	Std. Dev.	Min	Max	p-value
SANDPV01	3	0.78	0.83	0.12	0.64	0.87	
FA5.0PV01	3	0.88	0.88	0.12	0.76	1.00	0.2752
MDR7.5PV01	3	0.72	0.76	0.08	0.63	0.77	0.2752
APTPV01	3	0.18	0.16	0.12	0.08	0.31	0.0495
BIOPV01	3	0.44	0.44	0.28	0.17	0.72	0.1266
SANDPV03	3	0.72	0.73	0.05	0.67	0.76	
FA5.0PV03	3	1.03	1.08	0.25	0.76	1.25	0.1266
MDR7.5PV03	3	0.55	0.53	0.13	0.43	0.69	0.1266
APTPV03	3	0.17	0.20	0.08	0.08	0.24	0.0495
BIOPV03	3	0.31	0.09	0.39	0.09	0.76	0.2683
SANDPV10	3	0.65	0.63	0.11	0.56	0.77	
FA5.0PV10	3	0.76	0.83	0.28	0.45	1.00	0.5127
MDR7.5PV10	3	0.53	0.53	0.09	0.43	0.62	0.1266
APTPV10	3	0.12	0.12	0.05	0.08	0.17	0.0495
BIOPV10	3	0.50	0.70	0.36	0.09	0.72	0.8273
SANDPV30	3	0.75	0.76	0.02	0.73	0.77	
FA5.0PV30	3	0.59	0.83	0.45	0.07	0.88	0.5127
MDR7.5PV30	3	0.29	0.40	0.19	0.07	0.40	0.0463
APTPV30	3	0.24	0.20	0.10	0.16	0.35	0.0495
BIOPV30	3	1.47	0.78	1.30	0.65	2.97	0.5127

3.4.7.3 Zinc

The averaged normalized effluent concentrations from each column are summarized in Table 50 for total Zn and Table 51 filtered Zn. Values were omitted for those sample concentrations that all measured BDL. Additionally, mass balances of total Zn in Table

52 and filtered Zn in Table 53 were estimated using the same calculations as the previous mass balances. Zn effluent masses with BDL data were assumed to be half of the DL.

Table 50: Averaged results and standard deviations for normalized effluent total zinc concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND			0.06 ± 0.10	0.38 ± 0.66
FA5.0	0.07 ± 0.01	0.06 ± 0.00	0.06 ± 0.01	0.06
MDR7.5	0.07 ± 0.06	0.09 ± 0.09	0.16 ± 0.15	0.05 ± 0.04
APT				
BIO				

Table 51: Averaged results and standard deviations for normalized effluent filtered zinc concentrations from each column.

	PV01 (C _e /C _i)	PV03 (C _e /C _i)	PV10 (C _e /C _i)	PV30 (C _e /C _i)
SAND		0.14 ± 0.23		
FA5.0	0.08 ± 0.02	0.08 ± 0.01	0.08 ± 0.01	0.07 ± 0.01
MDR7.5	0.07 ± 0.06	0.08 ± 0.07	0.05 ± 0.05	0.05 ± 0.04
APT				
BIO				

Table 52: Averaged results and standard deviations of estimated total zinc mass balances of each column.

	Zn _{in} (mg)	Zn _{out} (mg)	% Removed
SAND	0.656 ± 0.060	0.159 ± 0.250	73 ± 43
FA5.0	0.788 ± 0.009	0.045 ± 0.006	94 ± 1
MDR7.5	0.894 ± 0.026	0.065 ± 0.057	93 ± 6
APT	0.855 ± 0.031	0.002	99
BIO	0.921 ± 0.026	0.002	99

Table 53: Averaged results and standard deviations of estimated filtered zinc mass balances of each column.

	Zn _{in} (mg)	Zn _{out} (mg)	% Removed
SAND	0.702 ± 0.028	0.007 ± 0.010	99 ± 0.02
FA5.0	0.775 ± 0.005	0.051 ± 0.001	93
MDR7.5	0.897 ± 0.036	0.044 ± 0.036	95 ± 0.04
APT	0.873 ± 0.031	0.002	99
BIO	0.891 ± 0.016	0.002	99

SAND showed between 94% to 100% Zn removal in the first 10 PVs but declined to 62% by PV30, as seen in Figure 55. One effluent sample at PV30 had a total Zn concentration nearly equal to the influent, which skewed the average at this sampling point. SAND was also able to decrease between 86% to 100% of filtered Zn, as seen in Figure 56. The primary removal mechanism in SAND is likely precipitation due to the elevated pH. Surface adsorption may not be present due to the effluent pH being below the PZC of SAND. This would cause H^+ to compete with Zn^{2+} for adsorption sites.

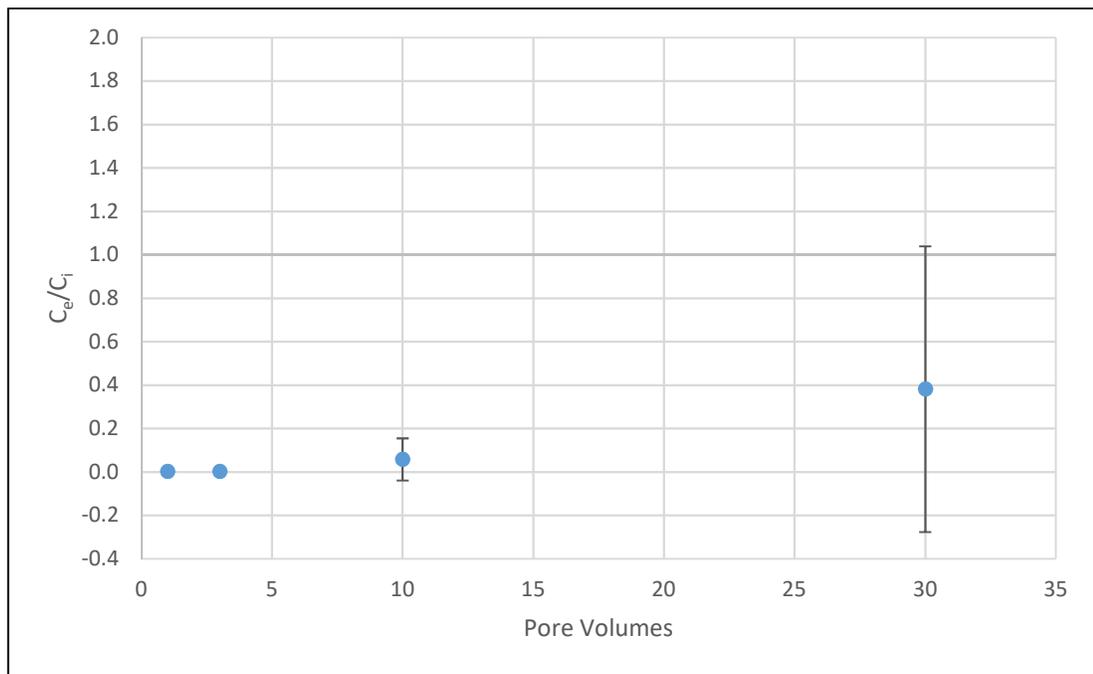


Figure 55: Normalized effluent total zinc concentrations of SAND columns.

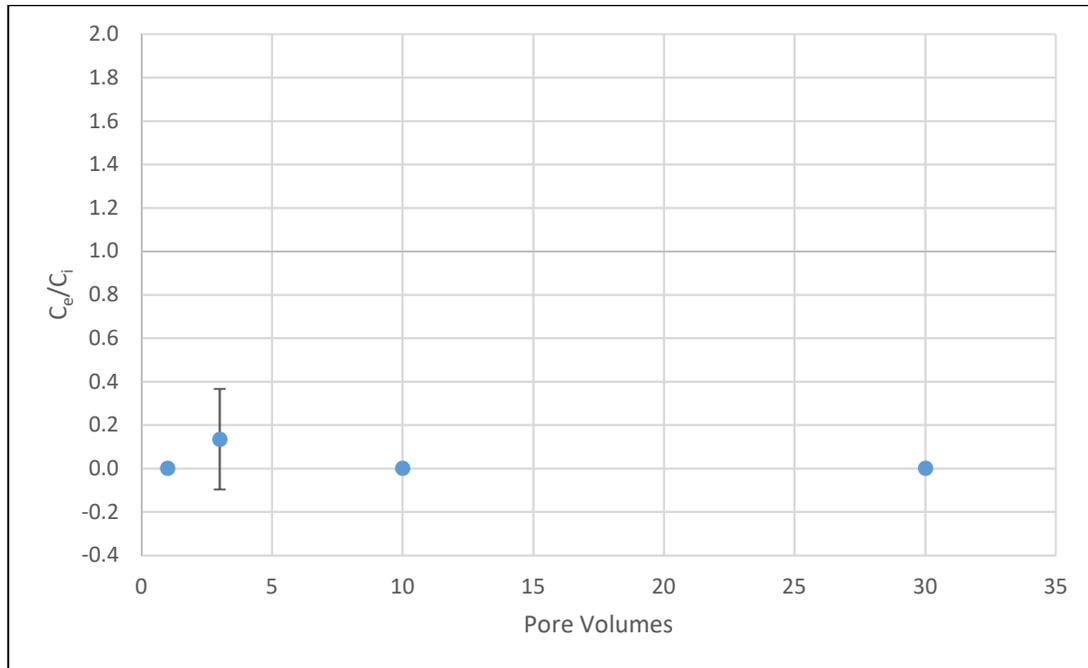


Figure 56: Normalized effluent filtered zinc concentrations of SAND columns.

FA5.0 showed over 93% removal of total and filtered Zn across all PVs, as seen in Figure 57 and Figure 58, respectively. Zn removal mechanisms in FA5.0 may include precipitation and surface adsorption due to elevated pH. Banerjee et al. (2003) observed pH dependent precipitation of Zn, where removal increased as pH increased. Additionally, Banerjee et al. (2003) observed enhanced surface adsorption due to increased speciation of AlO^- and SiO^- on FA surfaces, which readily bind to Zn^{2+} .

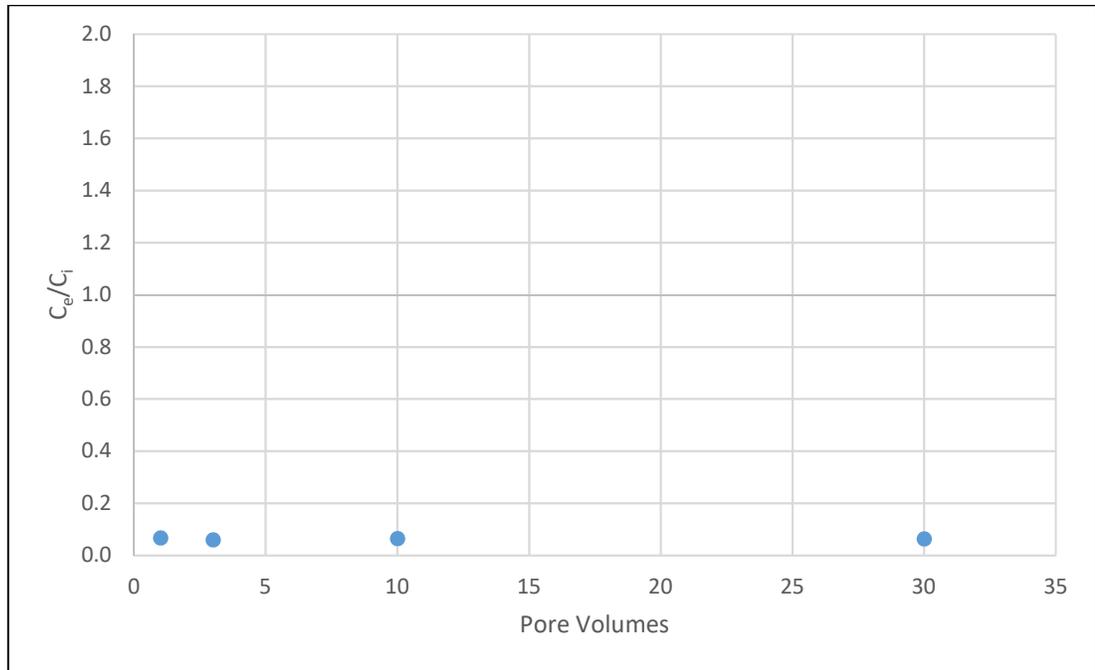


Figure 57: Normalized effluent total zinc concentrations of FA5.0 columns.

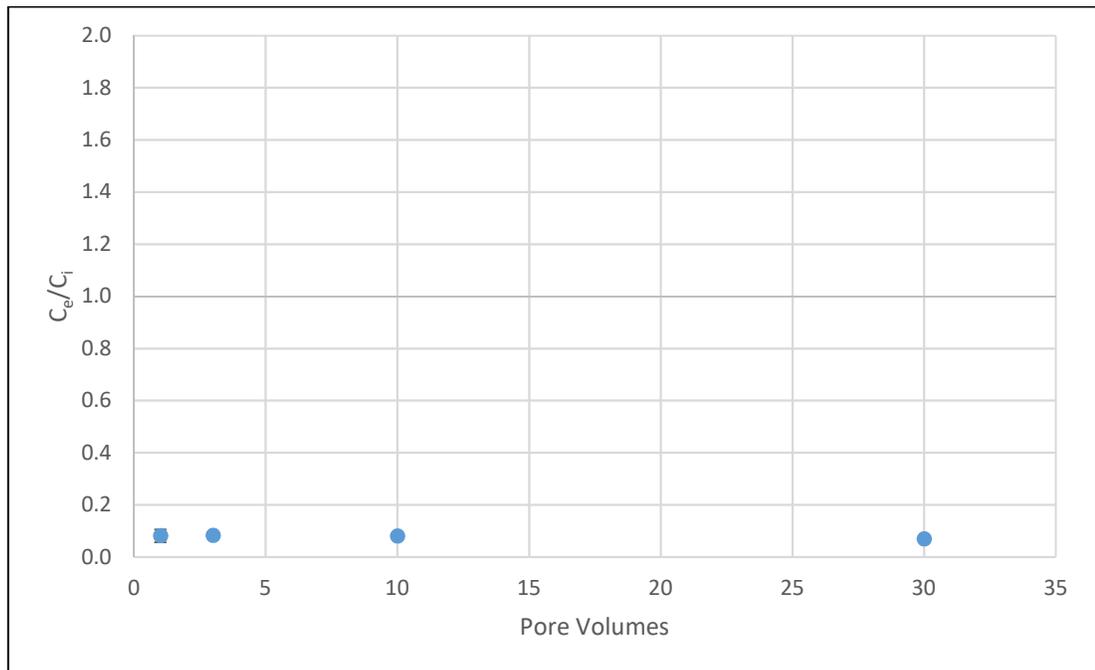


Figure 58: Normalized effluent filtered zinc concentrations of FA5.0 columns.

MDR7.5 was able to decrease total Zn concentrations at averages between 84% to 95% (Figure 59) and filtered Zn at averages between 92% to 95% (Figure 60). The primary removal mechanism in MDR7.5 is likely some precipitation and adsorption to the MDRs. Bolland et al. (1977) observed Zn precipitation at pH values above 7.3 as well as adsorption between pH values of five and nine. Additionally, Bolland et al. (1977) observed enhanced Zn^{2+} removal by adsorption in the presence of PO_4^{3-} , as well as the other way around. PO_4^{3-} adsorbed onto hydroxyl groups on goethite, creates additional adsorption sites for Zn^{2+} and at the same time, adsorbed Zn^{2+} creates adsorption sites for PO_4^{3-} (Bolland et al. (1977)). Because MDR7.5 showed great P removal, this may suggest possible enhancement of Zn removal (Table 28, Table 29, Table 30, and Table 31).

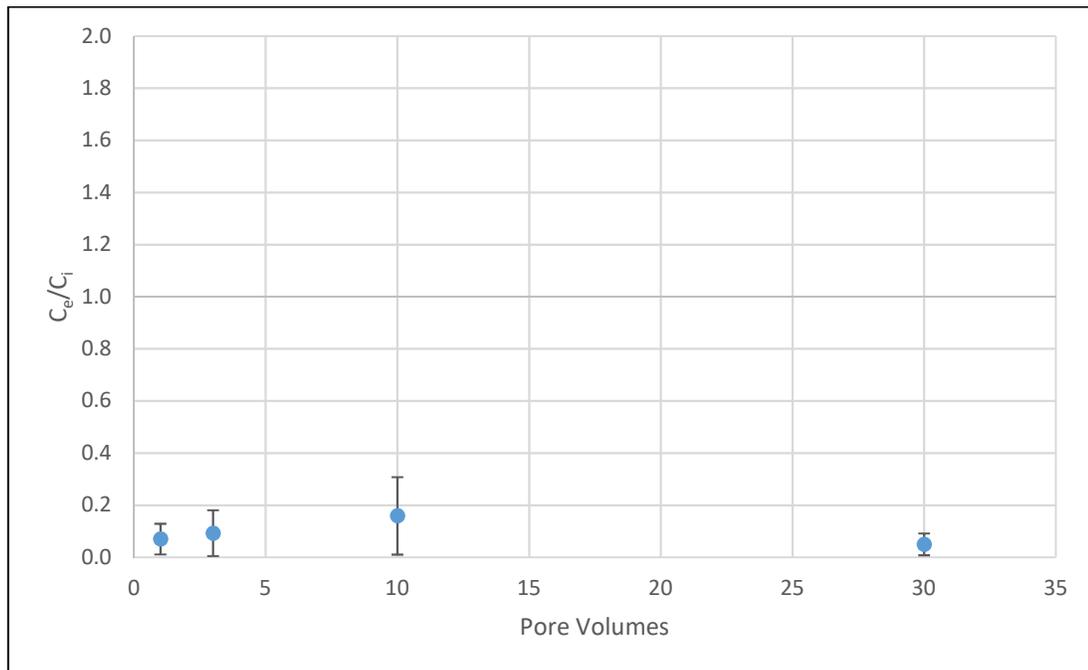


Figure 59: Normalized effluent total zinc concentrations of MDR7.5 columns.

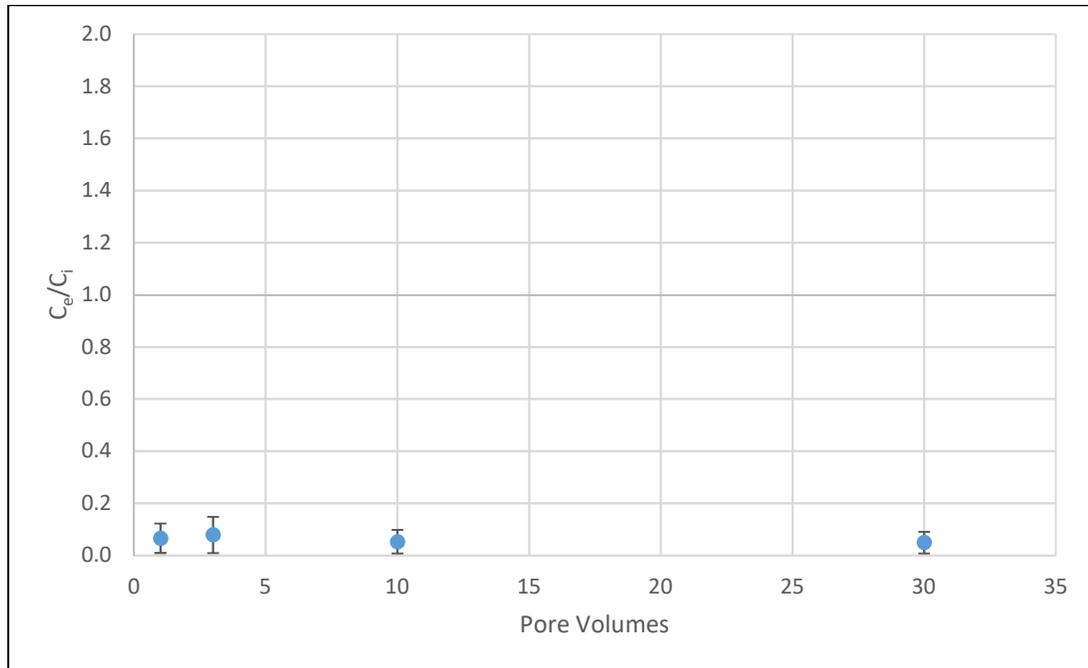


Figure 60: Normalized effluent filtered zinc concentrations of MDR7.5 columns.

APT (Figure 61 and Figure 62) and BIO (Figure 63 and Figure 64) both showed near complete removal of both total and filtered Zn. Bencheikh-Lehocine (1988) showed Zn removal by peat was attributed to complexation with humic substances. Additionally, Zn removal was enhanced with increasing pH by introducing precipitation as a removal mechanism and enhancing Zn-humic complexation. Because a layer of sand was placed in the last two-thirds of the columns, lengthwise, the effluent pH from APT and BIO columns may not be representative of the pH within the APT or BIO peat layers. The pH within the peat is most likely more acidic. However, additional “polishing” in the form of Zn precipitation may occur in the transition zone between the peat and sand, as well as within the sand layer from increases in pH.

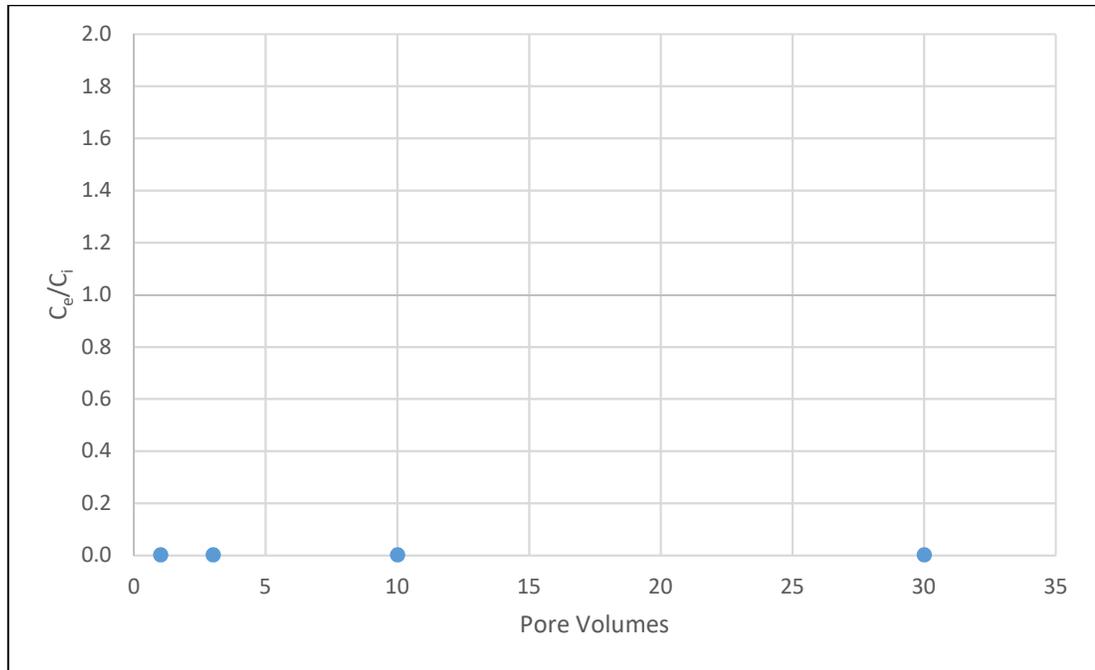


Figure 61: Normalized effluent total zinc concentrations of APT columns.

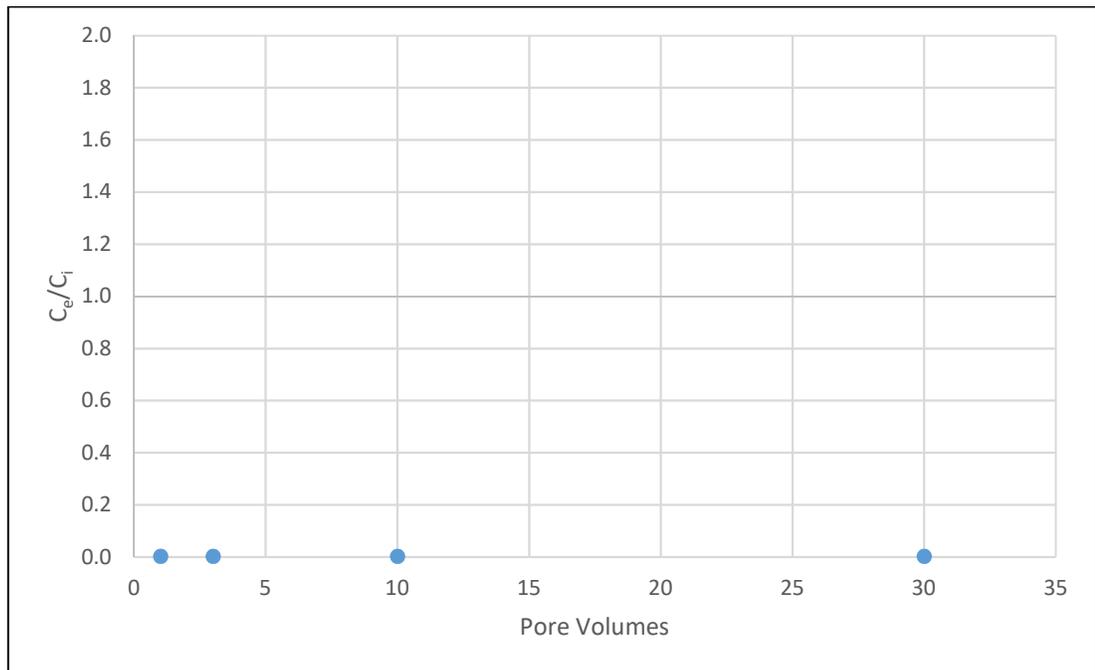


Figure 62: Normalized effluent filtered zinc concentrations of APT columns.

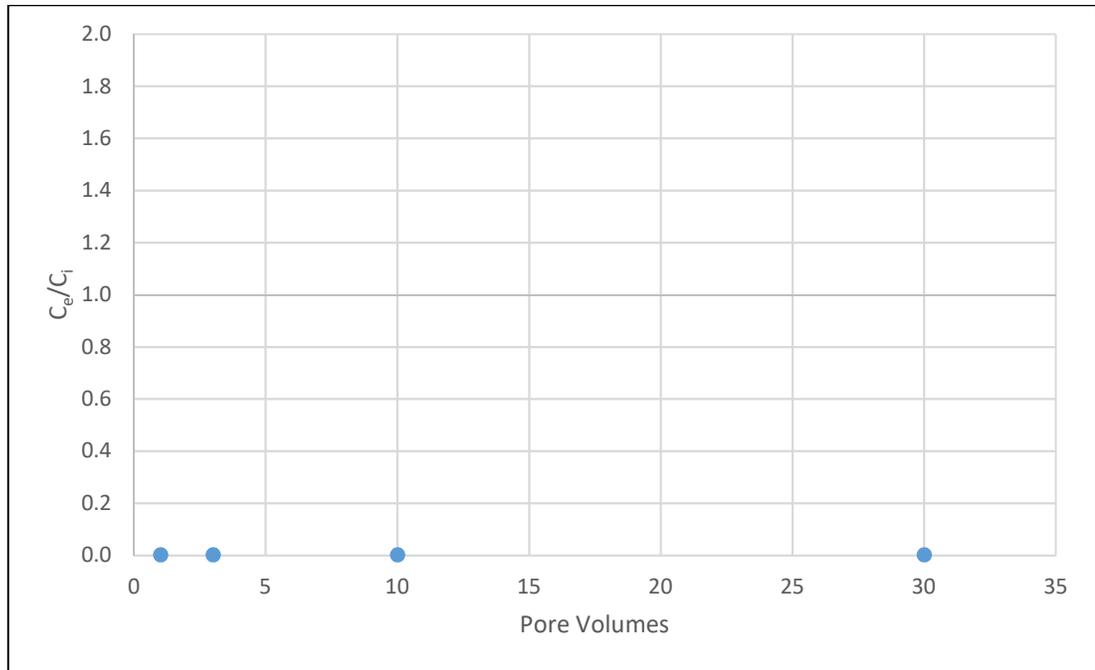


Figure 63: Normalized effluent total zinc concentrations of BIO columns.

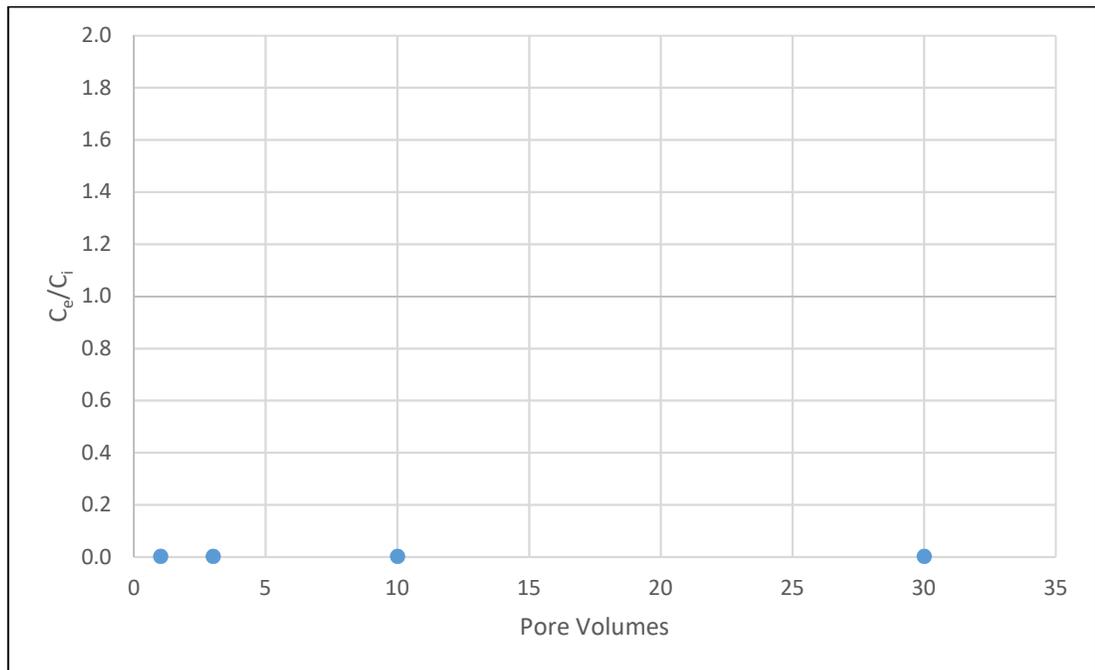


Figure 64: Normalized effluent filtered zinc concentrations of BIO columns.

3.5 Water Quality Criteria Exceedances

Recommended maximum limits for metals are available through the EPA National Recommended Water Quality Criteria (NRWQC) for Aquatic Life (EPA, 2018). These “criterion maximum concentrations” (CMC) are set as a function of hardness. Table 54 summarizes the number of hardness adjusted metals criteria exceedances by total metals in the effluent from the columns. Cr(III) and Cr(VI) were omitted from these exceedance counts because measurements consisted of total Cr rather than differentiating between the two Cr species. Some limitations to using the EPA NRWQC CMCs include being criteria for bodies of water and not discharges. Additionally, effluent data are representative of the laboratory columns and not field-scale BRCs. Hardness values and adjusted CMC for individual samples are found in (Appendix IX).

Table 54: Number of recommended water-quality metals criteria exceedances in column effluent samples (n=12).

	Ag	As	Cd	Cu	Pb	Hg	Ni	Se	Zn
SAND	12	0	0	11	12	0	0	4	1
FA5.0	12	3	1	9	0	0	0	1	0
MDR7.5	7	3	0	10	0	0	0	1	0
APT	11	0	0	12	0	0	0	6	0
BIO	11	0	0	12	5	0	0	3	0

3.6 Cost Analyses

The cost of the rain gardens at the Trailwoods residential neighborhood site in Norman, Oklahoma was \$29 per ft² in 2007. This cost is \$36 per ft² when adjusted for inflation to the year 2018 (Table 8). Using the EPA Opti-tool estimated pricing, the overall cost of BRC construction was \$126,083. This cost was calculated using the EPA pricing of \$15.46 per ft³ (\$16.08 per ft³ when converted to 2018 dollars). The WQV of 7,841 ft³

used in the cost estimate was calculated from assumptions of 2.5-acre runoff area, 90% impervious coverage, and one inch of rainfall. When converted to cost per ft², the EPA estimated cost was \$32 per ft². Table 55 summarizes the results of the cost analysis of different media if used in a BRC in Norman, OK. SAND, FA5.0, and MDR7.5 came out to be \$34.77, \$34.83, and \$35.31 per ft², respectively. Meanwhile APT and BIO came out to be \$60.04 per ft², nearly twice the cost of the other media as well as Trailwoods and the EPA Opti-tool estimate. The primary reason for the large price discrepancy between APT or BIO with SAND, FA5.0, and MDR7.5 is material transportation. Additionally, the maintenance costs per year were calculated based on a constant 6% of the construction cost. While APT and BIO maintenance costs were drastically greater than the other media, these costs are likely similar in real applications. Table 56 summarizes the costs of various existing BRCs in Oklahoma. The costs of the BRCs comprised of FA varied mainly due to varying planting costs, site conditions requiring tree removal and traffic control, and flat rates on material hauling and equipment use (Chavez, 2015).

Table 55: Cost analysis of different media in bioretention cells with itemized parameters and adjusted costs.

	SAND	FA5.0	MDR7.5	APT	BIO
Dimensions					
Width (ft)	5	5	5	5	5
Length (ft)	788	788	788	788	788
Total Area (ft ²)	3,940	3,940	3,940	3,940	3,940
Total Depth (ft)	1.5	1.5	1.5	1.5	1.5
Total Volume (ft ³)	5,910	5,910	5,910	5,910	5,910
Media Depth (ft)	0.5	0.5	0.5	0.5	0.5
Media Volume (ft ³)	1,970	1,970	1,970	1,970	1,970
#57 Stone Depth (ft)	0.5	0.5	0.5	0.5	0.5
#89 Stone Depth (ft)	0.25	0.25	0.25	0.25	0.25
6-inch Pipe Length (ft)	788	788	788	788	788
Construction Materials					
Media (\$)	7,880	7,890	8,390	36,800	36,800
#57 Stone (\$)	1,656	1,656	1,656	1,656	1,656
#89 Stone (\$)	621	621	621	621	621
6-inch Pipe (\$)	6,591	6,591	6,591	6,591	6,591
Fabric Liner (\$)	3,433	3,433	3,433	3,433	3,433
Vegetation, 65% Cover (\$)	6,243	6,243	6,243	6,243	6,243
Media Cover (\$)	644	644	644	644	644
Earthwork					
Excavation (\$)	1,431	1,431	1,431	1,431	1,431
Fill & Spread (\$)	311	311	311	311	311
Excavation Disposal (\$)	18,342	18,342	18,342	18,342	18,342
Transportation					
Media (\$)	583	721	873	6787	6787
#57 Stone (\$)	391	391	391	391	391
#89 Stone (\$)	195	195	195	195	195
Pre-Adjusted Construction Total (\$)	48,321	48,470	49,122	83,445	83,445
Cost of Required Land (\$)	2,416	2,423	2,456	4,172	4,172
Adjustments & Fees					
Developed Area Adjustment (\$)	101,475	101,786	103,157	175,235	175,235
Engineering Fees and Contingency (\$)	35,516	35,625	36,105	61,332	61,332
Adjusted Construction Total (\$)	136,991	137,412	139,261	236,567	236,567
Cost (\$ per ft ²)	34.77	34.88	35.35	60.04	60.04
O&M (\$/year)	3,044	3,054	3,095	5,257	5,257

Table 56: Costs of various existing bioretention cells with areas converted to square feet and costs adjusted for inflation (Coffman, 2014; Chavez, 2015).

Existing Bioretention Cell	Area (ft ²)	\$ per ft ²
Trailwoods Neighborhood Site, Norman, OK	3,940	36
Lendonwood Gardens, Grove, OK	248	47
Private Residence 1, Grove, OK	1,091	17
Private Residence 2, Grove, OK	324	30
Early Childhood Development Center, Grove, OK	518	28
Elm Creek Plaza, Grove, OK	680	26
Cherokee Queen Riverboats, Grove, OK	1,253	15
Grove High School, Grove, OK	1,609	15
Grand Lake Association, Grove, OK	1,858	23

3.7 Conclusions

3.7.1 Summary

All the objectives of this thesis were completed, which provided results and discussion on pollutant removal capabilities, material characterizations, and cost estimates of the reactive media. Overall, P and trace metals removal were observed in SAND, FA5.0, and MDR7.5. Trace metals removal was observed in APT and BIO, but P removal was poor or showed export. NO₃⁻ remained difficult to remove in all columns. Table 57 is a summarizes and organizes potential pollutant removal mechanisms by the reactive media.

Table 57: Summary of potential pollutant removal mechanisms by reactive media (Green=Removal; Red=Export; Gray=No Appreciable Change).

	SAND	FA5.0	MDR7.5	APT	BIO
Phosphorus	1. Calcium co-precipitation	1. Calcium co-precipitation	1. Calcium co-precipitation 2. Hydroxyl adsorption		1. Organic acid release
Nitrate					
Copper	1. Hydroxide/carbonate precipitation	1. Hydroxide/carbonate precipitation	1. Negative surface charge 2. Hydroxyl adsorption	1. Organic sorption 2. Hydroxide precipitation	1. Organic sorption 2. Hydroxide precipitation
Lead	1. Hydroxide precipitation	1. Hydroxide precipitation	1. Negative surface charge 2. Hydroxyl adsorption	1. Organic sorption 2. Hydroxide precipitation	1. Organic sorption 2. Hydroxide precipitation
Zinc	1. Hydroxide precipitation	1. Hydroxide precipitation 2. AlO ⁻ and SiO ⁻ adsorption	1. Negative surface charge 2. Hydroxyl adsorption	1. Organic sorption 2. Hydroxide precipitation	1. Organic sorption 2. Hydroxide precipitation

SAND showed some P removal abilities, but quickly declined by PV10 and PV30. FA5.0 and MDR7.5 showed similar P removal performance and both were able to remove a substantial amount of P across all PVs. APT and BIO performed poorly with P removal with BIO showing net export. Poor performance is likely due to TOC leaching, which is known to mobilize P, which may also be preexisting in APT and BIO.

Except for FA5.0, none of the columns showed appreciable ability to remove NO₃⁻. FA5.0 showed some ability to remove NO₃⁻ likely due to the formation of hydroxyapatite, which NO₃⁻ has an affinity toward. However, removable was not substantial because of competition for adsorption sites between other anions such as PO₄³⁻ and Cl⁻. Most N

export was associated with TOC in the form of organic N. NH_3 export was likely from preexisting NH_3 on media surfaces, which was eventually flushed or showed a decreasing trend in all cases. Some NO_3^- export from APT and BIO columns was suggested to be mineralized N from drying processes.

All columns showed the ability to remove at least 80% of total and filtered Cu, except for one effluent sample from FA5.0 columns. Surprisingly, SAND performed the best for Cu removal. The removal mechanism was likely precipitation, which was an important metals removal route, in general, for all columns. Among all metals, Pb was the most difficult to remove. APT performed the best with at least 77% removal of total Pb and 70% removal of filtered Pb. Filtered Pb was shown to have potential issues when sampling and analyzing. Outside of filtered Pb, MDR7.5 showed the ability to remove at least 45% of total Pb after the first PV. All columns removed a substantial amount of Zn, with APT and BIO removing nearly 100%. All other columns showed the ability to remove at least 90% of both total and filtered Zn. APT columns showed impressive ability to remove considerable amounts of all three metals that were studied. This is likely due to a variety of organic removal processes.

Although APT and BIO showed great metals removal capabilities overall, they are not suggested for BRC designs due to poor P and N removal performance and export in some cases. Because of signs of export, APT and BIO are likely to be internal sources of nutrients, which would be detrimental to runoff treatment in residential and agricultural settings. Implementing these media in BRCs would also increase construction costs by

nearly double. MDR7.5 and FA5.0 showed great abilities to remove P and metals. MDR7.5 and FA5.0 contributed a great deal of effluent hardness, compared to other media, which decreases the bioavailability of the metals. Hydroxyl-group adsorption was the primary mode of pollutant removal in MDR7.5, which suggested a two-fold pollutant removal enhancement where ternary complexes may have formed for P and Zn.

3.7.2 Concluding Remarks

Upon completion of the thesis objectives, the hypotheses were able to be addressed. The hypotheses were revisited and determined to be accepted or rejected. Based on the results and discussion, the conclusions for the hypotheses are as followed:

1. Effluents from laboratory treatment columns of all proposed reactive media will result in net decreases in Cu^{2+} , Pb^{2+} , and Zn^{2+} . Additionally, FA5.0 and MDR7.5 columns will result in net decreases in P. **ACCEPTED.**
2. Effluents from APT and BIO laboratory treatment columns will result in net decreases in NO_3^- . **REJECTED.**
3. Effluents from laboratory treatment columns of APTsorb and bioAPT will result in net increases in P concentrations. Due to the high composition of OM of peat, these media may be internal sources of nutrients (Liu et al., 2014; LeFevre et al., 2015). **ACCEPTED.**

3.7.3 Study Limitations and Recommendations

Based on the results of this research, FA5.0 and MDR7.5 showed great potential to remove nutrients and metals. The cost estimates of these media showed that their use can

yield comparable construction costs to existing BRCs. APT and BIO showed great metals removal capabilities but did not retain nutrients well and exported in many cases. These media can be applied if nutrient export is not a concern (likely based on determined total maximum daily loading of a water body). Additionally, the pricing of these products drastically increased the overall construction cost estimates of BRCs. Overall, several limitations of the column experiments were identified:

1. Synthetic stormwater was not created to entirely represent real stormwater water quality. This discounts for chemical interactions that may exist in the presence of other constituents such as particulate-associated pollutants, microbials, organic compounds, and other nutrients and metals.
2. Pollutant removal capacities of the media were not studied. This information would provide an idea of the lifetime of these media if used in BRCs. Additionally, knowing the media lifetime can allow for recurring media replacement frequencies and costs.
3. The pollutant removal data from this research is representative of columns, which were studied with more controls. Field-scale BRC experiments would account for variables that would be present in real-life BRC applications.

Based on the limitations, results, and discussion of this study, recommendations for further research were identified to provide more information to make BRC design recommendations. These recommendations include:

1. Field-scale BRC experiments using the reactive media used in this study.

2. Pollutant removal capacity experiments to determine pollutant breakthrough points of the reactive media.
3. Experiments that investigated the pollutant removal performance of nutrients and metals under reducing conditions.
4. Column experiments to investigate pollutant removal performance of the reactive media for other pollutants in urban stormwater, such as microbials and organic compounds.
5. Column experiments for APT and BIO amended with FA or MDRs to potentially improve their nutrient and metals removal capabilities.

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APPENDICES

Appendix I: Quikrete Product Data Sheets


CEMENT & CONCRETE PRODUCTS™

QUIKRETE® SAND & GRAVEL PRODUCTS

DIVISION 32

Aggregate
32 15 00

PRODUCT DESCRIPTION
QUIKRETE® provides a variety of sands and gravels for general and special uses as follows:



All Purpose Sand #1152:
A general use sand suitable for use as a fine aggregate in concrete, underlayment for brick pavers, traction on snow and ice, and mixing with potting soil. *Meets ASTM C33, Standard Specification for Concrete Aggregates.*
Sizes: 50 lb (22.6 kg) – 56 bags per pallet 70 lb (31.7 kg) – 42 bags per pallet



Play Sand #1113:
Is specially graded sand that has been washed, and screened for use in children's sandboxes. It is best used when kept damp.
Sizes: 50 lb (22.6 kg) – 56 bags per pallet



All Purpose Gravel #1151:
High quality clean gravel with an approximate top size of 3/8" (10 mm). Suitable for landscaping, concrete manufacture and a variety of other purposes. *Meets ASTM C33, Standard Specification for Concrete Aggregates.*
Sizes: 50 lb (22.6 kg) – 56 bags per pallet

Deco Pebbles # 9905-50
Use for landscaping around patios, decks, gardens, etc.

Marble Chips # 9906-50
Use for landscaping around patios, decks, gardens, etc.



Tubesand #1159:
This sand is designed in a tube shaped bag that fits along side the rear axle, above the wheel wells, or in the bed of a pick up truck. It is used for traction and vehicle weight for winter driving conditions.
Size: 60 lb (27.2 kg) – 42 bags per pallet

WARRANTY
The QUIKRETE® Companies warrant this product to be of merchantable quality when used or applied in accordance with the instructions herein. The product is not warranted as suitable for any purpose or use other than the general purpose for which it is intended. Liability under this warranty is limited to the replacement of its product (as purchased) found to be defective, or at the shipping companies' option, to refund the purchase price. In the event of a claim under this warranty, notice must be given to The QUIKRETE® Companies in writing. This limited warranty is issued and accepted in lieu of all other express warranties and expressly excludes liability for consequential damages.

The QUIKRETE® Companies
One Securities Centre
3490 Piedmont Rd., NE, Suite 1300, Atlanta, GA 30305
(404) 634-9100 • Fax: (404) 842-1425

* Refer to www.quikrete.com for the most current technical data, SDS, and guide specifications

Figure I-1: Quikrete® All Purpose Sand product data sheet.

2.1 Classification of the substance or mixture

Carcinogen – Category 1A
Specific Target Organ Toxicity Single Exposure – Category 3
Specific Target Organ Toxicity Repeat Exposure – Category 1
Eye Irritant – Category 2B

2.2a Signal word DANGER!

2.2b Hazard Statements

May cause cancer through chronic inhalation
May cause respiratory irritation
Causes damage to lungs through prolonged or repeated inhalation
Causes eye irritation if particles or dust get in eye

Industrial hygiene experts have studied long-term daily use of silica sands in sand-blasting and other occupations generating extreme volumes of dust. They have determined that long term, daily exposure to high concentrations of blasting sand dust causes damage to the lungs, may cause silicosis, and may cause cancer. **Do not use for sand blasting.** There are extensive OSHA precautions required for sand blasting.

2.2c Pictograms



2.2d Precautionary statements

Do not handle until all safety precautions have been read and understood.
Wear protective gloves, eye protection, and protective clothing.
Do not eat, drink or smoke when using this product.
Wash thoroughly after handling.
Use only in a well-ventilated area.
Do not breathe dust.

If inhaled: Remove person to fresh air and keep comfortable for breathing.
If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

Immediately seek medical advice or attention if symptoms are significant or persist.

Figure I-3: Quikrete® All Purpose Sand safety data sheet (2 of 9).

Dispose of contents/containers in accordance with all regulations.

2.3 Additional Information

2.3a HNOC – Hazards not otherwise classified: Not applicable

2.3b Unknown Acute Toxicity: None

SECTION III - HAZARDOUS INGREDIENTS/IDENTITY INFORMATION

<u>Hazardous Components</u>	<u>CAS No.</u>	<u>% by Weight</u>
Sand, Silica, Quartz	14808-60-7	100

SECTION IV – FIRST AID MEASURES

4.1 Description of the first-aid measures

General information:

After inhalation: Remove person to fresh air and keep comfortable for breathing.

After skin contact: Rinse skin with water.

After eye contact: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

After swallowing: If conscious, have the victim drink plenty of water and call a physician immediately. Never give anything by mouth to an unconscious person.

4.2 Most important symptoms/effects, acute and delayed

Inhalation: May cause respiratory tract irritation. Causes damage to organs through prolonged or repeated inhalation. This product contains crystalline silica. Prolonged or repeated inhalation of respirable silica from this product can cause silicosis.

Skin contact: Causes mechanical skin irritation.

Eye Contact: Causes eye irritation if particles or dust get in eye.

Ingestion: Ingestion of large quantities may cause discomfort and/or distress, nausea or vomiting.

4.3 Indication of immediate medical attention and special treatment needed:

Immediately seek medical advice or attention if symptoms are significant or persist.

SECTION V - FIRE FIGHTING MEASURES

5.1 Flammability of the Product: Non-flammable and non-combustible

5.2 Suitable extinguishing agents: Treat for surrounding material

5.3 Special hazards arising from the substance or mixture: None

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5/30/2017

Figure I-4: Quikrete® All Purpose Sand safety data sheet (3 of 9).

5.3a Products of Combustion: None
5.3b Explosion Hazards in Presence of Various Substances: Non-explosive in presence of shocks

SECTION VI – ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures: Wear personal protective equipment (See section VIII). Keep unprotected persons away.

6.2 Methods and material for containment and cleaning up:
 Do not allow to enter sewers/ surface or ground water. Dispose of unwanted materials and containers properly in accordance with all regulations.

SECTION VII - PRECAUTIONS FOR SAFE HANDLING AND STORAGE

7.1 Handling

Precautions for safe handling: Do not use for sand blasting. There are extensive OSHA precautions required for sand blasting. Ensure good ventilation/exhaustion at the workplace. **DO NOT BREATHE DUST.** In dusty environments, the use of an OSHA, MSHA or NIOSH approved respirator and tight fitting goggles is recommended. Wear appropriate PPE (See section 8). Do not mix with other chemical products, except as indicated by the manufacturer. Do not get in eyes, on skin or clothing. Good housekeeping is important to prevent accumulation of dust.

7.2 Storage

Requirements to be met by storerooms and receptacles: No special requirements.
Information about storage in one common storage facility: Not required.
Further information about storage conditions: Keep out of the reach of children.

SECTION VIII – EXPOSURE CONTROL MEASURES / PERSONAL PROTECTION

8.1 Components with limit values that require monitoring at the workplace:

Hazardous Components	CAS No.	PEL (OSHA) mg/M ³	TLV (ACGIH) mg/M ³
Silica Sand, crystalline	14808-60-7	0.1	0.025 (resp)

8.2 Exposure Controls

Use ventilation adequate to keep exposures below recommended exposure limits.

8.3 General protective and hygienic measures

Keep away from foodstuffs, beverages and feed. Immediately remove all soiled and contaminated clothing. Wash hands before breaks and at the end of work. Avoid contact with the eyes and skin.

Figure I-5: Quikrete® All Purpose Sand safety data sheet (4 of 9).

8.3a Personal protective equipment

Protection of hands:

Wear gloves of adequate length to offer appropriate skin protection from incidental contact. General duty work gloves have been found to offer adequate protection for most intended uses.

Eye protection:

Wear approved eye protection properly fitted dust- proof chemical safety glasses.

Respiratory protection:

A NIOSH-approved dust mask or filtering face piece is recommended in poorly ventilated areas or when permissible exposure limits may be exceeded. Respirators should be selected by and used under the direction of a trained health and safety professional, following requirements found in OSHA's respirator standard (29 CFR 1910.134) and ANSI's standard for respiratory protection (Z88.2).

SECTION IX - PHYSICAL/CHEMICAL CHARACTERISTICS

General Information

Appearance	Form: Granular Solid Color: Varies Odor: None
pH-value at 20°C (68 °F):	Not applicable
Boiling point/Boiling range:	Not applicable
Flash point:	Not applicable
Auto igniting:	Product is not self-igniting
Vapor pressure at 21°C (70°F)	Not applicable
Density at 25°C (77 °F):	2.5-2.8

Solubility in / Miscibility with

Water:	Insoluble
VOC content:	0 g/L VOC

SECTION X – STABILITY AND REACTIVITY

10.1 Reactivity

No dangerous reaction known under conditions of normal use.

10.2 Chemical stability

Stable under normal storage conditions. Keep in dry storage.

10.3 Possibility of hazardous reaction

No dangerous reaction known under conditions of normal use.

10.4 Thermal decomposition / conditions to be avoided

No decomposition if used according to specifications.

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5/30/2017

Figure I-6: Quikrete® All Purpose Sand safety data sheet (5 of 9).

10.5 Incompatible materials

Contact of silica with powerful oxidizing agents such as fluorine, chlorine trifluoride, manganese trioxide, or oxygen difluoride may cause fires

10.6 Hazardous Decomposition or By-products

Silica will dissolve in Hydrofluoric Acid and produce a corrosive gas – silicon tetrafluoride.

SECTION XI – TOXICOLOGICAL INFORMATION

11.1 Exposure Routes: Inhalation, skin contact, eye contact, or ingestion.

11.2 Symptoms related to physical/chemical/toxicological characteristics:

Inhalation: May cause respiratory tract irritation. Causes damage to organs through prolonged or repeated exposure. This product contains crystalline silica. Prolonged or repeated inhalation of respirable silica from this product can cause silicosis.

Skin contact: May cause mechanical skin irritation.

Eye Contact: Causes eye irritation if particles or dust gets in eye.

Ingestion: Ingestion of large quantities may cause discomfort and/or distress.

11.3 Delayed, immediate and chronic effects of short-term and long-term exposure

Short Term

Skin Corrosion/Irritation: Not applicable

Serious Eye Damage/Irritation: Causes eye irritation if particles or dust gets in eye

Respiratory Sensitization: Not applicable

Skin Sensitization: Not applicable

Specific Target Organ Toxicity-Single Exposure: (Category 3) May cause respiratory irritation

Aspiration Hazard: Not applicable

Long Term

Carcinogenicity: May cause cancer through chronic inhalation.

Germ Cell Mutagenicity: Not applicable

Reproductive Toxicity: Not applicable

Specific Target Organ Toxicity- Repeated Exposure: (Category 1) Causes damage to lungs through prolonged/repeated exposure

Synergistic/Antagonistic Effects: Not applicable

SECTION XII – ECOLOGICAL INFORMATION

12.1 Ecotoxicity

No further relevant information available.

12.2 Persistence and degradability

No further relevant information available.

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Figure I-7: Quikrete® All Purpose Sand safety data sheet (6 of 9).

12.3 Bioaccumulative potential:
No further relevant information available.

12.4 Mobility in soil
No further relevant information available.

12.5 Other Adverse Effects
No further relevant information available.

SECTION XIII – DISPOSAL CONSIDERATIONS

13.1 Waste Disposal Method
The packaging and material may be land filled; however, material should be covered to minimize generation of airborne dust. This product is not classified as a hazardous waste under the authority of the RCRA (40CFR 261) or CERCLA (40CFR 117&302). Disposal must be made in accordance with local, state and federal regulations.

13.2 Other disposal considerations
Uncleaned packaging
Recommendation: Disposal must be made in accordance with local, state and federal regulations.
Recommended cleansing agent: Water, if necessary with cleansing agents.

SECTION XIV – TRANSPORT INFORMATION

	DOT (U.S.)	TDG (Canada)
UN-Number	Not Regulated	Not Regulated
UN proper shipping name	Not Regulated	Not Regulated
Transport Hazard Class(es)	Not Regulated	Not Regulated
Packing Group (if applicable)	Not Regulated	Not Regulated

14.1 Environmental hazards:
Not applicable

14.2 Transport in bulk according to Annex II of Marpol 73/78 and the IBC Code
Not applicable

14.3 Special precautions for user
Do not handle until all safety precautions have been read and understood.

SECTION XV – OTHER REGULATORY INFORMATION

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Figure I-8: Quikrete® All Purpose Sand safety data sheet (7 of 9).

15.1 Safety, Health and Environmental Regulations/Legislations specific for the chemical

Canada

WHMIS Classification: Considered to be a D2A and D2B hazardous material under the Hazardous Products Act as defined by the Controlled Products Regulations and subject to the requirements of Health Canada's Workplace Hazardous Material Information (WHMIS). This document complies with the WHMIS requirements of the Hazardous Products Act (HPA) and the CPR.

15.2 US Federal Information

SARA 302/311/312/313 Components

No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302, 311, 312 or 313.

RCRA: Crystalline silica (quartz) is not classified as a hazardous waste under the Resource Conservation and Recovery Act, or its regulations, 40 CFR §261 et seq.

CERCLA: Crystalline silica (quartz) is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR §302.

Emergency Planning and Community Right to Know Act (SARA Title III): Crystalline silica (quartz) is not an extremely hazardous substance under Section 302 and is not a toxic chemical subject to the requirements of Section 313.

FDA: Silica is included in the list of substances that may be included in coatings used in food contact surfaces, 21 CFR §175.300(b)(3)(xxvi).

NTP: Respirable crystalline silica, primarily quartz dusts occurring in industrial and occupational settings, is classified as Known to be a Human Carcinogen.

OSHA Carcinogen: Crystalline silica (quartz) is not listed.

15.3 State Right to Know Laws

California Prop. 65 Components

WARNING: This product contains chemicals known to the State of California to cause cancer.

California Inhalation Reference Exposure Level (REL): California established a chronic REL of 3 µg for silica (crystalline, respirable). A chronic REL is an airborne level of a substance at or below which no adverse health effects are anticipated in individuals indefinitely exposed to the substance at that level.

Massachusetts Toxic Use Reduction Act: Silica, crystalline (respirable size, <10 microns) is "toxic" for purposes of the Massachusetts Toxic Use Reduction Act.

Figure I-9: Quikrete® All Purpose Sand safety data sheet (8 of 9).

15.4 Global Inventories

DSL All components of this product are on the Canadian DSL list.

TSCA No.: Crystalline silica (quartz) appears on the EPA TSCA inventory under the CAS No. 14808-60-7. All constituents are listed in the TSCA inventory.

SECTION XVI – OTHER INFORMATION

Last Updated: May 30, 2017

NOTE: The information and recommendations contained herein are based upon data believed to be correct. However, no guarantee or warranty of any kind, express or implied, is made with respect to the information contained herein. We accept no responsibility and disclaim all liability for any harmful effects which may be caused by exposure to silica contained in our products.

Prepared by

The QUIKRETE Companies, LLC

End of SDS

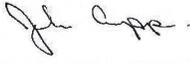
Figure I-10: Quikrete® All Purpose Sand safety data sheet (9 of 9).

Appendix II: Fly Ash Material Composition Analysis Report

Analytical Testing Service Laboratories, Inc.			
P.O. Box 1118, Joplin, Missouri 64802 (417) 782 6573			
Fly Ash Direct 4228 Airport Rd. Cincinnati, OH 45226 (513) 646-7577	March 09, 2017		
Attn: Scott Keith			
Re: 29400 - GRDA/Chouteau Fly Ash - 2000 Ton Composite - Unit 1 - 1/19-2/2/2017			
	AASHTO-M295 Class "C" <u>Requirements</u>	ASTM C-618 Class "C" <u>Requirements</u>	<u>Actual</u>
Fineness (+325 Mesh)	34% Max	34% Max	10.20%
Fineness Variation	5.0% Max	5.0% Max	4.70%
Moisture Content	3.0% Max	3% Max	0.08%
Density g/cm ³ C188	****	****	2.75
Density Variation	5.0% Max	5.0% Max	3.67%
Loss on Ignition	5.0% Max	6% Max	0.10%
Soundness	0.8% Max	0.8% Max	0.04%
S.A.I., 7 Days	75% Min	75% Min	98.80%
S.A.I., 28 Days	75% Min	75% Min	101.60%
Water Req. % Control	105% Max	105% Max	92.60%
Silica SiO ₂	****	****	37.61%
Aluminum Oxide Al ₂ O ₃ w/minor oxides	****	****	20.00%
Ferric Oxide Fe ₂ O ₃	****	****	6.15%
Total	50% Min	50% Min	63.76%
Sulfur Trioxide SO ₃	5% Max	5.0% Max	1.00%
Calcium Oxide CaO	****	****	26.88%
Magnesium Oxide MgO	****	****	5.06%
Available Alkalies Na ₂ O	1.50% Max	****	1.16%

We certify the above was tested in accordance with ASTM C-618 & AASHTO M295.

Analytical Testing Service Laboratories, Inc.



John K. Cupp, Manager

Figure II-1: Fly ash material composition report.

Appendix III: American Peat Technology Product and Safety Data Sheets



AMERICAN PEAT TECHNOLOGY, LLC

PRODUCT DATA SHEET



APTsorb is an innovative, environmentally-friendly sorption media for dissolved heavy metals. It is made of physically-, thermally-, and chemically-modified red-sedge peat harvested from the abundant reserves of North America. It capitalizes on the known sorption mechanisms and capacities of natural peat while improving on those qualities that have limited peat’s use in wastewater treatment in the past.

APTsorb is a low-cost alternative to traditional resins and excels in applications such as polishing prior to discharge, storm water treatment, and waste water with low pH.

PROPERTIES¹

Physical form	Granules
Matrix	Reed-sedge peat
Mechanisms of sorption	Chemical: ion-exchange, chemisorption, complexation Physical: surface adsorption Combination: adsorption-complexation
Ionic form	H ⁺ , Na ⁺
Total capacity ²	44.5 meq/100 g
Capacity at 50 ppb equilibrium ³	14 meq/100 g
Bulk density	0.7 g/cm ³
Particle size	12 X 50 mesh (>90 percent of granules)
Particle density	1.55 g/cm ³
Moisture content as shipped	9-14 percent
Expansion	up to 65 percent
pH of media ¹	4.9-5.2
Ash content	15-17 percent

Figure III-1: APTsorb product data sheet (1 of 2).

SUGGESTED OPERATING CONDITIONS

Maximum operating temperature	77°C (170°F)
pH of water	4 - 7.5
Recommended flow velocity m/h	Up to 1
Column pretreatment	Flush with five bed volumes clean water, discharge to drain
Regeneration	Not recommended
Sparging/fluffing	Water, air, CO ₂ or N ₂
Expansion precautions	Pre-wet media or allow for expansion, air sparge if needed

ELEMENTAL ANALYSIS

Element		Element	(ppm)	Element	(ppm)	Element	(ppm)
C	48 – 52 %	Be	<1	Li	<5	Na	<4800
H	4 – 5 %	B	<20	Mg	<1200	Sr	<18
N	2 – 3 %	Cd	<7	Mn	<31	Tl	<10
O	29 – 35 %	Ca	<5100	Hg	<60 ppb	Sn	<10
	(ppm)	Cr	<7	Mo	<3	Ti	<100
Al	<3500	Co	<2	Ni	<7	V	<6
Sb	<5	Cu	<6	K	<550	Zn	<10
As	<4	Fe	<3900	Se	<2		
Ba	<65	Pb	<7	Ag	<2		

¹ Test methods available upon request

² Measured using cadmium ion (22-25 mg of Cd/g)

³ Measured using cadmium ion (5-8 mg of Cd/g)

AMERICAN PEAT TECHNOLOGY, LLC

36203 350th AVE • AITKIN, MN, 56431
OFFICE - 218.927.7888 • FAX - 218.927.3272
WWW.AMERICANPEATTECH.COM

APTSorb is a trademark of American Peat Technology, LLC, Aitkin, Minnesota.

The user of this product must comply with all safety and regulatory standards. Consult your APT representative for further operating or usage information.

American Peat Technology makes no warranties as to the accuracy of these data and excludes any liability upon American Peat Technology arising out of the use, storage or disposal of its products. Suitable uses must be determined by the purchaser. Suggested uses should not be understood as recommending the use of our product in violation of any patent or as license to use the patents of American Peat Technology, LLC. Material Safety Data Sheets are available on request or can be downloaded from American Peat Technology's website.

Figure III-2: APTSorb product data sheet (2 of 2).

Section I. Identification and Company Information
SDS Name: APT[®]sorb

Synonyms: Peat, organic peat, reed-sedge peat

Recommended use: Water filtration media

Restrictions on use: none

Preparer's/Manufacturer's Name: American Peat Technology, LLC
 36203 350th Ave.
 Aitkin, MN 56431

Emergency Number: 218-927-1888

Section II. Hazards Identification

No known GHS hazards

Section III. Composition and Information on Ingredients

CAS #	Chemical name	Percent
Not available	Reed sedge peat	95 - 100
471-34-1	Calcium carbonate (ag lime)	0 - 5

Section IV. First Aid Measures
Eyes: Dust may cause mechanical irritation. Flush eyes with water for at least 15 minutes.

Inhalation: Dust may cause irritation of the upper respiratory tract. Move to fresh air. Seek medical attention if exposure results in difficulty breathing.

Skin: Not absorbed through skin.

Ingestion: Not available.

Section V. Fire Fighting Measures
General information: Will burn if involved in a fire.

Extinguishing media: Any available. **CAUTION:** Burning may continue inside bags or if material is piled. After fire is extinguished, spread material to assure that the material is not smoldering or starting to reheat.

Combustion products: Thermal decomposition products are those commonly observed with natural products such as wood or vegetable matter.

Special protective firefighting equipment and precautions: No special equipment or precautions necessary.

Dust explosion hazard: Per ASTM E1226, dust from APT[®]sorb is in the St 1 class with a $K_{st,max}$ of 78 m²-bar/s.

Figure III-3: APT[®]sorb safety data sheet (1 of 3).

Section VI. Accidental Release Measures

Precautions and equipment: No special equipment or precautions. Avoid generating dust.
Environmental precautions: None
Methods for containment: Vacuum or sweep up material and place in a suitable container.

Section VII. Handling and Storage

Handling: Minimize dust generation. Use a NIOSH-approved N95 particulate mask and/or eye protection if conditions are dusty.
Storage: Store in a dry place away from sources of ignition. Keep dry. If product gets wet, molding can occur. Periodically check bags for signs of internal heating.

Section VIII. Exposure Control and Personal Protection

Exposure limits: OSHA PEL: 15 mg/m³ (total, inert dust)
Engineering controls: Transfer product in a well-ventilated area to minimize dust accumulation.
Personal protective equipment
Eyes: Wear appropriate eyewear to protect against dust when transferring dry product.
Respirators: Use a NIOSH-approved N95 particulate mask to protect against dust when transferring dry product.

Section IX. Physical and chemical properties

Appearance: solid, brown, granular or fine grind	Odor: smoky, humic (no threshold)
pH: 4.9 – 7.0	Freezing/melting point: Not available
Boiling point: Not available	Flash point: Not available
Evaporation rate: Negligible	
Flammability: Not available	
Flammable limit (upper, lower): Not available	
Explosivity: (per ASTM E1226) P _{max} : 8.1 bar; (dP/dt) _{max} : 286 bar/s; K _{max} : 78 m-bar/s	
Vapor pressure: Not available	
Vapor density: Not available	
Specific gravity: 0.7	
Solubility: insoluble in water	
Autoignition temperature: 500° F (260° C)	
Decomposition temperature: Not available	

Section X. Stability and Reactivity

Reactivity: Not reactive
Chemical stability: Stable under normal temperatures and pressures.
Conditions to avoid: Dust generation, excess heat.
Incompatibilities with other materials: Has not been reported
Hazardous decomposition products: Thermal decomposition releases carbon monoxide, carbon dioxide, hydrocarbons

APTSorb SDS; American Peat Technology, Aitkin, MN

Figure III-4: APTSorb safety data sheet (2 of 3).

Section XI. Toxicological information	
<p>Routes of exposure: inhalation, eyes Symptoms of exposure: mechanical irritation of upper respiratory tract, eyes RTECS #: This material is not listed in the RTECS index. Effects of acute exposure: Dust may cause respiratory distress Effects of chronic exposure: Not available LD50/LC50: Not available Carcinogenicity: Not listed by OSHA, IARC, NTP or ACGIH Reproductive toxicity: Not available Teratogenicity: Not available Mutagenicity: Not available</p>	
Section XII. Ecological Information	
<p>APTsorb is derived from natural peat and has no known ecotoxicity or bioaccumulation potential.</p>	
Section XIII. Disposal Considerations	
<p>Chemical waste generators must determine if the used material is classified as a hazardous waste under EPA guidelines 40 CFR Parts 261.3. Generators must also consult state and local regulations.</p>	
Section XIV. Transport Information	
<p>UN Number: None US DOT: Not regulated</p>	<p>Special precautions: None Canada TDG: Not regulated</p>
Section XV. Regulatory Information	
<p>UNITED STATES TSCA: This material is not listed on the TSCA inventory. SARA Sections 302 and 304: This material is not listed as an EHS. EPCRA: This material is reportable under Section 313. CERCLA: This material does not have a reportable quantity. RCRA: This material is not listed on the RCRA lists. CAA: This material does not contain any hazardous air pollutants. CWA: This material is not listed as a hazardous substance, priority pollutant or toxic pollutant by the Clean Water Act.</p> <p>CANADA WHMIS: This product is not classified by the Controlled Products Regulations. DSL/NDSL: This material is not listed on the DSL or NDSL. However, there is no control measure imposed to this substance.</p>	
Section XVI. Additional Information	
<p>SDS creation date: 10/29/14; Revised: 01/15/15; 03.06.15</p> <p style="text-align: right;">APTsorb SDS; American Peat Technology, Aitkin, MN</p>	

Figure III-5: APTsorb safety data sheet (3 of 3).



PRODUCT DATA SHEET



BioAPT is the industry standard for granular and powdered microbial carriers. It is made from reed-sedge peat harvested from the abundant reserves of North America. Its humic substrate helps to minimize the shock of transition from the bag to the field while its high water retention capacity protects delicate microbes from desiccation. It is adaptable to a wide variety of formulations and displays excellent nutrient retention and shelf life. Once inoculated, the media is proven to sustain and multiply microbial growth for over a year.

PROPERTIES¹

Physical form	Granular	Powdered
Matrix	Reed-sedge peat	Reed-sedge peat
Bulk density	0.65 g/cm ³ or 40.6 lbs/ft ³	0.72 g/cm ³ or 45 lbs/ft ³
Particle size	10 X 50 mesh (>98 percent of media)	≤100 mesh (95 percent of media)
Uniformity coefficient (C _u)	1.75	6.2
Particle density	1.60 g/cm ³	ND
Moisture content as shipped	9 – 14 percent	9 – 14 percent
pH of media	6.2 – 7.0	6.2 – 7.0
Ash content	15 – 17 percent	15 – 17 percent

Powdered bioAPT has tested negative for the presence of salmonella and hydrogen-sulfide-producing enterobacteria. *Fusarium*, *Phytophthora*, *Pythium*, *Rhizoctonia* and *Sclerotinia* spp. were not recovered by standard cultural methods. Fecal coliform: <0.3 MPN/gm. Yeast: <10 cfu/gm. Mold: 100 cfu/gm.



Figure III-6: bioAPT product data sheet (1 of 2).

SUGGESTED CONDITIONS FOR USE¹

Heat of wetting	bioAPT generates heat upon wetting. When moisture content is raised from the shipping moisture content of 9 – 14% to 35%, expect a temperature increase of 6.5 to 13 degrees C.
Rewetting media	$Y = x \left(\frac{1-i}{1-D} \right) - x$ <p>Where: Y = mass of water needed (gms or lbs) x = mass of sample (gms or lbs) i = initial moisture content, expressed as decimal D = target moisture content, expressed as decimal</p>
Flowability	Granular media remains flowable and not sticky up to 40% moisture

ELEMENTAL ANALYSIS OF RAW PEAT USED IN BIOAPT PRODUCTION

Element		Element	(mg/kg)	Element	(mg/kg)	Element	(mg/kg)
C	40 - 45 %	Be	<1	Li	<4	Na	<860
H	4 - 6 %	B	<21	Mg	<2300	Sr	<52
N	2 - 3 %	Cd	<1	Mn	<250	Tl	<10
O	35 - 45 %	Ca	<32,000	Hg	<60 µg/L	Sn	<10
	(mg/kg)	Cr	<9	Mo	<4	Ti	<10
Al	<2500	Co	<2	Ni	<7	V	<4
Sb	<4	Cu	<7	K	<500	Zn	<30
As	<4	Fe	<5800	Se	<2		
Ba	<80	Pb	<7	Ag	<2		

¹Test methods available upon request

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bioAPT is a trademark of American Peat Technology, LLC, Aitkin, Minnesota.

The user of this product must comply with all safety and regulatory standards. Consult your APT representative for further operating or usage information.

American Peat Technology makes no warranties as to the accuracy of these data and excludes any liability upon American Peat Technology arising out of the use, storage or disposal of its products. Suitable uses must be determined by the purchaser. Suggested uses should not be understood as recommending the use of our product in violation of any patent or as license to use the patents of American Peat Technology, LLC. Safety Data Sheets are available on request or can be downloaded from American Peat Technology's website.

Figure III-7: bioAPT product data sheet (2 of 2).

Section I. Identification and Company Information

SDS Name: bioAPT
Synonyms: Peat, organic peat, reed-sedge peat
Recommended use: Microbial Carrier
Restrictions on use: none
Preparer's/Manufacturer's Name: American Peat Technology, LLC
 36203 350th Ave.
 Aitkin, MN 56431
Emergency Number: 218-927-1888

Section II. Hazards Identification

No known GHS hazards

Section III. Composition and Information on Ingredients

CAS #	Chemical name	Percent
Not available	Reed sedge peat	95
471-34-1	Calcium carbonate (ag lime)	5

Section IV. First Aid Measures

Eyes: Dust may cause mechanical irritation. Flush eyes with water for at least 15 minutes.
Inhalation: Dust may cause irritation of the upper respiratory tract. Move to fresh air. Seek medical attention if exposure results in difficulty breathing.
Skin: Not absorbed through skin.
Ingestion: Not available.

Section V. Fire Fighting Measures

General information: Will burn if involved in a fire.
Extinguishing media: Any available. **CAUTION:** Burning may continue inside bags or if material is piled. After fire is extinguished, spread material to assure that the material is not smoldering or starting to reheat.
Combustion products: Thermal decomposition products are those commonly observed with natural products such as wood or vegetable matter.
Special protective firefighting equipment and precautions: No special equipment or precautions necessary.
Dust explosion hazard: Per ASTM E1126, powdered bioAPT is in St 1 class with a K_{max} of 78 m·bar/s.

Figure III-8: bioAPT safety data sheet (1 of 3).

Section VI. Accidental Release Measures

Precautions and equipment: No special equipment or precautions. Avoid generating dust.
Environmental precautions: None
Methods for containment: Vacuum or sweep up material and place in a suitable container.

Section VII. Handling and Storage

Handling: Minimize dust generation. Use a NIOSH-approved N95 particulate mask and/or eye protection if conditions are dusty.
Storage: Store in a dry place away from sources of ignition. Keep dry. If product gets wet, molding can occur. Periodically check bags for signs of internal heating.

Section VIII. Exposure Control and Personal Protection

Exposure limits: OSHA PEL: 15 mg/m³ (total, inert dust)
Engineering controls: Transfer product in a well-ventilated area to minimize dust accumulation.
Personal protective equipment
Eyes: Wear appropriate eyewear to protect against dust when transferring dry product.
Respirators: Use a NIOSH-approved N95 particulate mask to protect against dust when transferring dry product.

Section IX. Physical and chemical properties

Appearance: solid, brown, granular or powdered	Odor: smoky, humic (no threshold)
pH: 6.0—7.0	Freezing/melting point: Not available
Boiling point: Not available	Flash point: Not available
Evaporation rate: Negligible	
Flammability: Not available	
Flammable limit (upper, lower): Not available	
Explosivity: (per ASTM E1226) P _{max} : 8.1 bar; (dP/dt) _{max} : 286 bar/s; K _{max} : 78 m-bar/s	
Vapor pressure: Not available	
Vapor density: Not available	
Specific gravity: 0.7	Solubility: insoluble in water
Autoignition temperature: 500° F (260° C)	Decomposition temperature: Not available

Section X. Stability and Reactivity

Reactivity: Not reactive
Chemical stability: Stable under normal temperatures and pressures.
Conditions to avoid: Dust generation, excess heat.
Incompatibilities with other materials: Has not been reported
Hazardous decomposition products: Thermal decomposition releases carbon monoxide, carbon dioxide, hydrocarbons

bioAPT SDS; American Peat Technology, Aitkin, MN

Figure III-9: bioAPT safety data sheet (2 of 3).

Section XI. Toxicological information

Routes of exposure: inhalation, eyes
Symptoms of exposure: mechanical irritation of upper respiratory tract, eyes
RTECS #: This material is not listed in the RTECS index.
Effects of acute exposure: Dust may cause respiratory distress
Effects of chronic exposure: Not available
LD50/LC50: Not available
Carcinogenicity: Not listed by OSHA, IARC, NTP or ACGIH
Reproductive toxicity: Not available
Teratogenicity: Not available
Mutagenicity: Not available

Section XII. Ecological Information

APTSorb is derived from natural peat and has no known ecotoxicity or bioaccumulation potential.

Section XIII. Disposal Considerations

Chemical waste generators must determine if the used material is classified as a hazardous waste under EPA guidelines 40 CFR Parts 261.3. Generators must also consult state and local regulations.

Section XIV. Transport Information

UN Number: None	Special precautions: None
US DOT: Not regulated	Canada TDG: Not regulated

Section XV. Regulatory Information

UNITED STATES

TSCA: This material is not listed on the TSCA inventory.
SARA Sections 302 and 304: This material is not listed as an EHS.
EPCRA: This material is reportable under Section 313.
CERCLA: This material does not have a reportable quantity.
RCRA: This material is not listed on the RCRA lists.
CAA: This material does not contain any hazardous air pollutants.
CWA: This material is not listed as a hazardous substance, priority pollutant or toxic pollutant by the Clean Water Act.

CANADA

WHMIS: This product is not classified by the Controlled Products Regulations.
DSL/NDSL: This material is not listed on the DSL or NDSL. However, there is no control measure imposed to this substance.

Section XVI. Additional Information

SDS creation date: 10/29/14; **Revised:** 01/15/15; 03.06.15

bioAPT SDS; American Peat Technology, Aitkin, MN

Figure III-10: bioAPT safety data sheet (3 of 3).

Appendix IV: Raw In-Situ Data by Individual Sample

Table IV-1: Raw in-situ data by individual sample (1 of 2).

Sample	pH	SC ($\mu\text{S}/\text{cm}$)	ORP (mV)	DO (mg/L)	T ($^{\circ}\text{C}$)
SS1.03	6.27	39.44	157	6.98	21.2
SAND1PV01	9.65	52.20	145	6.15	21.0
SAND1PV03	9.81	56.68	126	7.22	21.0
SAND1PV10	9.69	58.17	126	7.59	20.9
SAND1PV30	9.80	56.02	119	6.68	20.9
SAND2PV01	9.70	57.83	126	7.11	21.1
SAND2PV03	9.77	57.28	125	7.50	20.8
SAND2PV10	9.78	54.60	122	7.59	20.9
SAND2PV30	9.85	57.90	118	6.66	20.9
SS2.04	6.35	23.81	130	8.74	21.5
SAND3PV01	9.67	52.80	110	8.56	22.2
SAND3PV03	9.76	53.02	113	8.50	21.9
SAND3PV10	9.79	55.67	112	7.05	22.1
SAND3PV30	9.85	56.75	128	8.52	21.8
SS1.01	7.14	31.22	198	7.42	20.1
FA5.01PV01	11.36	759.50	124	7.41	19.0
FA5.01PV03	11.47	658.00	102	7.50	19.2
FA5.01PV10	11.28	454.90	73	7.12	19.3
FA5.01PV30	11.12	453.20	58	7.44	19.7
FA5.02PV01	11.52	956.10	123	7.27	19.0
FA5.02PV03	11.57	886.40	108	7.58	19.1
FA5.02PV10	11.35	556.30	60	7.13	19.1
FA5.02PV30	11.11	341.90	59	7.38	19.8
SS1.05	6.40	22.42	130	8.04	21.4
FA5.03PV01	11.27	532.80	120	8.08	21.6
FA5.03PV03	11.22	497.10	86	7.88	21.6
FA5.03PV10	11.09	382.30	140	7.87	21.8
FA5.03PV30	10.94	292.60	111	8.22	21.7
MDR7.53PV01	7.91	296.00	158	6.68	21.5
MDR7.53PV03	7.50	233.90	181	6.98	21.6
MDR7.53PV10	8.35	169.20	180	6.73	21.7
MDR7.53PV30	7.55	105.40	153	7.32	21.6

Table IV-2: Raw in-situ data by individual sample (2 of 2).

Sample	pH	Conductivity ($\mu\text{S}/\text{cm}$)	ORP (mV)	DO (mg/L)	T ($^{\circ}\text{C}$)
SS2.01	6.60	20.73	207	7.56	20.2
MDR7.51PV01	8.03	265.10	195	3.82	17.3
MDR7.51PV03	8.11	225.10	178	5.19	18.9
MDR7.51PV10	8.05	176.70	118	5.54	19.1
MDR7.51PV30	8.12	103.80	119	5.91	19.7
MDR7.52PV01	7.73	272.30	203	3.40	17.2
MDR7.52PV03	7.91	227.50	181	5.54	19.0
MDR7.52PV10	8.16	156.90	125	5.99	19.3
MDR7.52PV30	8.22	111.80	125	5.96	19.8
SS2.03	7.71	22.09	103	7.77	21.4
APT1PV01	7.41	68.11	90	7.41	21.3
APT1PV03	7.60	58.24	75	7.60	21.1
APT1PV10	7.71	56.10	89	7.71	21.3
APT1PV30	7.56	52.51	94	7.56	19.9
APT3PV01	7.68	67.98	84	7.68	21.3
APT3PV03	8.08	58.44	78	8.08	21.2
APT3PV10	7.85	55.97	87	7.85	20.9
APT3PV30	7.69	55.16	96	7.69	19.9
SS2.02	7.12	21.71	135	5.72	21.1
APT2PV01	9.17	59.63	97	5.30	20.9
APT2PV03	9.30	50.30	100	5.03	20.9
APT2PV10	9.28	46.21	112	7.20	20.7
APT2PV30	9.55	49.58	86	6.29	19.7
BIO2PV01	8.80	58.22	110	4.52	20.9
BIO2PV03	9.15	50.10	96	4.88	21.0
BIO2PV10	9.18	53.85	99	7.02	20.5
BIO2PV30	9.51	55.04	97	6.02	19.6
SS1.04	7.14	22.46	162	7.72	19.7
BIO1PV01	8.96	73.80	124	7.15	19.7
BIO1PV03	9.29	67.60	107	7.11	20.2
BIO1PV10	9.23	64.54	113	7.43	20.3
BIO1PV30	9.52	62.72	105	7.38	20.1
BIO3PV01	9.19	71.71	115	7.42	19.7
BIO3PV03	9.35	69.38	101	7.45	20.2
BIO3PV10	9.41	63.03	106	7.62	20.4
BIO3PV30	9.33	60.42	108	7.35	19.8

Appendix V: Raw Nutrients Data by Individual Sample

Table V-1: Raw nutrients data by individual sample (1 of 2).

Sample	P (mg/L as P)		N (mg/L as N)		
	Total	Dissolved	NO ₃ ⁻	NH ₃	Total
SS1.03	0.56	0.55	1.4	BDL	1.56
SAND1PV01	0.16	0.11	1.3	0.056	1.64
SAND1PV03	0.16	0.15	1.3	0.041	1.56
SAND1PV10	0.44	0.43	1.4	0.029	1.59
SAND1PV30	0.52	0.52	1.4	0.005	1.61
SAND2PV01	0.24	0.14	1.1	0.064	1.64
SAND2PV03	0.16	0.14	1.4	0.044	1.57
SAND2PV10	0.51	0.51	1.2	0.027	1.60
SAND2PV30	0.51	0.50	1.4	BDL	1.62
SS2.04	0.54	0.54	1.6	BDL	1.78
SAND3PV01	0.12	0.10	1.0	0.033	1.80
SAND3PV03	0.10	0.10	0.9	0.029	1.74
SAND3PV10	0.27	0.27	1.5	0.019	1.74
SAND3PV30	0.48	0.47	1.5	BDL	1.84
SS1.01	0.52	0.51	1.6	0.098	1.91
FA5.01PV01	0.02	0.02	1.4	BDL	1.79
FA5.01PV03	0.03	0.02	1.3	BDL	1.77
FA5.01PV10	0.03	0.03	1.5	BDL	1.74
FA5.01PV30	0.04	0.03	1.4	BDL	1.81
FA5.02PV01	0.03	0.01	1.3	0.015	1.70
FA5.02PV03	0.03	0.02	1.6	BDL	1.78
FA5.02PV10	0.03	0.03	1.4	BDL	1.74
FA5.02PV30	0.05	0.04	1.4	BDL	1.79
SS1.05	0.55	0.55	1.4	BDL	1.69
FA5.03PV01	0.05	0.05	1.2	0.016	1.53
FA5.03PV03	0.06	0.06	0.9	0.024	1.57
FA5.03PV10	0.13	0.13	1.2	BDL	1.57
FA5.03PV30	0.13	0.13	1.3	BDL	1.62
MDR7.53PV01	0.08	0.08	1.4	0.046	1.54
MDR7.53PV03	0.02	0.02	1.2	0.067	1.60
MDR7.53PV10	0.10	0.10	1.6	0.075	1.57
MDR7.53PV30	0.08	0.08	1.4	0.064	1.59

Table V-2: Raw nutrients data by individual sample (2 of 2).

Sample	P (mg/L as P)		N (mg/L as N)		
	Total	Dissolved	NO ₃ ⁻	NH ₃	Total
SS2.01	0.53	0.53	1.5	BDL	1.80
MDR7.51PV01	0.03	0.02	1.5	0.221	1.86
MDR7.51PV03	0.02	0.02	1.5	0.146	1.76
MDR7.51PV10	0.09	0.09	1.7	0.164	1.75
MDR7.51PV30	0.08	0.08	1.5	0.028	1.75
MDR7.52PV01	0.02	0.01	1.5	0.242	1.84
MDR7.52PV03	0.02	0.01	1.5	0.156	1.73
MDR7.52PV10	0.08	0.05	1.3	0.215	1.80
MDR7.52PV30	0.04	0.03	1.3	0.027	1.70
SS2.03	0.57	0.57	1.3	BDL	1.74
APT1PV01	0.35	0.25	0.5	0.880	2.76
APT1PV03	0.50	0.40	1.0	0.670	2.56
APT1PV10	0.55	0.55	1.5	0.300	2.22
APT1PV30	0.60	0.50	1.5	0.068	1.87
APT3PV01	0.40	0.25	1.0	1.120	2.90
APT3PV03	0.45	0.40	0.5	0.783	2.72
APT3PV10	0.55	0.55	1.5	0.315	2.20
APT3PV30	0.55	0.50	1.0	0.061	1.86
SS2.02	0.63	0.63	1.6	BDL	1.78
APT2PV01	0.15	0.10	1.4	0.451	2.30
APT2PV03	0.25	0.25	1.8	0.348	2.19
APT2PV10	0.55	0.50	1.4	0.175	1.95
APT2PV30	0.60	0.55	1.4	0.017	1.81
BIO2PV01	0.40	0.35	1.0	0.156	2.44
BIO2PV03	0.60	0.60	2.0	0.136	2.29
BIO2PV10	0.70	0.65	1.4	0.108	2.14
BIO2PV30	0.65	0.60	1.6	0.018	1.97
SS1.04	0.54	0.54	1.5	BDL	1.82
BIO1PV01	0.65	0.60	1.6	0.886	3.67
BIO1PV03	0.85	0.75	1.6	0.825	3.17
BIO1PV10	0.85	0.75	1.8	0.325	2.58
BIO1PV30	0.75	0.75	1.4	0.168	2.06
BIO3PV01	0.60	0.60	1.4	0.801	3.52
BIO3PV03	0.75	0.70	1.6	0.552	2.96
BIO3PV10	0.75	0.75	1.6	0.261	2.49
BIO3PV30	0.80	0.75	1.2	0.055	2.03

Appendix VI: Raw Metals Data by Individual Sample - Copper, Lead, and Zinc

Table VI-1: Raw copper, lead, and zinc data by individual sample (1 of 2).

Sample	Cu (mg/L)		Pb (mg/L)		Zn (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS1.03	0.025	0.023	0.030	0.018	0.100	0.104
SAND1PV01	0.002	0.001	0.026	0.018	BDL	BDL
SAND1PV03	0.003	0.002	0.022	0.017	BDL	BDL
SAND1PV10	0.002	0.005	0.019	0.015	0.017	BDL
SAND1PV30	0.001	BDL	0.022	BDL	BDL	BDL
SAND2PV01	0.003	0.001	0.025	0.016	BDL	BDL
SAND2PV03	0.002	0.001	0.020	BDL	BDL	BDL
SAND2PV10	0.002	BDL	0.023	BDL	BDL	BDL
SAND2PV30	BDL	BDL	0.023	BDL	BDL	BDL
SS2.04	0.021	0.020	0.025	0.019	0.085	0.097
SAND3PV01	0.001	0.001	0.016	0.020	BDL	BDL
SAND3PV03	0.001	0.001	0.019	0.018	BDL	0.039
SAND3PV10	0.001	BDL	0.014	0.014	BDL	BDL
SAND3PV30	0.001	BDL	0.019	0.014	0.097	BDL
SS1.01	0.027	0.024	0.024	0.008	0.098	0.096
FA5.01PV01	0.007	0.003	0.021	0.025	0.006	0.007
FA5.01PV03	0.005	0.003	0.030	0.023	0.006	0.009
FA5.01PV10	0.005	0.001	0.024	0.025	0.006	0.008
FA5.01PV30	0.005	0.001	0.020	0.017	0.006	0.007
FA5.02PV01	0.007	0.004	0.024	0.025	0.006	0.006
FA5.02PV03	0.009	0.003	0.026	0.027	0.006	0.007
FA5.02PV10	0.005	0.002	0.020	0.017	0.006	0.008
FA5.02PV30	0.005	0.001	0.021	0.010	0.006	0.007
SS1.05	0.023	0.025	0.029	BDL	0.096	0.095
FA5.03PV01	BDL	0.003	0.022	0.023	0.008	0.010
FA5.03PV03	BDL	BDL	0.022	BDL	0.005	0.008
FA5.03PV10	BDL	0.003	0.013	BDL	0.007	0.007
FA5.03PV30	0.023	BDL	BDL	BDL	0.006	0.006
MDR7.53PV01	BDL	0.005	0.022	0.012	BDL	BDL
MDR7.53PV03	0.004	0.004	0.020	BDL	BDL	BDL
MDR7.53PV10	0.005	BDL	0.018	BDL	BDL	BDL
MDR7.53PV30	BDL	0.003	BDL	BDL	BDL	BDL

Table VI-2: Raw copper, lead, and zinc data by individual sample (2 of 2).

Sample	Cu (mg/L)		Pb (mg/L)		Zn (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS2.01	0.031	0.024	0.030	BDL	0.101	0.102
MDR7.51PV01	0.005	0.001	0.019	0.017	0.010	0.009
MDR7.51PV03	0.005	0.001	0.016	0.021	0.018	0.014
MDR7.51PV10	0.004	BDL	0.013	0.015	0.030	0.007
MDR7.51PV30	0.005	BDL	0.012	0.013	0.008	0.008
MDR7.52PV01	0.004	0.001	0.023	0.022	0.011	0.011
MDR7.52PV03	0.005	0.001	0.013	0.019	0.010	0.010
MDR7.52PV10	0.004	BDL	0.016	0.019	0.018	0.009
MDR7.52PV30	0.004	BDL	0.012	0.009	0.007	0.007
SS2.03	0.023	0.022	0.025	0.019	0.093	0.095
APT1PV01	0.003	0.002	BDL	BDL	BDL	BDL
APT1PV03	0.002	0.002	0.005	BDL	BDL	BDL
APT1PV10	0.005	0.001	BDL	BDL	BDL	BDL
APT1PV30	0.001	0.001	0.004	0.005	BDL	BDL
APT3PV01	0.004	0.003	0.004	BDL	BDL	BDL
APT3PV03	0.002	0.001	BDL	BDL	BDL	BDL
APT3PV10	0.002	0.002	0.003	0.005	BDL	BDL
APT3PV30	0.001	BDL	0.005	BDL	BDL	BDL
SS2.02	0.023	0.023	0.029	0.020	0.099	0.101
APT2PV01	0.002	0.003	0.009	0.014	BDL	BDL
APT2PV03	0.002	0.002	0.007	BDL	BDL	BDL
APT2PV10	0.004	0.002	0.005	BDL	BDL	BDL
APT2PV30	0.002	0.002	0.010	BDL	BDL	BDL
BIO2PV01	0.003	0.003	0.021	BDL	BDL	BDL
BIO2PV03	0.003	0.003	0.022	BDL	BDL	BDL
BIO2PV10	0.002	0.002	0.021	BDL	BDL	BDL
BIO2PV30	0.004	0.003	0.086	BDL	BDL	BDL
SS1.04	0.024	0.023	0.023	0.023	0.104	0.098
BIO1PV01	0.003	0.002	0.004	BDL	BDL	BDL
BIO1PV03	0.003	0.003	BDL	BDL	BDL	BDL
BIO1PV10	0.002	0.002	BDL	0.004	BDL	BDL
BIO1PV30	0.001	0.002	0.018	0.005	BDL	BDL
BIO3PV01	0.003	0.003	0.010	BDL	BDL	BDL
BIO3PV03	0.003	0.002	BDL	BDL	BDL	BDL
BIO3PV10	0.002	0.002	0.016	BDL	BDL	BDL
BIO3PV30	0.002	0.001	0.015	BDL	BDL	BDL

**Appendix VII: Raw Metals Data by Individual Sample - Silver, Arsenic,
Cadmium, Mercury, Nickel, and Selenium**

Table VII-1: Raw silver, arsenic, and cadmium data by individual sample (1 of 2).

Sample	Ag (mg/L)		As (mg/L)		Cd (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS1.03	BDL	BDL	BDL	BDL	0.00017	0.00035
SAND1PV01	0.004	0.002	BDL	BDL	0.00020	0.00019
SAND1PV03	0.005	0.004	BDL	BDL	0.00007	0.00013
SAND1PV10	0.003	0.003	BDL	BDL	0.00042	0.00031
SAND1PV30	0.003	0.002	BDL	BDL	0.00014	0.00038
SAND2PV01	0.004	0.003	BDL	BDL	0.00026	0.00018
SAND2PV03	0.004	0.003	BDL	BDL	0.00009	0.00048
SAND2PV10	0.003	BDL	BDL	BDL	0.00016	0.00020
SAND2PV30	0.002	0.002	BDL	BDL	0.00021	BDL
SS2.04	BDL	BDL	BDL	BDL	0.00015	0.00029
SAND3PV01	0.003	BDL	BDL	BDL	0.00032	0.00045
SAND3PV03	0.003	0.004	BDL	BDL	0.00024	0.00012
SAND3PV10	0.003	0.002	BDL	BDL	0.00041	0.00011
SAND3PV30	0.003	0.003	BDL	BDL	0.00015	0.00012
SS1.01	BDL	BDL	BDL	BDL	BDL	BDL
FA5.01PV01	0.044	0.038	BDL	BDL	BDL	0.00046
FA5.01PV03	0.053	0.034	0.163	BDL	BDL	BDL
FA5.01PV10	0.033	BDL	BDL	0.149	BDL	0.00131
FA5.01PV30	0.030	0.020	BDL	BDL	BDL	BDL
FA5.02PV01	0.066	0.046	BDL	0.150	BDL	BDL
FA5.02PV03	0.050	0.059	BDL	BDL	0.00060	BDL
FA5.02PV10	0.031	0.026	0.141	BDL	BDL	0.00249
FA5.02PV30	0.043	BDL	BDL	BDL	0.00048	0.00234
SS1.05	BDL	0.009	BDL	BDL	0.00017	0.00019
FA5.03PV01	0.031	0.029	0.051	BDL	0.00073	0.00051
FA5.03PV03	0.019	0.025	BDL	BDL	0.00054	0.00024
FA5.03PV10	0.011	0.017	BDL	BDL	0.00030	0.00065
FA5.03PV30	0.006	0.012	BDL	BDL	0.00061	0.00040
MDR7.53PV01	0.020	0.018	BDL	BDL	0.00059	0.00038
MDR7.53PV03	0.014	BDL	BDL	BDL	0.00103	0.00012
MDR7.53PV10	0.009	BDL	BDL	BDL	0.00059	0.00015
MDR7.53PV30	BDL	0.009	BDL	BDL	BDL	0.00031

Table VII-2: Raw silver, arsenic, and cadmium data by individual sample (2 of 2).

Sample	Ag (mg/L)		As (mg/L)		Cd (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS2.01	0.007	BDL	BDL	BDL	BDL	0.00013
MDR7.51PV01	0.036	BDL	BDL	BDL	BDL	BDL
MDR7.51PV03	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.51PV10	BDL	0.034	BDL	BDL	BDL	BDL
MDR7.51PV30	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.52PV01	0.045	BDL	0.139	BDL	BDL	BDL
MDR7.52PV03	0.039	0.044	0.179	BDL	BDL	BDL
MDR7.52PV10	0.024	0.022	0.157	BDL	BDL	0.00105
MDR7.52PV30	BDL	BDL	BDL	BDL	BDL	BDL
SS2.03	BDL	BDL	BDL	BDL	BDL	0.00047
APT1PV01	0.004	0.002	BDL	BDL	0.00045	0.00010
APT1PV03	0.004	BDL	BDL	BDL	0.00049	0.00024
APT1PV10	0.004	BDL	0.012	BDL	0.00018	0.00017
APT1PV30	0.003	BDL	BDL	BDL	0.00032	0.00005
APT3PV01	0.007	0.003	BDL	BDL	0.00012	0.00012
APT3PV03	0.004	BDL	BDL	BDL	0.00016	0.00016
APT3PV10	0.004	0.003	BDL	BDL	0.00009	0.00009
APT3PV30	0.003	0.004	BDL	BDL	0.00015	0.00015
SS2.02	BDL	BDL	BDL	BDL	0.00019	0.00018
APT2PV01	BDL	0.003	BDL	BDL	0.00040	0.00013
APT2PV03	0.005	0.002	BDL	BDL	0.00026	0.00044
APT2PV10	0.003	BDL	BDL	BDL	0.00027	0.00020
APT2PV30	0.003	BDL	BDL	BDL	0.00038	0.00006
BIO2PV01	0.003	0.004	BDL	BDL	0.00019	0.00046
BIO2PV03	0.003	0.005	BDL	BDL	0.00019	0.00022
BIO2PV10	0.006	0.003	BDL	BDL	0.00020	0.00022
BIO2PV30	0.021	0.003	BDL	BDL	0.00058	0.00028
SS1.04	BDL	BDL	BDL	BDL	0.00019	0.00013
BIO1PV01	0.003	0.004	BDL	BDL	0.00014	0.00010
BIO1PV03	0.005	0.003	BDL	BDL	0.00037	0.00015
BIO1PV10	0.003	0.003	BDL	BDL	0.00021	0.00020
BIO1PV30	0.004	0.003	BDL	BDL	0.00015	0.00036
BIO3PV01	0.005	0.001	BDL	BDL	0.00017	0.00005
BIO3PV03	0.004	0.004	BDL	BDL	0.00041	0.00010
BIO3PV10	BDL	0.003	BDL	BDL	0.00014	0.00013
BIO3PV30	0.004	0.003	0.016	BDL	0.00013	0.00020

**Table VII-3: Raw mercury, nickel, and selenium data by individual sample
(1 of 2).**

Sample	Hg (mg/L)		Ni (mg/L)		Se (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS1.03	BDL	BDL	BDL	BDL	BDL	BDL
SAND1PV01	BDL	BDL	BDL	BDL	0.017	0.015
SAND1PV03	BDL	BDL	BDL	BDL	BDL	BDL
SAND1PV10	BDL	BDL	BDL	BDL	BDL	BDL
SAND1PV30	BDL	BDL	BDL	BDL	0.018	0.015
SAND2PV01	BDL	BDL	BDL	BDL	BDL	BDL
SAND2PV03	BDL	BDL	BDL	BDL	BDL	0.014
SAND2PV10	BDL	BDL	BDL	BDL	0.014	BDL
SAND2PV30	BDL	BDL	BDL	BDL	BDL	0.019
SS2.04	BDL	BDL	BDL	BDL	BDL	BDL
SAND3PV01	BDL	BDL	BDL	BDL	0.014	BDL
SAND3PV03	BDL	BDL	BDL	BDL	BDL	0.015
SAND3PV10	BDL	BDL	BDL	BDL	BDL	0.013
SAND3PV30	BDL	BDL	BDL	BDL	BDL	0.015
SS1.01	BDL	BDL	BDL	BDL	BDL	BDL
FA5.01PV01	BDL	BDL	BDL	BDL	BDL	BDL
FA5.01PV03	BDL	BDL	BDL	BDL	BDL	BDL
FA5.01PV10	BDL	BDL	BDL	BDL	BDL	BDL
FA5.01PV30	BDL	BDL	BDL	BDL	BDL	BDL
FA5.02PV01	BDL	BDL	BDL	BDL	BDL	BDL
FA5.02PV03	BDL	BDL	BDL	BDL	BDL	BDL
FA5.02PV10	BDL	BDL	BDL	BDL	BDL	BDL
FA5.02PV30	BDL	BDL	BDL	BDL	BDL	BDL
SS1.05	BDL	BDL	BDL	BDL	BDL	BDL
FA5.03PV01	BDL	BDL	BDL	BDL	BDL	0.046
FA5.03PV03	BDL	BDL	BDL	BDL	BDL	BDL
FA5.03PV10	BDL	BDL	BDL	BDL	BDL	BDL
FA5.03PV30	BDL	BDL	BDL	BDL	0.045	BDL
MDR7.53PV01	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.53PV03	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.53PV10	BDL	BDL	BDL	BDL	BDL	0.017
MDR7.53PV30	BDL	BDL	BDL	BDL	0.176	BDL

**Table VII-4: Raw mercury, nickel, and selenium data by individual sample
(2 of 2).**

Sample	Hg (mg/L)		Ni (mg/L)		Se (mg/L)	
	Total	Filtered	Total	Filtered	Total	Filtered
SS2.01	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.51PV01	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.51PV03	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.51PV10	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.51PV30	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.52PV01	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.52PV03	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.52PV10	BDL	BDL	BDL	BDL	BDL	BDL
MDR7.52PV30	BDL	BDL	BDL	BDL	BDL	BDL
SS2.03	BDL	BDL	BDL	BDL	0.012	BDL
APT1PV01	BDL	BDL	BDL	BDL	0.020	BDL
APT1PV03	BDL	BDL	BDL	BDL	0.019	BDL
APT1PV10	BDL	BDL	0.012	BDL	BDL	BDL
APT1PV30	BDL	BDL	BDL	BDL	0.015	0.015
APT3PV01	BDL	BDL	BDL	BDL	0.017	BDL
APT3PV03	BDL	BDL	BDL	BDL	BDL	BDL
APT3PV10	BDL	BDL	BDL	BDL	0.014	BDL
APT3PV30	BDL	BDL	BDL	BDL	BDL	BDL
SS2.02	BDL	BDL	BDL	BDL	0.016	0.019
APT2PV01	BDL	BDL	BDL	BDL	BDL	BDL
APT2PV03	BDL	BDL	BDL	BDL	BDL	BDL
APT2PV10	BDL	BDL	BDL	BDL	BDL	0.014
APT2PV30	BDL	BDL	BDL	BDL	0.015	BDL
BIO2PV01	BDL	BDL	BDL	BDL	BDL	0.017
BIO2PV03	BDL	BDL	BDL	BDL	BDL	BDL
BIO2PV10	BDL	BDL	BDL	BDL	BDL	0.018
BIO2PV30	BDL	BDL	BDL	BDL	0.021	BDL
SS1.04	BDL	BDL	BDL	BDL	BDL	BDL
BIO1PV01	BDL	BDL	BDL	BDL	0.015	0.016
BIO1PV03	BDL	BDL	BDL	BDL	BDL	BDL
BIO1PV10	BDL	BDL	BDL	BDL	BDL	BDL
BIO1PV30	BDL	BDL	BDL	BDL	BDL	BDL
BIO3PV01	BDL	BDL	BDL	BDL	BDL	BDL
BIO3PV03	BDL	BDL	BDL	BDL	BDL	BDL
BIO3PV10	BDL	BDL	BDL	BDL	0.017	0.019
BIO3PV30	BDL	BDL	BDL	BDL	BDL	0.017

Appendix VIII: Raw TOC/N Data by Individual Sample and Calibration Reports

aj-Analyzer multi N/C 2100 S; multiWin 4.05; Serial No: N5-325/J

AnalysesTable

AnalysesTable: 030718

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Type Calibration function	Density DF
BLANK			3/7/2018 6:28:31 PM	1
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.02mg/l		Concentration [1, 2, 3, 4] = 0	
IC	156.0µg/l ± 31.88µg/l	291.4AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.18mg/l ± 26.45µg/l	505.0AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	401.7µg/l ± 470.0ng/l	1.06AU CR!	e = (0.0015999*F + 0.19914)/V	1
SS202			3/7/2018 7:08:27 PM	2
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.28mg/l		Concentration [1, 2, 3, 4] = 0	
IC	229.4µg/l ± 9.25µg/l	338.3AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.51mg/l ± 135.3µg/l	711.6AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	1.78mg/l ± 21.98µg/l	431.3AU CR!	e = (0.0015999*F + 0.19914)/V	1
APT2PV1			3/7/2018 7:48:49 PM	3
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	4.95mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.98mg/l ± 212.6µg/l	1.454AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	6.93mg/l ± 272.9µg/l	4.057AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	2.30mg/l ± 7.95µg/l	594.5AU CR!	e = (0.0015999*F + 0.19914)/V	1
BIO2PV1			3/7/2018 8:34:00 PM	4
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	12.32mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.14mg/l ± 100.9µg/l	916.9AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	13.45mg/l ± 118.1µg/l	8.085AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	2.44mg/l ± 9.15µg/l	639.4AU CR!	e = (0.0015999*F + 0.19914)/V	1
APT2PV3			3/7/2018 9:16:05 PM	5
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	4.05mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.09mg/l ± 124.2µg/l	887.2AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	5.14mg/l ± 97.95µg/l	2.951AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	2.19mg/l ± 910.0ng/l	560.0AU CR!	e = (0.0015999*F + 0.19914)/V	1
BIO2PV3			3/7/2018 10:00:59 PM	6
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	10.50mg/l		Concentration [1, 2, 3, 4] = 0	
IC	688.8µg/l ± 71.78µg/l	631.2AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	11.19mg/l ± 54.66µg/l	6.689AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	2.29mg/l ± 11.89µg/l	592.5AU CR!	e = (0.0015999*F + 0.19914)/V	1
APT2PV10			3/7/2018 10:45:40 PM	7
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	3.21mg/l		Concentration [1, 2, 3, 4] = 0	
IC	629.4µg/l ± 58.81µg/l	593.4AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	3.84mg/l ± 49.95µg/l	2.150AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	1.95mg/l ± 7.76µg/l	484.5AU CR!	e = (0.0015999*F + 0.19914)/V	1
BIO2PV10			3/7/2018 11:30:45 PM	8
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	8.33mg/l		Concentration [1, 2, 3, 4] = 0	
IC	509.5µg/l ± 66.53µg/l	516.9AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	8.84mg/l ± 20.73µg/l	5.236AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	2.14mg/l ± 16.83µg/l	545.3AU CR!	e = (0.0015999*F + 0.19914)/V	1
APT2PV30			3/8/2018 12:13:15 AM	9
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.68mg/l		Concentration [1, 2, 3, 4] = 0	
IC	463.3µg/l ± 87.01µg/l	487.4AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	3.14mg/l ± 102.2µg/l	1.718AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	1.81mg/l ± 11.53µg/l	440.3AU CR!	e = (0.0015999*F + 0.19914)/V	1
BIO2PV30			3/8/2018 12:50:36 AM	10
DIFF TN		IC, TC, TN	500.0µl 3 (3-4) 1 in 1 Sample	
TOC	6.68mg/l		Concentration [1, 2, 3] = 0	
IC	273.2µg/l ± 11.55µg/l	366.2AU CR!	e = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	6.96mg/l ± 147.1µg/l	4.073AU CR!	e = (8.100E-4*F + 0.17911)/V	1
TN	1.97mg/l ± 29.89µg/l	492.6AU CR!	e = (0.0015999*F + 0.19914)/V	1

Figure VIII-1: Raw TOC/N Data Report 1 (1 of 3).

AnalysesTable

AnalysesTable: 030718

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Type	Density DF
SS104			3/8/2018 1:22:31 AM	11
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.01mg/l		Concentration [1,2,3,4] = 0	
IC	98.80µg/l ± 9.73µg/l	254.9AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	1.11mg/l ± 36.70µg/l	461.4AU CR!	c = (8.100E-4*I + 0.17911)/V	1
TN	1.82mg/l ± 10.27µg/l	444.4AU	c = (0.0015999*I - 0.19914)/V	1
APT1PV1			3/8/2018 2:01:57 AM	12
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	10.81mg/l		Concentration [1,2,3,4] = 0	
IC	513.0µg/l = 40.40µg/l	519.2AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	11.32mg/l ± 117.5µg/l	6.769AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.76mg/l ± 18.04µg/l	737.1AU	c = (0.0015999*I - 0.19914)/V	1
APT3PV1			3/8/2018 2:45:47 AM	13
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	11.17mg/l		Concentration [1,2,3,4] = 0	
IC	507.4µg/l = 13.25µg/l	515.6AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	11.68mg/l ± 103.7µg/l	6.987AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.90mg/l ± 27.51µg/l	780.5AU	c = (0.0015999*I - 0.19914)/V	1
APT1PV3			3/8/2018 3:28:46 AM	14
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	7.90mg/l		Concentration [1,2,3,4] = 0	
IC	301.0µg/l = 72.50µg/l	383.9AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	8.21mg/l ± 44.71µg/l	4.844AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.56mg/l ± 27.69µg/l	675.4AU	c = (0.0015999*I - 0.19914)/V	1
APT3PV3			3/8/2018 4:11:12 AM	15
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	8.46mg/l		Concentration [1,2,3,4] = 0	
IC	428.7µg/l = 113.7µg/l	465.4AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	8.89mg/l ± 46.84µg/l	5.267AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.72mg/l ± 32.50µg/l	727.1AU	c = (0.0015999*I - 0.19914)/V	1
APT1PV10			3/8/2018 4:56:04 AM	16
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	5.77mg/l		Concentration [1,2,3,4] = 0	
IC	252.1µg/l = 28.09µg/l	352.8AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	6.02mg/l ± 40.72µg/l	3.497AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.22mg/l ± 17.69µg/l	570.2AU	c = (0.0015999*I - 0.19914)/V	1
APT3PV10			3/8/2018 5:40:34 AM	17
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	5.96mg/l		Concentration [1,2,3,4] = 0	
IC	183.8µg/l = 5.56µg/l	309.2AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	6.15mg/l ± 83.99µg/l	3.572AU	c = (8.100E-4*I + 0.17911)/V	1
TN	2.20mg/l ± 11.39µg/l	563.6AU	c = (0.0015999*I - 0.19914)/V	1
APT1PV30			3/8/2018 6:25:40 AM	18
DIFF_TN		IC; TC; TN	500.0µl 3 (3-4) 1 in 1 Sample	
TOC	4.13mg/l		Concentration [1,2,3] = 0	
IC	122.2µg/l ± 4.12µg/l	269.9AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	4.25mg/l ± 80.43µg/l	2.405AU CR!	c = (8.100E-4*I + 0.17911)/V	1
TN	1.87mg/l = 3.30µg/l	461.2AU	c = (0.0015999*I - 0.19914)/V	1
APT3PV30			3/8/2018 6:57:13 AM	19
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	4.13mg/l		Concentration [1,2,3,4] = 0	
IC	94.63µg/l = 18.16µg/l	252.3AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	4.22mg/l ± 27.41µg/l	2.386AU CR!	c = (8.100E-4*I + 0.17911)/V	1
TN	1.86mg/l = 8.23µg/l	455.6AU	c = (0.0015999*I - 0.19914)/V	1
SS203			3/8/2018 7:38:49 AM	20
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	972.7µg/l		Concentration [1,2,3,4] = 0	
IC	106.2µg/l = 10.40µg/l	259.7AU CR!	c = (2.563E-9*F + 7.818E-4*I - -0.15006)/V	1
TC	1.08mg/l ± 16.41µg/l	444.9AU CR!	c = (8.100E-4*I + 0.17911)/V	1
TN	1.74mg/l = 8.07µg/l	420.3AU	c = (0.0015999*I - 0.19914)/V	1

Figure VIII-2: Raw TOIC/N Data Report 1 (2 of 3).

AnalysesTable

AnalysesTable: 030718

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Type	Density DF
BIO1PV1			3/8/2018 8:18:59 AM	21
DIFF TN		IC, TC, TN	500.0µl 3 (3-4) 1 in 1 Sample	
TOC	22.43mg/l		Concentration [1,2,3]=0	
IC	193.2µg/l ± 3.52µg/l	315.2AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	22.62mg/l ± 154.5µg/l	1.374E4AU	c = (8.100E-4*m + 0.17911)/V	1
TN	3.67mg/l ± 6.17µg/l	1.021AU	c = (0.0015999*m + 0.19914)/V	1
BIO3PV1			3/8/2018 8:52:37 AM	22
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	22.38mg/l		Concentration [1,2,3,4]=0	
IC	116.8µg/l ± 25.61µg/l	266.4AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	22.50mg/l ± 20.08µg/l	1.367E4AU	c = (8.100E-4*m + 0.17911)/V	1
TN	3.52mg/l ± 25.71µg/l	974.1AU	c = (0.0015999*m + 0.19914)/V	1
BIO1PV3			3/8/2018 9:38:09 AM	23
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	19.39mg/l		Concentration [1,2,3,4]=0	
IC	126.5µg/l ± 33.33µg/l	272.6AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	19.52mg/l ± 56.62µg/l	1.183E4AU	c = (8.100E-4*m + 0.17911)/V	1
TN	3.17mg/l ± 41.68µg/l	866.0AU	c = (0.0015999*m + 0.19914)/V	1
BIO3PV3			3/8/2018 10:22:10 AM	24
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	18.48mg/l		Concentration [1,2,3,4]=0	
IC	126.0µg/l ± 12.11µg/l	272.3AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	18.61mg/l ± 12.12µg/l	1.126E4AU	c = (8.100E-4*m + 0.17911)/V	1
TN	2.96mg/l ± 8.47µg/l	799.5AU	c = (0.0015999*m + 0.19914)/V	1
BIO1PV10			3/8/2018 11:07:25 AM	25
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	14.66mg/l		Concentration [1,2,3,4]=0	
IC	119.5µg/l ± 4.40µg/l	268.2AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	14.78mg/l ± 38.44µg/l	8.903AU	c = (8.100E-4*m + 0.17911)/V	1
TN	2.58mg/l ± 16.29µg/l	681.0AU	c = (0.0015999*m + 0.19914)/V	1
BIO3PV10			3/8/2018 11:52:29 AM	26
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	13.96mg/l		Concentration [1,2,3,4]=0	
IC	114.7µg/l ± 14.97µg/l	265.0AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	14.08mg/l ± 16.91µg/l	8.468AU	c = (8.100E-4*m + 0.17911)/V	1
TN	2.49mg/l ± 32.22µg/l	653.0AU	c = (0.0015999*m + 0.19914)/V	1
BIO1PV30			3/8/2018 12:36:57 PM	27
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	10.01mg/l		Concentration [1,2,3,4]=0	
IC	90.47µg/l ± 16.80µg/l	249.6AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	10.10mg/l ± 42.27µg/l	6.016AU	c = (8.100E-4*m + 0.17911)/V	1
TN	2.06mg/l ± 28.12µg/l	517.9AU	c = (0.0015999*m + 0.19914)/V	1
BIO3PV30			3/8/2018 1:22:05 PM	28
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	9.40mg/l		Concentration [1,2,3,4]=0	
IC	112.3µg/l ± 6.52µg/l	263.5AU CR!	c = (2.563E-9*m ² + 7.818E-4*m + -0.15006)/V	1
TC	9.51mg/l ± 19.79µg/l	5.650AU	c = (8.100E-4*m + 0.17911)/V	1
TN	2.03mg/l ± 10.77µg/l	511.4AU	c = (0.0015999*m + 0.19914)/V	1

Figure VIII-3: Raw TOC/N Data Report 1 (3 of 3).

AnalysesTable

AnalysesTable: 031118

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Calibration function Type	Density DF
BLANK				
DIFF TN		IC, TC, TN	3/11/2018 1:42:57 PM	1
TOC	1.69mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	66.36µg/l ± 14.32µg/l	234.2AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	1.76mg/l ± 18.71µg/l	864.9AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	447.1µg/l ± 510.0ng/l	15.26AU CR!	c = (0.0015999* T + 0.19914)/V	1
SS101				
DIFF TN		IC, TC, TN	3/11/2018 2:25:38 PM	2
TOC	1.85mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	201.9µg/l ± 24.63µg/l	320.7AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.05mg/l ± 27.24µg/l	1,047AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.91mg/l ± 2.54µg/l	472.4AU	c = (0.0015999* T + 0.19914)/V	1
FA1PV1				
DIFF TN		IC, TC, TN	3/11/2018 3:09:01 PM	3
TOC	2.19mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	297.8µg/l ± 85.99µg/l	381.9AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.48mg/l ± 43.33µg/l	1,312AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.79mg/l ± 14.99µg/l	436.0AU	c = (0.0015999* T + 0.19914)/V	1
FA2PV1				
DIFF TN		IC, TC, TN	3/11/2018 3:51:17 PM	4
TOC	2.45mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	249.8µg/l ± 41.06µg/l	351.3AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.70mg/l ± 3.77µg/l	1,448AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.70mg/l ± 17.62µg/l	407.6AU	c = (0.0015999* T + 0.19914)/V	1
FA1PV3				
DIFF TN		IC, TC, TN	3/11/2018 4:33:12 PM	5
TOC	2.02mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	221.4µg/l ± 37.66µg/l	333.2AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.24mg/l ± 46.22µg/l	1,161AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.77mg/l ± 14.54µg/l	429.8AU	c = (0.0015999* T + 0.19914)/V	1
FA2PV3				
DIFF TN		IC, TC, TN	3/11/2018 5:14:48 PM	6
TOC	2.15mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	155.8µg/l ± 1.88µg/l	291.3AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.31mg/l ± 32.48µg/l	1,204AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.78mg/l ± 3.70µg/l	430.3AU	c = (0.0015999* T + 0.19914)/V	1
FA1PV10				
DIFF TN		IC, TC, TN	3/11/2018 5:53:08 PM	7
TOC	1.87mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	116.9µg/l ± 3.65µg/l	266.5AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	1.99mg/l ± 15.34µg/l	1,005AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.74mg/l ± 10.15µg/l	420.0AU	c = (0.0015999* T + 0.19914)/V	1
FA2PV10				
DIFF TN		IC, TC, TN	3/11/2018 6:31:42 PM	8
TOC	2.03mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	125.7µg/l ± 5.59µg/l	272.1AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.15mg/l ± 15.78µg/l	1,108AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.74mg/l ± 2.59µg/l	418.3AU	c = (0.0015999* T + 0.19914)/V	1
FA1PV30				
DIFF TN		IC, TC, TN	3/11/2018 7:09:43 PM	9
TOC	1.92mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	143.5µg/l ± 33.85µg/l	283.5AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	2.06mg/l ± 26.75µg/l	1,051AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.81mg/l ± 5.78µg/l	440.2AU	c = (0.0015999* T + 0.19914)/V	1
FA2PV30				
DIFF TN		IC, TC, TN	3/11/2018 7:49:21 PM	10
TOC	1.78mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	192.0µg/l ± 14.53µg/l	314.4AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T - 0.15006)/V	1
TC	1.98mg/l ± 10.33µg/l	998.9AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.79mg/l ± 27.67µg/l	434.1AU	c = (0.0015999* T + 0.19914)/V	1

Figure VIII-4: Raw TOC/N Data Report 2 (1 of 5).

AnalysesTable

AnalysesTable: 031118

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Type	Density DF
SS201			3/11/2018 8:26:07 PM	11
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.41mg/l		Concentration [1, 2, 3, 4] = 0	
IC	86.58µg/l ± 1.10µg/l	247.1AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	1.50mg/l ± 50.61µg/l	705.6AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.80mg/l ± 6.66µg/l	439.2AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR751PV1			3/11/2018 9:05:33 PM	12
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.97mg/l		Concentration [1, 2, 3, 4] = 0	
IC	2.28mg/l ± 268.3µg/l	1.641AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	5.25mg/l ± 197.2µg/l	3.019AU	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.86mg/l ± 5.51µg/l	456.5AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR752PV1			3/11/2018 9:47:10 PM	13
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.74mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.08mg/l ± 103.9µg/l	877.3AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	3.82mg/l ± 93.32µg/l	2.135AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.84mg/l ± 55.72µg/l	449.8AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR751PV3			3/11/2018 10:29:06 PM	14
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.72mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.59mg/l ± 203.7µg/l	1.203AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	4.31mg/l ± 126.3µg/l	2.439AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.76mg/l ± 13.20µg/l	425.3AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR752PV3			3/11/2018 11:06:59 PM	15
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.47mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.42mg/l ± 115.1µg/l	1.093AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	3.89mg/l ± 103.9µg/l	2.177AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.73mg/l ± 23.09µg/l	415.9AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR751PV10			3/11/2018 11:44:14 PM	16
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.29mg/l		Concentration [1, 2, 3, 4] = 0	
IC	760.4µg/l ± 53.60µg/l	676.8AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	3.05mg/l ± 23.98µg/l	1.665AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.75mg/l ± 4.81µg/l	422.7AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR752PV10			3/12/2018 12:20:57 AM	17
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.14mg/l		Concentration [1, 2, 3, 4] = 0	
IC	1.16mg/l ± 85.93µg/l	933.9AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	3.31mg/l ± 64.41µg/l	1.821AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.80mg/l ± 63.64µg/l	438.5AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR751PV30			3/12/2018 12:59:42 AM	18
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.06mg/l		Concentration [1, 2, 3, 4] = 0	
IC	481.6µg/l ± 89.18µg/l	499.1AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	2.55mg/l ± 42.97µg/l	1.350AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.75mg/l ± 10.66µg/l	423.6AU	$e = (0.0015999 * I + 0.19914) / V$	I
MDR752PV30			3/12/2018 1:40:57 AM	19
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	2.05mg/l		Concentration [1, 2, 3, 4] = 0	
IC	472.5µg/l ± 50.84µg/l	493.4AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	2.53mg/l ± 93.59µg/l	1.338AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.70mg/l ± 11.32µg/l	407.9AU	$e = (0.0015999 * I + 0.19914) / V$	I
SS103			3/12/2018 2:22:05 AM	20
DIFF_TN		IC; TC; TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	889.6µg/l		Concentration [1, 2, 3, 4] = 0	
IC	64.42µg/l ± 20.08µg/l	233.0AU CR!	$e = (2.563E-9 * P + 7.818E-4 * I - 0.15006) / V$	I
TC	954.0µg/l ± 26.34µg/l	367.8AU CR!	$e = (8.100E-4 * I + 0.17911) / V$	I
TN	1.56mg/l ± 16.81µg/l	364.5AU	$e = (0.0015999 * I + 0.19914) / V$	I

Figure VIII-5: Raw TOC/N Data Report 2 (2 of 5).

AnalysesTable

AnalysesTable: 031118

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Calibration function Type	Density DF
SAND1PV1			3/12/2018 3:01:54 AM	21
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.39mg/l		Concentration [1, 2, 3, 4] = 0	
IC	149.1µg/l ± 25.38µg/l	287.0AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.53mg/l ± 77.72µg/l	726.1AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.64mg/l ± 15.70µg/l	388.0AU	c = (0.0015999*F + 0.19914)/V	1
SAND2PV1			3/12/2018 3:40:50 AM	22
DIFF TN		IC, TC, TN	500.0µl 3 (3-4) 1 in 1 Sample	
TOC	1.43mg/l		Concentration [1, 2, 3] = 0	
IC	136.4µg/l ± 5.85µg/l	278.9AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.57mg/l ± 41.14µg/l	746.4AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.64mg/l ± 16.63µg/l	387.5AU	c = (0.0015999*F + 0.19914)/V	1
SAND1PV3			3/12/2018 4:09:06 AM	23
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.23mg/l		Concentration [1, 2, 3, 4] = 0	
IC	115.8µg/l ± 12.93µg/l	265.8AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.35mg/l ± 23.96µg/l	610.3AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.56mg/l ± 3.36µg/l	363.0AU	c = (0.0015999*F + 0.19914)/V	1
SAND2PV3			3/12/2018 4:43:53 AM	24
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.28mg/l		Concentration [1, 2, 3, 4] = 0	
IC	72.46µg/l ± 12.25µg/l	238.1AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.35mg/l ± 13.39µg/l	613.7AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.57mg/l ± 13.46µg/l	367.1AU	c = (0.0015999*F + 0.19914)/V	1
SAND1PV10			3/12/2018 5:20:42 AM	25
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.21mg/l		Concentration [1, 2, 3, 4] = 0	
IC	78.48µg/l ± 7.70µg/l	241.9AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.29mg/l ± 12.04µg/l	575.1AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.59mg/l ± 3.91µg/l	373.2AU	c = (0.0015999*F + 0.19914)/V	1
SAND2PV10			3/12/2018 5:56:59 AM	26
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.26mg/l		Concentration [1, 2, 3, 4] = 0	
IC	98.53µg/l ± 24.33µg/l	254.7AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.36mg/l ± 22.47µg/l	619.9AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.60mg/l ± 5.61µg/l	376.4AU	c = (0.0015999*F + 0.19914)/V	1
SAND1PV30			3/12/2018 6:36:01 AM	27
DIFF TN		IC, TC, TN	500.0µl 3 (3-4) 1 in 1 Sample	
TOC	1.20mg/l		Concentration [1, 2, 3] = 0	
IC	92.16µg/l ± 2.59µg/l	250.7AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.29mg/l ± 39.80µg/l	577.1AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.61mg/l ± 3.93µg/l	380.0AU	c = (0.0015999*F + 0.19914)/V	1
SAND2PV30			3/12/2018 7:05:45 AM	28
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.15mg/l		Concentration [1, 2, 3, 4] = 0	
IC	67.77µg/l ± 11.73µg/l	235.1AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.22mg/l ± 58.71µg/l	530.5AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.62mg/l ± 13.21µg/l	381.1AU	c = (0.0015999*F + 0.19914)/V	1
SS204			3/12/2018 7:42:26 AM	29
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	881.7µg/l		Concentration [1, 2, 3, 4] = 0	
IC	54.62µg/l ± 18.24µg/l	226.7AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	936.4µg/l ± 8.16µg/l	356.9AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.78mg/l ± 41.84µg/l	431.1AU	c = (0.0015999*F + 0.19914)/V	1
SAND3PV1			3/12/2018 8:19:04 AM	30
DIFF TN		IC, TC, TN	500.0µl 4 (3-4) 1 in 1 Sample	
TOC	1.18mg/l		Concentration [1, 2, 3, 4] = 0	
IC	81.64µg/l ± 11.93µg/l	244.0AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V	1
TC	1.26mg/l ± 20.12µg/l	555.7AU CR!	c = (8.100E-4*F + 0.17911)/V	1
TN	1.80mg/l ± 6.69µg/l	438.8AU	c = (0.0015999*F + 0.19914)/V	1

Figure VIII-6: Raw TOC/N Data Report 2 (3 of 5).

AnalysesTable

AnalysesTable: 031118

Sample ID	Method	Parameter	Time of analysis	Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity Rep. Dilution Calibration function Type	Density DF
SAND3PV3				
DIFF TN		IC, TC, TN	3/12/2018 8:56:12 AM	31
TOC	1.26mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	37.84µg/l ± 9.84µg/l	216.0AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.30mg/l ± 26.44µg/l	578.3AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.80mg/l ± 10.92µg/l	437.5AU	c = (0.0015999* T + 0.19914)/V	1
SAND3PV10				
DIFF TN		IC, TC, TN	3/12/2018 9:35:40 AM	32
TOC	1.10mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	65.75µg/l ± 17.40µg/l	233.8AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.16mg/l ± 36.07µg/l	497.6AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.74mg/l ± 14.28µg/l	420.2AU	c = (0.0015999* T + 0.19914)/V	1
SAND3PV30				
DIFF TN		IC, TC, TN	3/12/2018 10:14:42 AM	33
TOC	1.17mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	48.48µg/l ± 10.15µg/l	222.8AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.21mg/l ± 1.48µg/l	528.1AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.84mg/l ± 14.22µg/l	451.9AU	c = (0.0015999* T + 0.19914)/V	1
SS105				
DIFF TN		IC, TC, TN	3/12/2018 10:51:55 AM	34
TOC	988.6µg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	44.43µg/l ± 14.50µg/l	220.2AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.03mg/l ± 45.58µg/l	416.5AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.69mg/l ± 6.01µg/l	404.7AU	c = (0.0015999* T + 0.19914)/V	1
MDR753PV1				
DIFF TN		IC, TC, TN	3/12/2018 11:31:55 AM	35
TOC	2.06mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	539.9µg/l ± 36.73µg/l	536.3AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	2.60mg/l ± 42.69µg/l	1,386.0AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.54mg/l ± 13.56µg/l	358.0AU	c = (0.0015999* T + 0.19914)/V	1
FA503PV1				
DIFF TN		IC, TC, TN	3/12/2018 12:08:09 PM	36
TOC	1.19mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	67.81µg/l ± 4.83µg/l	235.1AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.25mg/l ± 102.3µg/l	553.5AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.53mg/l ± 26.90µg/l	353.1AU	c = (0.0015999* T + 0.19914)/V	1
MDR753PV3				
DIFF TN		IC, TC, TN	3/12/2018 12:43:44 PM	37
TOC	2.30mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	82.96µg/l ± 7.89µg/l	244.8AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	2.38mg/l ± 65.82µg/l	1,251.0AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.60mg/l ± 5.07µg/l	375.3AU	c = (0.0015999* T + 0.19914)/V	1
FA503PV3				
DIFF TN		IC, TC, TN	3/12/2018 1:20:02 PM	38
TOC	1.14mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	54.30µg/l ± 19.32µg/l	226.5AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.19mg/l ± 860.0ng/l	514.0AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.59mg/l ± 3.33µg/l	371.4AU	c = (0.0015999* T + 0.19914)/V	1
MDR753PV10				
DIFF TN		IC, TC, TN	3/12/2018 1:55:55 PM	39
TOC	2.13mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	96.53µg/l ± 37.20µg/l	253.5AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	2.22mg/l ± 64.83µg/l	1,151.0AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.57mg/l ± 31.14µg/l	367.3AU	c = (0.0015999* T + 0.19914)/V	1
FA503PV10				
DIFF TN		IC, TC, TN	3/12/2018 2:31:33 PM	40
TOC	1.05mg/l		500.0µl 4 (3-4) 1 in 1 Sample	
IC	74.72µg/l ± 14.26µg/l	239.5AU CR!	c = (2.563E-9* T^2 + 7.818E-4* T + -0.15006)/V	1
TC	1.13mg/l ± 2.28µg/l	473.6AU CR!	c = (8.100E-4* T + 0.17911)/V	1
TN	1.57mg/l ± 7.75µg/l	366.7AU	c = (0.0015999* T + 0.19914)/V	1

Figure VIII-7: Raw TOC/N Data Report 2 (4 of 5).

AnalysesTable

AnalysesTable: 031118

Sample ID	Method	Parameter	Time of analysis			Rack pos.
Param.	Concentration ± SD	Area units [AU]	Sample quantity	Rep.	Dilution	Density
			Calibration function			DF
MDR753PV30			3/12/2018 3:06:44 PM			41
DIFF TN		IC, TC, TN	500.0µl	4 (3-4)	1 in 1 Sample	
TOC	1.86mg/l		Concentration [1, 2, 3, 4] = 0			
IC	57.05µg/l ± 31.16µg/l	228.3AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V			1
TC	1.92mg/l ± 24.57µg/l	963.0AU CR!	c = (8.100E-4*F + 0.17911)/V			1
TN	1.59mg/l ± 14.40µg/l	373.3AU	c = (0.0015999*F + 0.19914)/V			1
FA503PV30			3/12/2018 3:43:58 PM			42
DIFF TN		IC, TC, TN	500.0µl	4 (3-4)	1 in 1 Sample	
TOC	1.03mg/l		Concentration [1, 2, 3, 4] = 0			
IC	70.79µg/l ± 7.09µg/l	237.0AU CR!	c = (2.563E-9*F ² + 7.818E-4*F + -0.15006)/V			1
TC	1.10mg/l ± 16.11µg/l	456.7AU CR!	c = (8.100E-4*F + 0.17911)/V			1
TN	1.62mg/l ± 7.16µg/l	381.6AU	c = (0.0015999*F + 0.19914)/V			1

Figure VIII-8: Raw TOC/N Data Report 2 (5 of 5).

CalibrationReport

Calibration: Cal_Diff_5_180201_1746
 Calibration of: 2/1/2018 5:46:55 PM -0600 Method: Diff_5

Comment

Accidentally added second "100 mg/L TC." Don't use that point!

User: Admin
 Calibration channel: IC-500ppm
 Quadratic Regression [µg]: $c = (k2 \cdot P^2 + k1 \cdot I + k0) / V$
 $k0 = -0.15006$ $k1 = 7.818E-4$ $k2 = 2.563E-9$
 Residual SD: 164.1AU Linearity: False
 Procedure standard deviation: 290.7µg/l Variance homogeneity: OK
 Procedure variation coefficient: 0.79286%
 Qual. of rep.: 0.99997
 Correlation coefficient: 0.99999

Calibration with fixed sample volume: 500.0µl

No.	Rep.	c-nom.	m-Nominal	I-Net	c-act.	c-Delta
B	3-5			460.8AU/ml		
1	3-5	2.500mg/l	1.25µg	1,751AU	2.454mg/l	-1.84%
2	3-5	5.000mg/l	2.50µg	3,296AU	4.910mg/l	-1.81%
3	3-5	12.500mg/l	6.25µg	8,178AU	12.829mg/l	2.63%
4	3-5	25.000mg/l	12.50µg	1.526E4AU	24.757mg/l	-0.97%
5	3-5	50.000mg/l	25.00µg	2.937E4AU	50.053mg/l	0.11%
7	3-5	125.000mg/l	62.50µg	6.59E4AU	125.000mg/l	0.00%

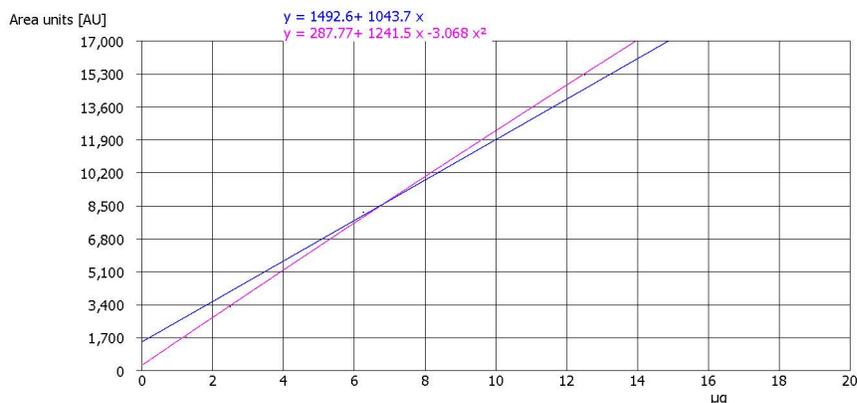


Figure VIII-9: Total carbon and total inorganic carbon calibration report.

Calibration Report

Calibration: Cal_TN_only_180306_1434
 Calibration of: 3/6/2018 2:34:34 PM -0600 Method: TN_only

User: Admin
 Calibration channel: TN
 Linear Regression [µg]: $c = (k1 \cdot I + k0) / V$
 $k0 = 0.20011$ $k1 = 0.0015999$

Residual SD: 40.343AU Linearity: OK
 Procedure standard deviation: 129.2µg/l Variance homogeneity: OK
 Procedure variation coefficient: 2.7931% Detection limit: 385.0µg/l
 Qual. of rep.: 0.99929 Identification limit: 769.9µg/l
 Correlation coefficient: 0.99964 Quantification limit: 1.53mg/l

Calibration with fixed sample volume: 500.0µl

No.	Rep.	c-nom.	m-Nominal	I-Net	c-act.	c-Delta
B	3-4			1.21AU/ml		
1	3-4	1.000mg/l	0.500µg	217.7AU	1.097mg/l	9.68%
2	3-4	2.500mg/l	1.25µg	650.6AU	2.482mg/l	-0.71%
3	3-4	5.000mg/l	2.50µg	1,394AU	4.859mg/l	-2.82%
4	3-4	10.000mg/l	5.00µg	3,019AU	10.062mg/l	0.62%

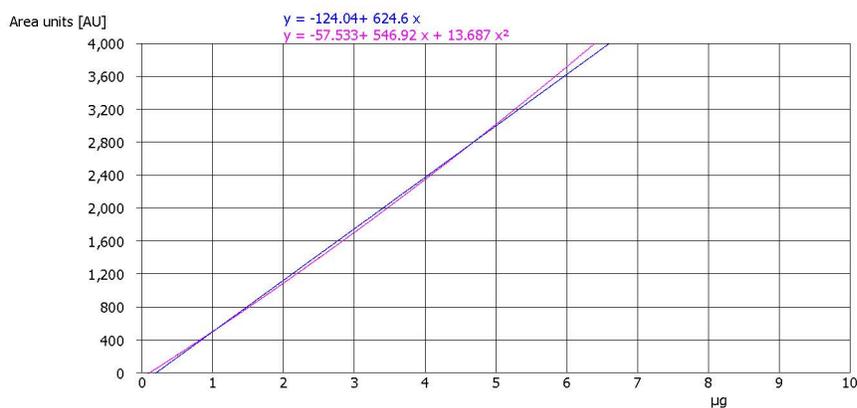


Figure VIII-10: Total nitrogen calibration report.

**Appendix IX: EPA Recommended Water Quality Criteria for Aquatic Life –
Hardness Adjusted Metals Limits by Individual Sample**

Table IX-1: Hardness adjusted EPA Recommended Water Quality Criteria for Aquatic Life for arsenic, cadmium, chromium(III), chromium(IV), and copper by individual sample (1 of 2).

Sample	Hardness (mg/L as CaCO ₃)	As (µg/L)	Cd (µg/L)	Cr(III) (µg/L)	Cr(VI) (µg/L)	Cu (µg/L)
SS1.03M	0.00	0.00	0.00	0.00	0.00	0.00
SAND1PV01	35.55	0.04	0.68	244.26	40.75	0.96
SAND1PV03	28.67	124.49	0.56	204.82	40.75	0.96
SAND1PV10	24.43	4.00	0.48	179.62	40.75	0.96
SAND1PV30	21.03	5.00	0.42	158.91	40.75	0.96
SAND2PV01	40.04	1.39	0.76	269.25	40.75	0.96
SAND2PV03	28.84	7.00	0.56	205.79	40.75	0.96
SAND2PV10	25.11	76.28	0.49	183.75	40.75	0.96
SAND2PV30	21.31	9.00	0.42	160.62	40.75	0.96
SS2.04	0.00	0.00	0.00	0.00	0.00	0.00
SAND3PV01	27.95	26.63	0.54	200.56	40.75	0.96
SAND3PV03	23.80	12.00	0.47	175.81	40.75	0.96
SAND3PV10	23.59	13.00	0.46	174.56	40.75	0.96
SAND3PV30	19.72	14.00	0.39	150.74	40.75	0.96
SS1.01	0.00	0.00	0.00	0.00	0.00	0.00
FA5.01PV01	214.59	16.00	3.66	1064.86	40.75	0.96
FA5.01PV03	193.49	17.00	3.32	978.27	40.75	0.96
FA5.01PV10	132.52	18.00	2.33	717.53	40.75	0.96
FA5.01PV30	108.71	19.00	1.94	610.08	40.75	0.96
FA5.02PV01	279.28	20.00	4.68	1321.31	40.75	0.96
FA5.02PV03	214.86	21.00	3.66	1065.94	40.75	0.96
FA5.02PV10	144.47	22.00	2.53	770.12	40.75	0.96
FA5.02PV30	122.82	23.00	2.17	674.24	40.75	0.96
SS1.05	0.00	0.00	0.00	0.00	0.00	0.00
FA5.03PV01	182.45	25.00	3.15	932.31	40.75	0.96
FA5.03PV03	162.87	26.00	2.83	849.55	40.75	0.96
FA5.03PV10	108.87	27.00	1.94	610.83	40.75	0.96
FA5.03PV30	65.54	28.00	1.21	403.10	40.75	0.96
MDR7.53PV01	185.79	29.00	3.20	946.27	40.75	0.96
MDR7.53PV03	148.55	30.00	2.60	787.90	40.75	0.96
MDR7.53PV10	92.03	31.00	1.66	532.31	40.75	0.96
MDR7.53PV30	51.57	32.00	0.97	331.27	40.75	0.96

Table IX-2: Hardness adjusted EPA Recommended Water Quality Criteria for Aquatic Life for arsenic, cadmium, chromium(III), chromium(IV), and copper by individual sample (2 of 2).

Sample	Hardness (mg/L as CaCO ₃)	As (µg/L)	Cd (µg/L)	Cr(iii) (µg/L)	Cr(vi) (µg/L)	Cu (µg/L)
SS2.01	0.00	0.00	0.00	0.00	0.00	0.00
MDR7.51PV01	154.30	34.00	2.69	812.75	40.75	0.96
MDR7.51PV03	117.89	35.00	2.09	651.99	40.75	0.96
MDR7.51PV10	83.61	36.00	1.52	492.05	40.75	0.96
MDR7.51PV30	52.76	37.00	0.99	337.47	40.75	0.96
MDR7.52PV01	161.26	38.00	2.80	842.69	40.75	0.96
MDR7.52PV03	135.61	39.00	2.38	731.19	40.75	0.96
MDR7.52PV10	85.74	40.00	1.55	502.32	40.75	0.96
MDR7.52PV30	56.80	41.00	1.06	358.52	40.75	0.96
SS2.03	0.00	0.00	0.00	0.00	0.00	0.00
APT1PV01	47.48	43.00	0.89	309.58	40.75	0.96
APT1PV03	33.68	44.00	0.65	233.69	40.75	0.96
APT1PV10	26.31	45.00	0.51	190.91	40.75	0.96
APT1PV30	22.61	46.00	0.45	168.59	40.75	0.96
APT3PV01	67.60	47.00	1.24	413.45	40.75	0.96
APT3PV03	37.97	48.00	0.73	257.81	40.75	0.96
APT3PV10	27.72	49.00	0.54	199.23	40.75	0.96
APT3PV30	23.80	50.00	0.47	175.81	40.75	0.96
SS2.02	0.00	0.00	0.00	0.00	0.00	0.00
APT2PV01	28.66	52.00	0.56	204.76	40.75	0.96
APT2PV03	24.78	53.00	0.49	181.76	40.75	0.96
APT2PV10	24.36	54.00	0.48	179.21	40.75	0.96
APT2PV30	19.66	55.00	0.39	150.35	40.75	0.96
BIO2PV01	33.86	56.00	0.65	234.69	40.75	0.96
BIO2PV03	30.20	57.00	0.59	213.73	40.75	0.96
BIO2PV10	26.74	58.00	0.52	193.43	40.75	0.96
BIO2PV30	22.98	59.00	0.45	170.85	40.75	0.96
SS1.04	0.00	0.00	0.00	0.00	0.00	0.00
BIO1PV01	55.43	61.00	1.03	351.41	40.75	0.96
BIO1PV03	47.05	62.00	0.89	307.28	40.75	0.96
BIO1PV10	39.24	63.00	0.75	264.81	40.75	0.96
BIO1PV30	28.86	64.00	0.56	205.90	40.75	0.96
BIO3PV01	54.67	65.00	1.02	347.48	40.75	0.96
BIO3PV03	44.27	66.00	0.84	292.31	40.75	0.96
BIO3PV10	37.57	67.00	0.72	255.53	40.75	0.96
BIO3PV30	33.22	68.00	0.64	231.05	40.75	0.96

Table IX-3: Hardness adjusted EPA Recommended Water Quality Criteria for Aquatic Life for lead, mercury, nickel, selenium, silver, and zinc by individual sample (1 of 2).

Sample	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Ag (µg/L)	Zn (µg/L)
SS1.03M	0.00	0.00	0.00	0.00	0.00	0.00
SAND1PV01	20.61	0.85	195.20	0.00	0.54	48.79
SAND1PV03	16.20	0.85	162.74	0.00	0.38	40.66
SAND1PV10	13.52	0.85	142.10	0.00	0.28	35.50
SAND1PV30	11.42	0.85	125.21	0.00	0.22	31.27
SAND2PV01	23.54	0.85	215.87	0.00	0.67	53.96
SAND2PV03	16.30	0.85	163.53	0.00	0.38	40.86
SAND2PV10	13.95	0.85	145.48	0.00	0.30	36.34
SAND2PV30	11.59	0.85	126.60	0.00	0.23	31.62
SS2.04	0.00	0.00	0.00	0.00	0.00	0.00
SAND3PV01	15.74	0.85	159.24	0.00	0.36	39.79
SAND3PV03	13.13	0.85	138.99	0.00	0.27	34.72
SAND3PV10	13.00	0.85	137.96	0.00	0.27	34.46
SAND3PV30	10.62	0.85	118.57	0.00	0.20	29.61
SS1.01	0.00	0.00	0.00	0.00	0.00	0.00
FA5.01PV01	146.70	0.85	893.34	0.00	11.96	223.79
FA5.01PV03	131.43	0.85	818.41	0.00	10.01	204.99
FA5.01PV10	87.63	0.85	594.17	0.00	5.22	148.75
FA5.01PV30	70.72	0.85	502.50	0.00	3.71	125.77
FA5.02PV01	193.57	0.85	1116.40	0.00	18.82	279.76
FA5.02PV03	146.89	0.85	894.27	0.00	11.99	224.02
FA5.02PV10	96.17	0.85	639.21	0.00	6.06	160.04
FA5.02PV30	80.72	0.85	557.18	0.00	4.58	139.48
SS1.05	0.00	0.00	0.00	0.00	0.00	0.00
FA5.03PV01	123.47	0.85	778.72	0.00	9.05	195.04
FA5.03PV03	109.37	0.85	707.42	0.00	7.44	177.15
FA5.03PV10	70.83	0.85	503.13	0.00	3.72	125.93
FA5.03PV30	40.65	0.85	327.51	0.00	1.56	81.92
MDR7.53PV01	125.88	0.85	790.77	0.00	9.34	198.06
MDR7.53PV03	99.09	0.85	654.46	0.00	6.35	163.87
MDR7.53PV10	58.99	0.85	436.48	0.00	2.79	109.22
MDR7.53PV30	31.19	0.85	267.41	0.00	1.03	66.87

Table IX-4: Hardness adjusted EPA Recommended Water Quality Criteria for Aquatic Life for lead, mercury, nickel, selenium, silver, and zinc by individual sample (2 of 2).

Sample	Pb (µg/L)	Hg (µg/L)	Ni (µg/L)	Se (µg/L)	Ag (µg/L)	Zn (µg/L)
SS2.01	0.00	0.00	0.00	0.00	0.00	0.00
MDR7.51PV01	103.21	0.85	675.79	0.00	6.78	169.22
MDR7.51PV03	77.22	0.85	538.20	0.00	4.27	134.72
MDR7.51PV10	53.12	0.85	402.42	0.00	2.36	100.69
MDR7.51PV30	31.98	0.85	272.58	0.00	1.07	68.16
MDR7.52PV01	108.21	0.85	701.52	0.00	7.32	175.67
MDR7.52PV03	89.83	0.85	605.86	0.00	5.43	151.68
MDR7.52PV10	54.60	0.85	411.10	0.00	2.47	102.86
MDR7.52PV30	34.71	0.85	290.17	0.00	1.22	72.56
SS2.03	0.00	0.00	0.00	0.00	0.00	0.00
APT1PV01	28.46	0.85	249.35	0.00	0.89	62.34
APT1PV03	19.40	0.85	186.49	0.00	0.49	46.61
APT1PV10	14.71	0.85	151.34	0.00	0.32	37.81
APT1PV30	12.39	0.85	133.09	0.00	0.25	33.24
APT3PV01	42.06	0.85	336.20	0.00	1.64	84.10
APT3PV03	22.19	0.85	206.40	0.00	0.61	51.59
APT3PV10	15.59	0.85	158.15	0.00	0.35	39.51
APT3PV30	13.13	0.85	138.99	0.00	0.27	34.72
SS2.02	0.00	0.00	0.00	0.00	0.00	0.00
APT2PV01	16.19	0.85	162.69	0.00	0.37	40.65
APT2PV03	13.75	0.85	143.85	0.00	0.29	35.94
APT2PV10	13.48	0.85	141.77	0.00	0.28	35.41
APT2PV30	10.58	0.85	118.25	0.00	0.20	29.53
BIO2PV01	19.52	0.85	187.31	0.00	0.50	46.81
BIO2PV03	17.17	0.85	170.05	0.00	0.41	42.49
BIO2PV10	14.97	0.85	153.40	0.00	0.33	38.32
BIO2PV30	12.62	0.85	134.94	0.00	0.26	33.70
SS1.04	0.00	0.00	0.00	0.00	0.00	0.00
BIO1PV01	33.78	0.85	284.22	0.00	1.17	71.08
BIO1PV03	28.17	0.85	247.44	0.00	0.88	61.86
BIO1PV10	23.01	0.85	212.20	0.00	0.64	53.04
BIO1PV30	16.31	0.85	163.62	0.00	0.38	40.88
BIO3PV01	33.27	0.85	280.94	0.00	1.14	70.25
BIO3PV03	26.32	0.85	235.00	0.00	0.79	58.75
BIO3PV10	21.92	0.85	204.52	0.00	0.60	51.12
BIO3PV30	19.10	0.85	184.31	0.00	0.48	46.06

Appendix X: Graphs of Points of Zero Charge by pH Drift Method

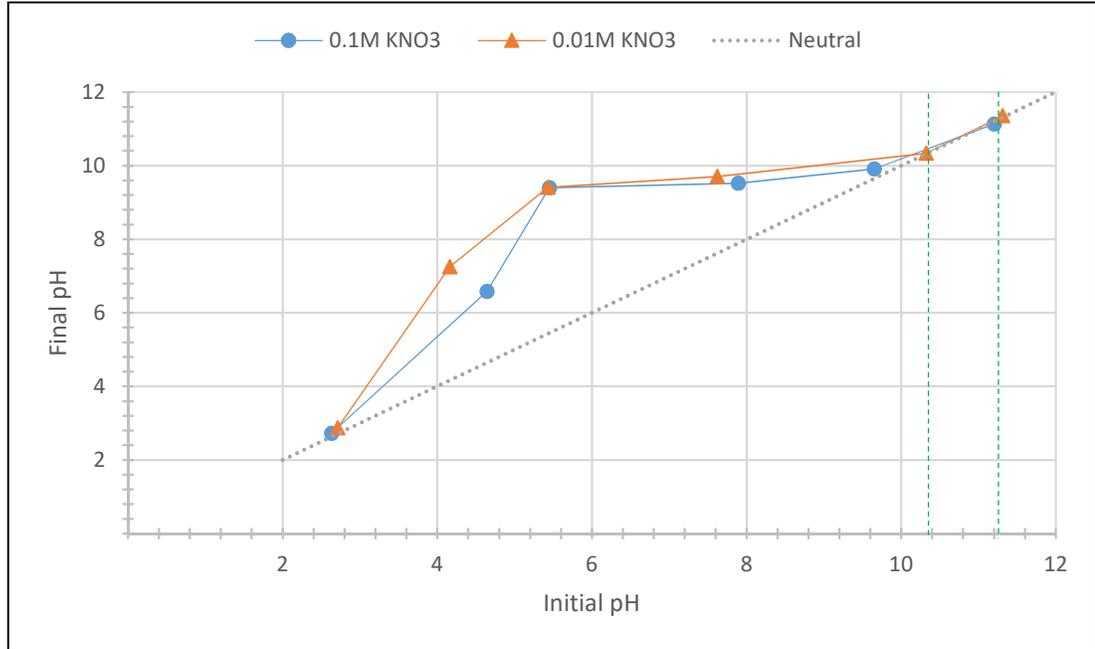


Figure X-1: SAND point of zero charge graph.

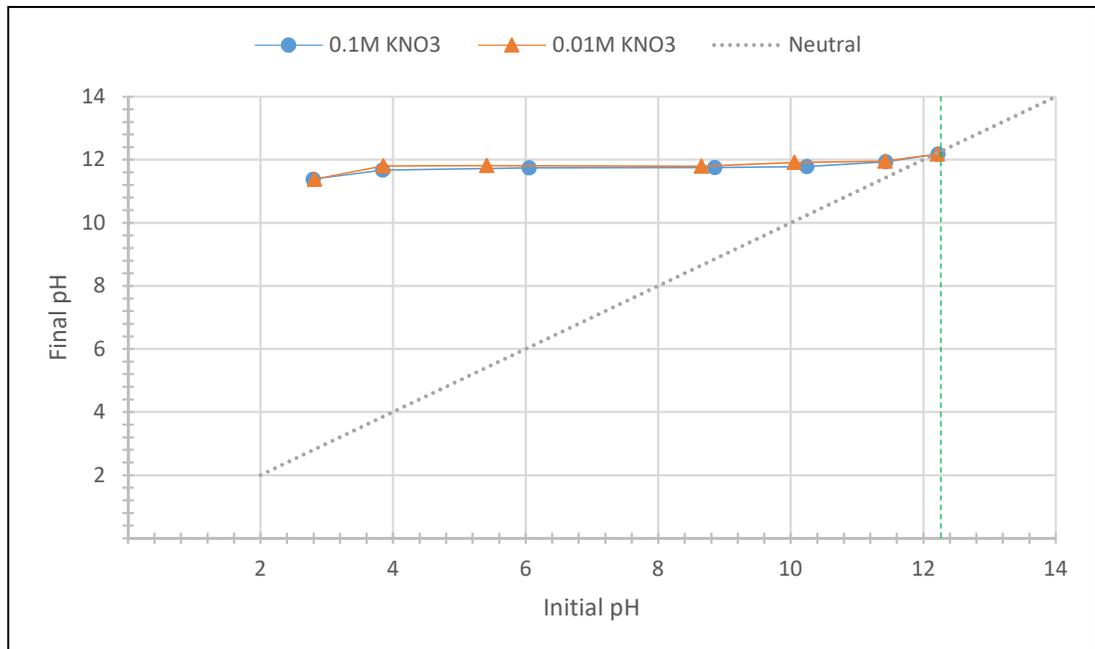


Figure X-2: FA point of zero charge graph.

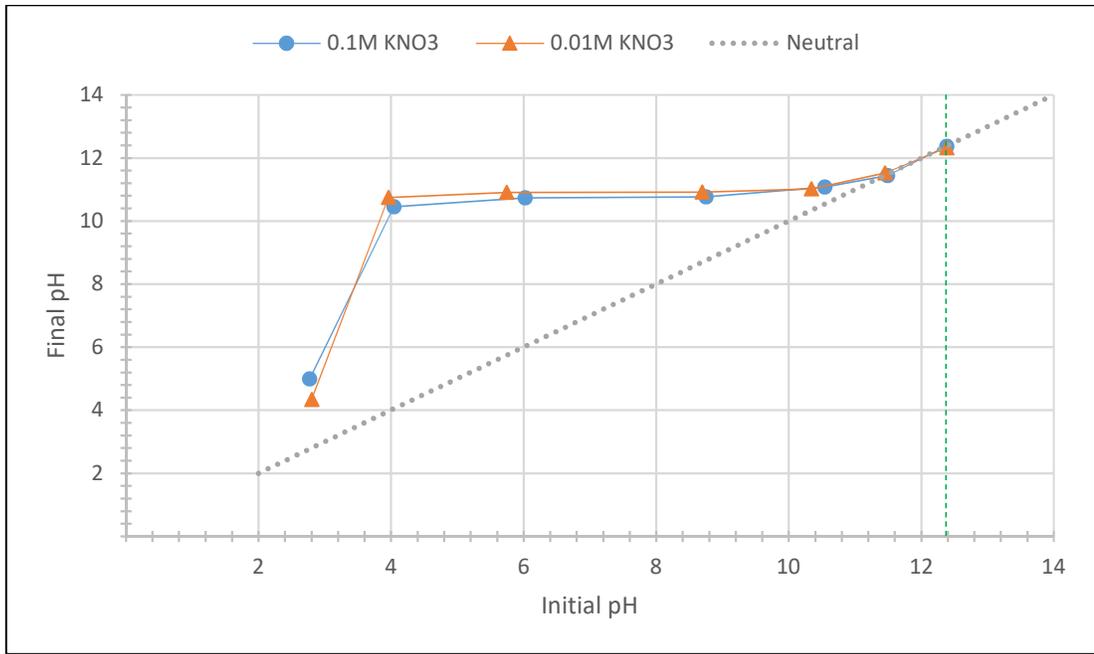


Figure X-3: FA5.0 point of zero charge graph.

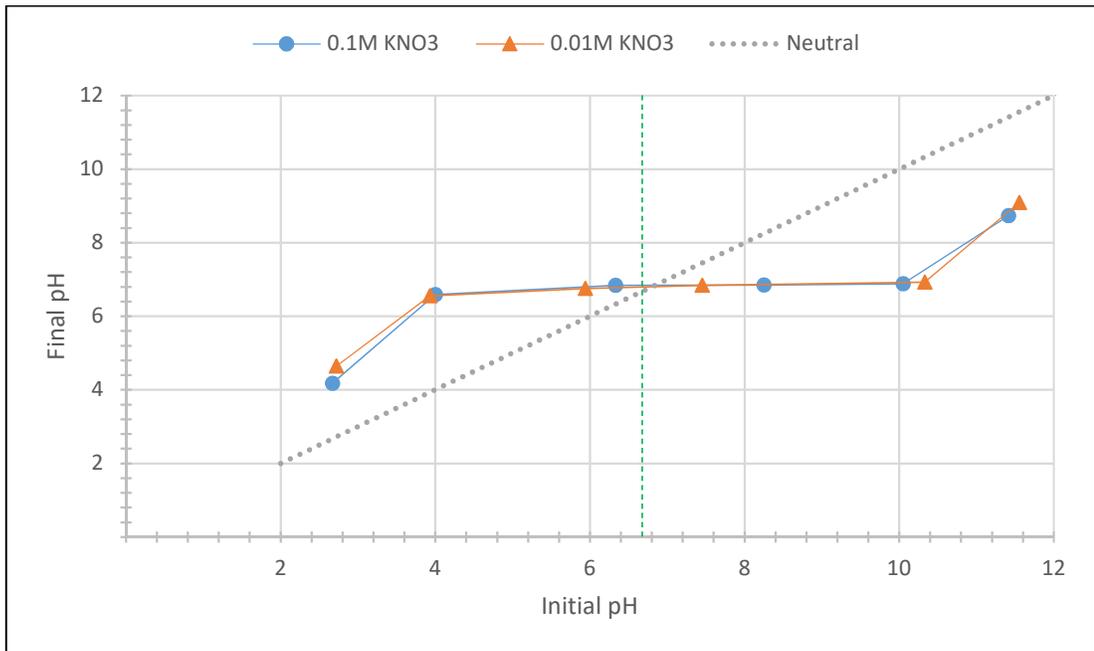


Figure X-4: MDR point of zero charge graph.

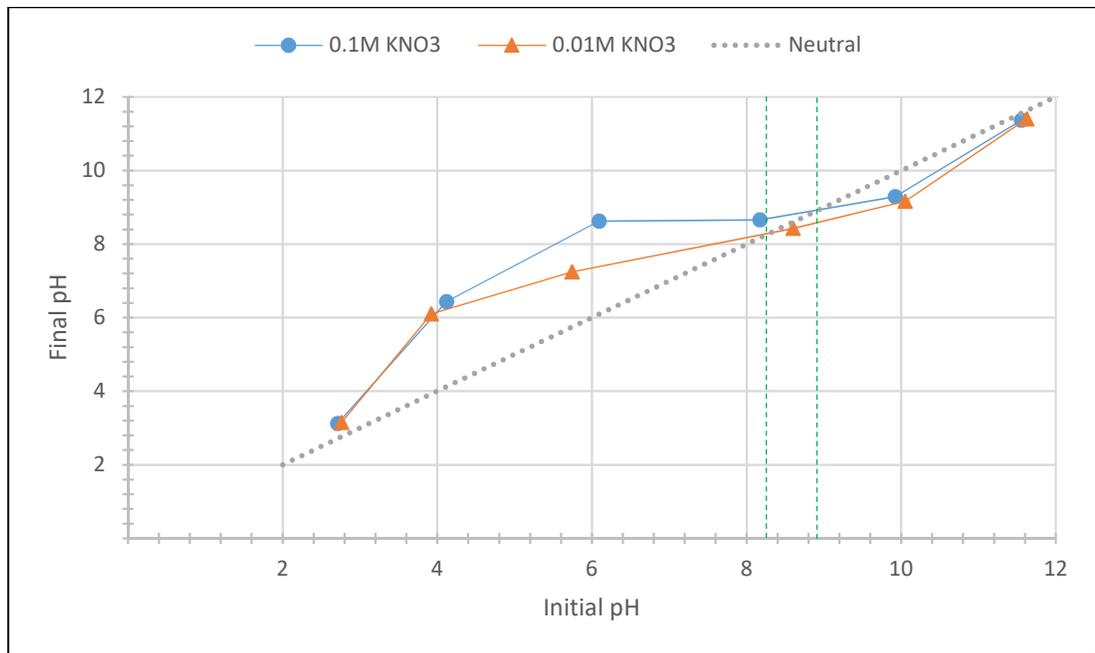


Figure X-5: MDR7.5 point of zero charge graph.

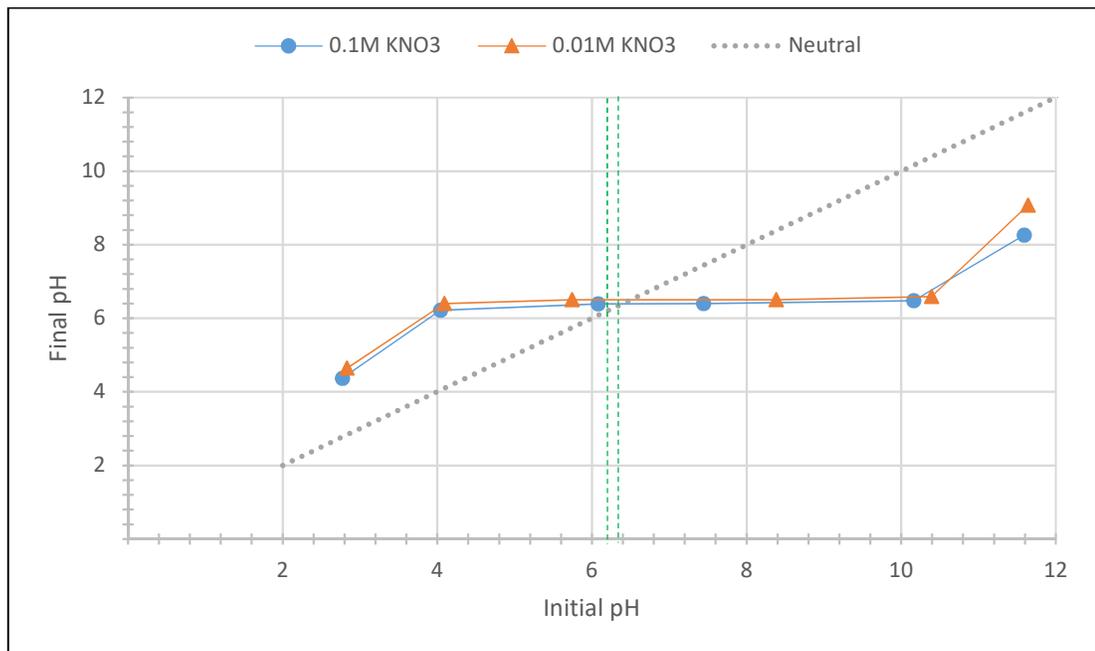


Figure X-6: APT point of zero charge graph.

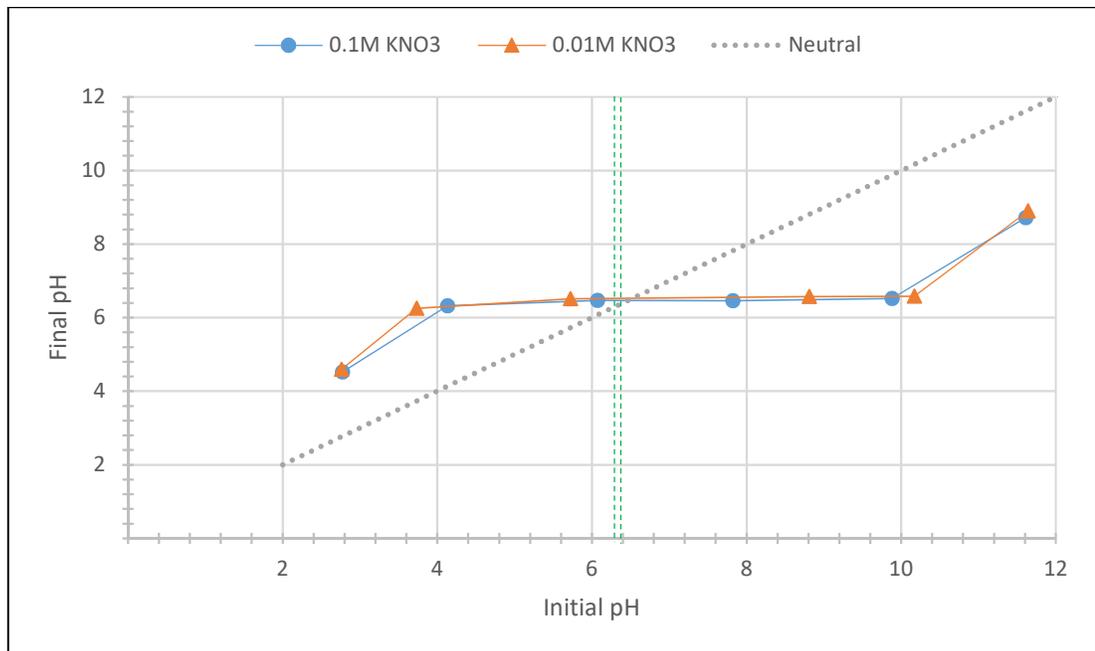


Figure X-7: BIO point of zero charge graph.