Nutrient Removal Rates of Permeable Reactive Concrete

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Abstract: Nitrogen and phosphorus contained in stormwater runoff contaminate both surface and groundwaters, causing problems for natural aquatic systems and human health. Pervious concrete specifically designed for pollutant removal, otherwise known as permeable reactive concrete (PRC), may be used as a novel component of existing infrastructure to remove nutrients from runoff. This research compares the removal and retention of dissolved, inorganic nitrate-nitrogen (NO_3-N) and orthophosphate-phosphorus (PO_4-P) for three PRC mixtures. The control PRC was ordinary portland cement (OPC) and was compared against other mixtures containing 25% replacement with Class C fly ash or with drinking water treatment residual waste (DWTR). Concrete specimens were jar-tested for 72 h in three different concentrations of nitrate or phosphate. The control mixture removed 60% of NO_3-N and more than 80% PO_4-P, and the fly ash mixture removed up to 39% of NO_3-N and more than 91% PO_4-P. The DWTR mixture leached NO_3-N while removing more than 80% PO_4-P. Linear isotherms were determined for the range of nutrient concentrations tested. Column leach tests were conducted on specimens after initial jar testing and used as an indication of removal permanence. Inorganic removal mechanisms were investigated, including crystallographic substitution, adsorption, and physical solute filtering in cement pore space. Results indicate PRC can be one of the leading methods to remove nitrate from surface waters and is as efficient as other methods for orthophosphate removal. **DOI: 10.1061/JSWBAY.0000850.** *© 2018 American Society of Civil Engineers.*

Introduction

Nutrients contained in surface water runoff have negative impacts on surface and groundwater systems. High concentrations of phosphorus and nitrogen promote growth of algae in aquatic systems, including lakes, coastal areas, large rivers, and wetlands (USEPA 1993b). Excessive amounts of nutrients have been problematic for wildlife and societal functions for areas in the United States such as the Florida Bay, the Chesapeake Bay, and the Gulf of Mexico by creating preferential conditions for eutrophication (Zhang et al. 2015; Scade-Poole and Moller 2016; Wendel 2015). Additionally, high levels of nitrate-nitrogen cause fatal symptoms in infants under 6 months of age as blue baby syndrome when ingested from drinking water (WHO 2011). Receiving waters that serve as surface water sources have been greatly impacted by nitrogen, to the extent that public drinking water treatment facilities are forced to remove nitrate in order to protect human health (Stets et al. 2015). Current methods for nutrient remediation, such as anion exchange and reverse osmosis, are costly and require significant maintenance (King et al. 2012). In the Midwestern United States, major municipalities are engaging in litigation with upstream farmers to pay for past and future nitrate reduction at drinking water treatment facilities (Metre et al. 2016). Ideally, nutrient pollution should be intercepted and retained before entering water systems to reduce potential remediation costs and environmental impacts. Stormwater best management practices (BMPs) can be effective at removing nutrients before pollution enters water systems; however, structural BMPs that use plants for nutrient uptake can increase the amount of nutrients discharged as plants decay (NCHRP 2006). A considerable amount of research has been performed regarding removal effectiveness of installed permeable pavement systems for hydrocarbons, fecal coliforms, nutrients, metals, and other contaminants (Scholz and Grabowiecki 2007; Imran et al. 2013; ACI 2011). In most cases, permeable pavements have been studied without investigating or comparing pollutant removal potential of individual pavement material mixture proportions, storage layer materials, and soil microbe interactions. Instead, studies have focused on system-wide performance through field installation monitoring of nutrients at the inlet and outlet.

The research presented herein aimed to characterize the nutrient mass removal rates and retention capacity of three permeable reactive concrete (PRC) mix designs, one ordinary portland cement (OPC) control, and two with 25% replacement of OPC with fly ash (FA) or drinking water treatment residual waste (DWTR) by weight in standard laboratory conditions. Mass removal rates determined for each mixture can serve as basis for future PRC designs. This investigation presents the first critical bench-scale examination of inorganic, dissolved nitrate and phosphate removal by pervious concrete in its purest form. Removal mechanisms for nitrate and phosphate are discussed and the effects of a supplementary cementitious material (SCM) and a waste mineral filler on removal are compared to the control.

Literature Summary

Examination of pervious concrete as a water quality best management practice has just begun and is typically limited to consideration of the material as a component of a greater permeable pavement system. The literature compares different permeable pavement systems, not different permeable pavement mixture

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proportions In particular, little is known about the fundamental performance of pervious concrete under the influence of nutrient-laden solutions. Field studies generally compare nutrient removal in significantly different permeable pavement systems. The common comparisons are between conventional asphalt and permeable interlocking concrete pavers, porous asphalt, or pervious concrete (Beecham et al. 2012; Bean et al. 2007; Brown and Borst 2015; Collins et al. 2010; Drake et al. 2014; Huang et al. 2016; James and Shahin 1998). These field studies do not evaluate the effects of physical or chemical properties of similar pervious concrete mixtures. Of the early laboratory studies, Park and Tia (2004) investigated permeable concrete coated in a biofilm for nutrient removal, noting that aggregate size influenced microbial growth, which in turn influenced nutrient removal. Soto-Perez and Hwang (2016) investigated the effects of fly ash for fecal coliform and phosphorus removal. Other studies investigated the removal for particular permeable pavement system designs (Tota-Maharaj and Scholz 2010; Kamali et al. 2017). However, the literature lacks a fundamental examination of the removal capacity of the concrete materials themselves as a potential mechanism for physical or chemical nutrient reduction.

Nutrient removal is traditionally thought to occur through chemical or physical sorption, biological uptake, biological transformation processes, and filtration (NCHRP 2006), all of which may be present in permeable pavement systems. Nitrification and filtration are acknowledged contributors to nitrogen species reduction in the reported literature (Bean et al. 2007; Brown and Borst 2015; Drake et al. 2014). Ammonia as nitrogen (NH_4-N) reduction because of nitrification is a commonly observed phenomenon in permeable pavement systems because the conditions present in the filtering action into the aggregate base holding zone are aerobic. Total nitrogen (TN) reductions are generally attributed to the reduction of ammonia or filtration of particulate bound organic nitrogen (Brown and Borst 2015). An increase in nitrite-nitrogen (NO_2-N) or nitrate-nitrogen (NO_3-N) is commonly observed in permeable pavements because of the nitrification of NH_4-N and lack of anaerobic conditions for denitrification because most systems are designed to completely empty in 72 h. Nitrifying bacteria perform best in the optimal pH range of 7.6–8.8 S/U (standard units), which may influence the reduction of nitrogen species in permeable pavement systems (Brown and Borst 2015) because these systems may retain higher pH values for many years.

Phosphorus, on the other hand, may be removed through filtration, adsorption, precipitation, or biological uptake within a permeable pavement system. Permeable pavement systems present a beneficial environment for phosphorus removal with elevated pH and, in the case of limestone storage aggregate or pervious concrete, provide favorable calcium ions for phosphorus attenuation. Dissolved phosphorus may be removed through chemical or physical adsorption and subsequent precipitation and filtration (Brown and Borst 2015). Portland cement and Class C fly ash contain significant amounts of calcium compounds, which are favorable for phosphorus removal (Agyei et al. 2002). DWTR also has a high calcite calcium content and has been used as an internal curing agent in cement mortar because of its flocculated structure and high accessible moisture content (Nowasell and Kevern 2016). The chemical composition and loss on ignition (LOI) of OPC, class C fly ash, and DWTR are shown in Table 1.

Table 1. Chemical Composition of Cementitious Materials

Compound	Portland cement (%)	Class C fly ash (%)	DWTR (%)
SiO_2	20.49	40.71	5.84
AL_2O_3	4.26	18.99	1.55
Fe_2O_3	3.14	6.05	0.78
CaO	63.48	20.10	43.93
MgO	2.11	4.82	4.24
SO_3	2.90	0.83	0.31
Na_2O	0.18	1.46	—
K_2O	0.47	0.65	0.20
CO_2	1.48	0.00	—
$CaCO_3$	3.41	0.00	—
P_2O_5	—	—	0.10
Loss on ignition	2.20	0.08	42.59

The removal of nitrogen species and orthophosphate for permeable interlocking concrete pavement (PICP) was monitored in North Carolina, where, notably, the PICP system effluent had significantly lower TKN and NH_4-N concentrations than the control asphalt pavement runoff, whereas NO_2-N concentrations increased and TN concentrations were not significantly different (Bean et al. 2007). Removal was attributed to nitrification through aerobic conditions presumably present in the pavement system. Total phosphorus (TP) concentrations were significantly decreased by the PICP, whereas there was no significant difference in orthophosphate concentrations between infiltrate and exfiltrate.

Drake et al. (2014) investigated the effluent concentrations of PICP and pervious concrete in field conditions. Permeable pavement systems reduced TN loadings through nitrification and filtration of organic nitrogen; however, NO_3 concentrations increased. One solution would be through adjustable storage to increase anoxic conditions favorable for denitrification (Drake et al. 2014). PICPs had greater phosphorus removal than the pervious concrete, which was attributed to larger pervious concrete influent concentrations. With the limited amount of research, it was unclear if the nutrients bound in the system were permanent. Similarly, Collins et al. (2010) found that NO_3 and NO_2 concentrations increased through permeable pavement systems, whereas TKN and NH_3 concentrations decreased. TN and organic nitrogen levels did not decease as seen in Drake et al. (2014).

Brown and Borst (2015) compared the nutrient concentrations in the discharged effluent of permeable concrete, PICP, and porous asphalt in a side-by-side-by-side field study. Results indicated higher dissolved PO_4 removal from the porous asphalt attributed to the unexpectedly higher pH of the effluent from the porous asphalt when compared to the effluent of other porous asphalt reported in the literature. The high pH of the porous asphalt was suggested to negatively influence the nitrification process of NO_2 to NO_3 as out of range for optimal transformation. NO_3 was the predominant nitrogen species in PICP and pervious concrete effluent, suggesting nitrification processes occurred. However, the TN concentrations were no different from the rainfall concentrations.

Other laboratory studies have focused on the removal capacity of individual unhydrated cementitious materials (Gray and Schwab 1993; Ugurlu and Salman 1998; Kirk et al. 2003; Zhang et al. 2008; Sikdar 2007). Individually, fly ash has been effective in removing phosphorus (Ugurlu and Salman 1998; Kirk et al. 2003; Zhang et al. 2008). Phosphorus removal was also observed for pervious concrete with OPC and 10 and 35% fly ash replacement in a column study by Soto-Pérez and Hwang (2016). However, a reduction in phosphorus removal was observed with the addition of fly ash in the mix design, likely because of the decrease in available calcium ions. Molle et al. (2002) found significant removal capacity in recycled crushed concrete when compared to calcite in batch isotherms and breakthrough curve testing.

The literature reviewing water treatment residuals (WTRs) and nutrient removal capacity tends to focus on removal of phosphorus species rather than nitrogen species, for primarily alum and ferric-based WTR (Krishna et al. 2017). Of the studies comparing alum, ferric, and lime-based WTR, Elliot et al. (2002) found that alum-WTR decreased phosphorus leachability in sandy soil better than lime and ferric WTR, whereas Adhikari et al. (2016) found higher phosphorus removal for alum-based drinking water treatment residuals when compared to the ferric and lime counterparts. Ippolito et al. (2003) discussed how calcium in lime sludge may form less soluble forms of phosphate crystals over longer periods of time. The DWTR used in the current study was derivative of lime-softening industrial drinking water treatment, with lower organic content compared to other WTRs. In order to avoid confusion with the different reagents and types of water treatment residuals, the acronym DWTR will be used to differentiate between the by-product used in this study and other water treatment residual sources.

Reported nutrient removal from field studies is quite variable, with permeable pavement system age, composition, structural design, drainage design, climate, and influent chemistry all strongly influencing performance. Additionally, field testing introduces other nutrient removal mechanisms such as natural biological process and filtration that make it difficult to quantify, or at best classify, exactly how the contaminant removal occurs. Although it is important to understand how permeable pavement systems behave in the environment, it is necessary to compare the performance of individual components in standardized laboratory settings to reduce the number of variables and error pathways and to allow active design of systems for pollutant removal in the future. In the case of pervious concrete or PRC, a significant amount of removal can occur in the concrete structure, requiring testing of individual sets of mixture proportions. Permeable pavement components must be characterized at the fundamental level to establish a foundation for future designs. The significance and novelty of this study includes characterizing the removal capacity of dissolved, inorganic NO_3-N and PO_4-P by PRC at the most fundamental level while eliminating competing removal mechanisms. In addition, this study aims to elucidate the effects of SCM replacement on removal capacity.

Methods

Mixing, curing, and testing occurred in multiple steps to ensure that the mixes were properly handled such that all specimens received the same treatment and underwent the same controlled conditions in order to eliminate error. The following methods describe the three-stage approach of mixing and curing, bench-scale testing, and drying and leachability studies.

Mix Designs and Concrete Batching

Mixtures included in the study included an OPC mixture as a control and two mixtures that replaced 25% of the portland cement with either ASTM C618 Class C fly ash or DWTR, as shown in Table 2. To avoid competition for available reaction or nucleation sites by ions present in tap water, 18 MΩ deionized (DI) water was used as the concrete mixing water and as the reagent solution solvent [ASTM D1193-06 (ASTM 2011)]. The coarse aggregate was nominally an 8-mm limestone from Randolph, MO. The Class C fly ash was obtained from La Cygne, Kansas. The chemical properties are shown in Table 1. The porosity of the wet concrete was fixed at 25% and controlled for all samples. Pervious reactive concrete does not meet the technical criteria for traditional pervious concrete applications for structural or pavement applications [ACI 522.1-13 (ACI 2013)]. Mixtures in this study were designed to maximize cement porosity, reactive material, and available surface area, which reduces the cement paste thickness needed for durability concerns [ACI 201 (ACI 2015)]. The acronym PRC has previously been used to describe a series of mixture proportions used in similar remedial applications and will be used throughout this study to describe the materials tested (Holmes et al. 2017).

Table 2. Permeable Reactive Concrete Mix Design Proportions

Mixture	Cement (kg/m^3)	Fly ash/DWTR (dry) (kg/m^3)	Coarse aggregate (kg/m^3)	Mixing water (kg/m^3)
PC	270	0	1,500	110
FA25	200	70	1,490	110
DWTR25	200	70	1,485	110

Freshly mixed PRC was prepared and cured in accordance with ASTM C192 (ASTM 2016). DWTR had a moisture content of 59%. The freshly mixed concrete was weighed to produce exactly 25% voids for all samples as determined from the mixture proportions. Fresh PRC was placed into 100 × 200 mm plastic cylinder molds in three tamped lifts with each lift being compacted by a rubber tamper. Sufficient compaction effort was applied to place the specified mass (±0.1 grams) into each plastic mold, but limited in effort to prevent overconsolidation. Specimens were then sealed and stored for 24 h in the mold. After 24 h, molds were stripped and placed in a 100% humidity, 23°C curing room for 6 additional days. After moist curing, specimens were transferred to a 50% relative humidity, 23°C environmental chamber for 14 days to slowly dry before testing.

Bench-Scale Testing

Removal rates of cylinder specimens were determined by performing bench-scale jar testing. Each specimen was placed in a continuously stirred batch reactor containing 750 mL of nutrient solution. Specimens were suspended in solution by a nonreactive nylon string, as shown in Fig. 1. Nonreactive coated, magnetic stir bars were used to continuously mix the solution for the 72 h at 400 rpm. Each batch reactor contained a solution of nitrate or phosphate at increasing concentrations to determine if reactivity changed because of contaminant mass. Jar testing was performed for concentrations of 2.2 mg, 1.1 mg, or 0.2 mg NO_3-N/L and 3.3, 1.6, or 0.3 mg PO_4-P/L separately in the form of potassium nitrate (MP Biomedicals, LLC, cat no. 191428, lot no. 9328K) and potassium

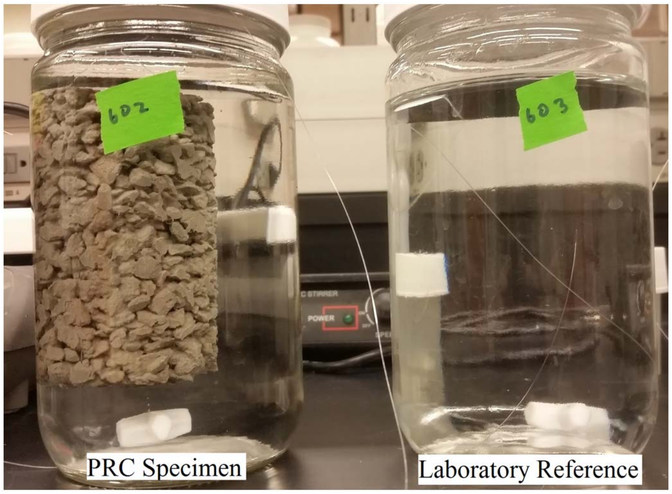

Fig. 1. Bench-scale jar test, 4 × 8 in. with PRC specimen and LR

phosphate (Fisher Scientific, BP 362-800, lot no. 141262A) dissolved in ASTM Grade I deionized water. The concentrations selected reflected state regulations for reservoirs in Missouri while allowing a detectable range of at least one order of magnitude for isotherm determination (State of Missouri 2014).

Once jar testing was completed, the concrete specimens were allowed to drip dry over the jar, then were placed into the drying environmental chamber for 28 days. After the 28 days of drying, the specimens were leach-tested similarly to the original jar test by placing the previously tested specimen in 750 mL of DI water for 72 h. For each mixture, three replicate specimens were tested at each of the six concentrations (three for NO_3-N and three for PO_4-P) and subsequently leach tested. Additionally, three specimens for each mixture were jar-tested in 750 mL of DI water to establish a background concentration of NO_2-N, NO_3-N, and PO_4-P. Specimens were only jar-tested once; i.e., no additional testing was completed after leach testing. One laboratory reference (LR) containing the corresponding stock solution (NO_3-N, PO_4-P, or DI water), nylon string, and stir bar with no specimen was jar-tested for each concentration and each leach test.

Upon completion of jar testing and leachability testing, pH, temperature, and conductivity were measured for each batch reactor. Each effluent sample was pH-adjusted using a 1.0 N HCl solution to a pH of less than 8 to be consistent with the ion chromatography reagents and reduce peak-to-peak interference. Solutions were stored in accordance with nitrate and phosphate standards until further testing occurred (Clesceri et al. 1989). Triplicate samples of all batch-testing effluents were analyzed for NO_2-N, NO_3-N, and PO_4-P using an ion chromatography system (ICS-90) with an automated sampler (AS40). ICS-90 hardware included a 4 × 250-mm AS23 column (064149), an AG23 guard column (064147), an AMMS 300 suppressor (064558), a D5 stabilizer, and a 50 μL injection loop; 4.5 mM sodium carbonate/0.8 mm sodium bicarbonate eluent and 2.0 n sulfuric acid regenerate were used at a flow rate of 1.0 mL/min. A 5% relative standard deviation (RSD) was used for the triplicate analysis of analytes measured with the ICS-90 following the standard method. Throughout testing, the ion chromatograph underwent routine quality control to ensure that the results were consistent with EPA Method 300.0 (USEPA 1993a). All specimen and laboratory equipment was handled with nonreactive gloved hands and all miscellaneous laboratory instruments and jars were thoroughly cleaned with ASTM Type I DI water prior to experimental testing. Jars were cleaned with a 9N HCl solution to remove any residuals, particularly phosphorus.

Mass removal rates of NO_3-N and PO_4-P were determined for each specimen by comparing the post-jar-test concentrations to the corresponding LR stock solution concentrations. Average background concentrations from the specimen were subtracted from the reference sample in which only deionized water and a specimen were tested. Mass leached percentages of NO_3-N and PO_4-P were determined for each specimen by comparing the initial mass removed to the mass leached. Average mass removal rates, mass removed, mass leached percentages, and mass leached were determined for each mix design at each concentration using a RSD of 15%. Average pH was determined by converting pH to hydronium concentrations.

Results and Discussion

The results of this study are discussed in sections for pH and conductivity, nitrate-nitrogen performance, and orthophosphate performance. Elaboration on nitrate-nitrogen removal is investigated through additional experimentation. Nitrate-nitrogen performance is divided into four sections because of the amount of discussion required.

pH and Conductivity

The pH and conductivity of the jar testing and leach testing effluents are shown in Figs. 2 and 3. The initial pHs of the stock solutions were similar to the corresponding LR, and final pH was similar among each mixture proportion. However, once the PRC specimens were introduced, pH rose into the 12.0 S/U range and remained consistent for the entire test. Leaching did not significantly reduce the overall pH when compared to initial jar testing. The conductivity varied slightly between the three mixture proportions, with FA25 having a lower conductivity than PC and DWTR25. Leach testing reduced the overall conductivity when compared to the original jar testing, with PC having the highest leaching conductivity. Because the pH after leaching remained high, there is further potential for removal on the specimen.

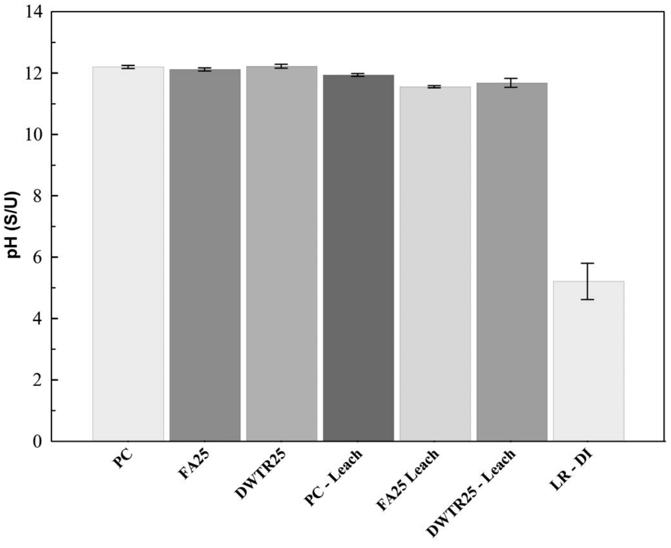

Fig. 2. pH of jar-testing effluent (one standard deviation)

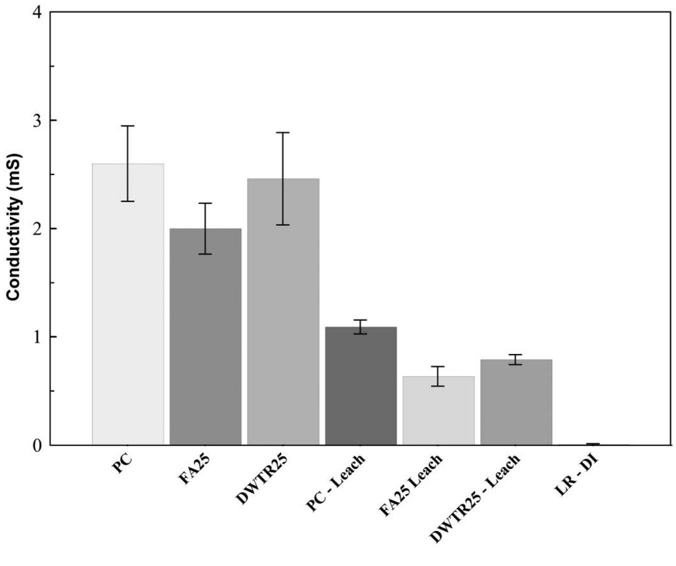

Fig. 3. Conductivity of jar-testing effluent (one standard deviation)

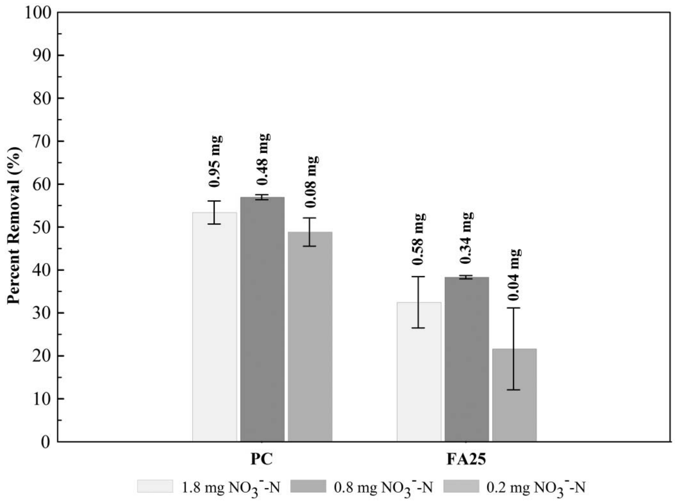

Fig. 4. Nitrate-nitrogen removal rates and mass removed for PC and FA25

Nitrate-Nitrogen Removal

Fig. 4 shows the mass removal and percent removal rates of NO_3-N for the PC and FA25 mix designs. DWTR25 significantly increased the concentration of nitrate-nitrogen by as much as 1.21 mg of NO_3-N, resulting in negative removal rates, which are not included in this figure. The PC series had higher mass removal rates for NO_3-N. NO_3-N mass removal rates had no particular trend within the range of concentrations tested, similar to what was found for cadmium, lead, and zinc (Holmes et al. 2017). The PC series removed as much as 0.95 mg of NO_3-N for the higher concentrations, resulting in an average mass removal of 53%. As much as 0.58 mg of NO_3-N was removed by the FA25 series, with a corresponding removal of 32%. Generally, the PC series removed 45–60% of the original NO_3-N, whereas the FA25 series removed 12–39%. Mass removal was also expressed as mass removed per dose in a linear isotherm, as shown in Fig. 5. Linear, Freundlich, and Langmuir isotherms were compared for the data with coefficients shown in Tables 3 and 4. Isotherm fittings were not significantly different; therefore, a linear isotherm fit was assumed for the range of concentrations tested.

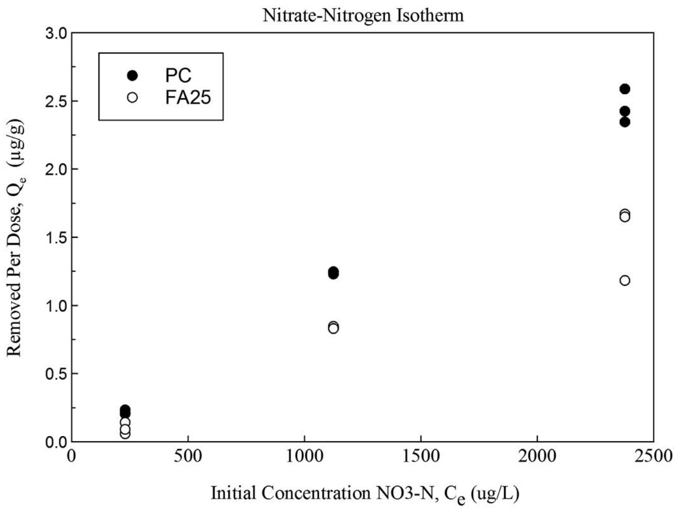

Fig. 5. Nitrate-nitrogen adsorption isotherm

Table 3. Nitrate-Nitrogen Isotherm

	Linear		Freundlich			Langmuir		
Mixture	k	R^2	k	n	R^2	K	q_m	R^2
PC	0.0010	0.994	0.0014	0.96	0.995	0.000038	29.38	0.995
FA25	0.0007	0.934	0.0013	0.91	0.938	0.000111	7.23	0.942

Table 4. Orthophosphate-Phosphorus Isotherm

	Linear		Freundlich			Langmuir		
Mixture	k	R^2	k	n	R^2	K	q_m	R^2
PC	0.0033	0.992	0.0058	0.88	0.999	0.000113	25.00	1.000
FA25	0.0026	0.998	0.0042	0.94	0.999	0.000055	53.38	1.000
DWTR25	0.0024	0.990	0.0064	0.87	0.998	0.000139	21.60	0.999

Nitrate-Nitrogen Leaching

Fig. 6 shows the mass and percentage of leached NO_3-N from the specimen during leach testing. In most cases, a greater mass of NO_3-N as high as 0.10 mg, leached from the FA25 specimen. The percentage of NO_3-N leached increased as initial concentrations decreased. Because the FA25 specimen removed less NO_3-N originally, and a higher mass leached off of the specimen after initial jar testing, the overall percentage leached was greater than that of the PC specimen. The percentage leached was as high as 66% for the FA25 specimen. Mass leached increased as initial mass removed increased, indicating that nitrate removal may not necessarily be permanent, especially for the fly ash mix. As little as 13% of initially removed NO_3-N was leached from the PC specimen, which is an indicator of longer-term retention. This shows a novel and permanent means of inorganic removal of nitrogen not attributable to nitrification or degassing.

Studies on WTR do not tend to focus on leachability of nitrate from the residuals. Loss on ignition for the DWTR used in this study represents the majority of organic material contained within the sample, which may serve as the source of excess NO_3-N observed from the DWTR. Levels of nitrogen and other organic materials have been found to leach from alum-based drinking water treatment waste (Ippolito et al. 2003). Both Gallimore et al. (1999) and Ippolito et al. (2003) reported higher concentrations of NO_3-N

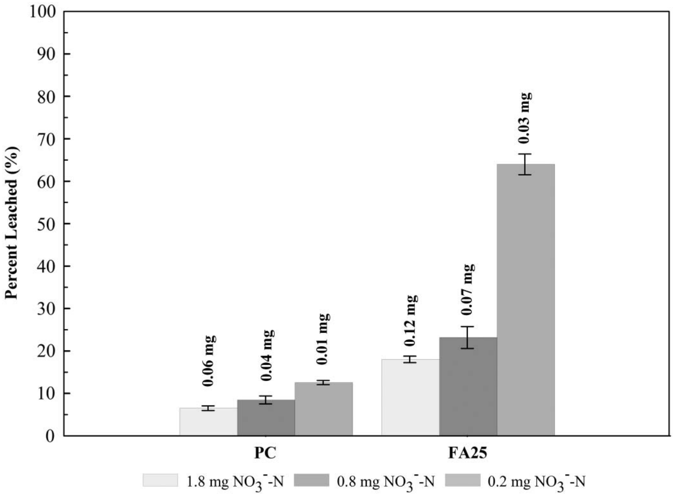

Fig. 6. Nitrate-nitrogen leaching rates and mass leached of PC and FA25 (one standard deviation)

than other species of nitrogen in alum-based drinking water treatment waste. Small amounts of nitrogen leaching were observed from six alum-based drinking water treatment sludges by Hidalgo et al. (2017). Nitrogen species were also found in an alum sludge reuse investigation (Maiden et al. 2015). Repeated studies for Florida water treatment plants have shown little to no phosphorus or nitrogen in lime, alum, and ferric sludges (Townsend et al. 2001). The composition of a WTR will depend on the condition of the raw water source and plant operating conditions, and not all residuals will contain excess nitrogen or phosphorus (Babatunde and Zhao 2006). Reuse of industrial waste byproducts in applications where they are in contact with free water should be examined for leachability prior to use.

Nitrate was the only solute introduced to the system in this study; however, ion chromatography allows for the examination of nitrite as well. NO_2-N was found at masses below 0.02 mg for the background and all other jar testing, indicating that no NO_3-N was reduced to NO_2-N. Solutions were examined for biological activity with the absence of growth noted, reducing the likelihood of denitrification, dissimilatory nitrate reduction to ammonia, or anaerobic ammonia oxidation occurrence (Denk et al. 2017). Although there are other nitrogen-reducing species, it would be highly unlikely for NH_4-N to occur in the absence of growing bacterial colonies. Ammonia was only analyzed for a few aliquots but was nondetectable using colorimetry standard methodology EPA Method 350.1. Because no additional testing was performed after leach testing, it is unknown how well the specimens may continue to remove NO_3-N.

Comparison of Nitrate-Nitrogen Removal Field Studies

The literature shows varied success of the nitrogen-removal capabilities of pervious concrete as part of infiltration systems. In general, the potential to remove nitrogen has been studied on established systems complete with gravel underlays, engineered soils, pipes, and so on. The removal capacities in this study are substantially higher than those noted in the field for a variety of reasons. Primarily, the enhanced removal capacities found in this study may be attributable to the increased surface area, resulting in more reaction sites and higher porosity, and to the lack of other nitrogen species that may be oxidized to NO_3-N such as field studies demonstrate (Bean et al. 2007; Brown and Borst 2015; Collins et al. 2010; Drake et al. 2014). Comparisons between a complete system and a component of the system are difficult because traditional pervious concrete has substantially more cement paste at a different water-to-cement ratio, resulting in less macroporosity (rapid water flow) and microporosity (hydrated cement pores) than the specimens examined in this study. Additionally, the absence of biological activity noted in this study may also contribute to deviations from systems where additional removal mechanisms of biological activity can occur. These modifications to the concrete and lack of system components may lead to a demonstration of maximum NO_3-N removal, or they may show an average capability of the material without the addition of appurtenances for infiltration systems.

Fate of Nitrate-Nitrogen in PRC

The fate of nitrate within the PRC material was investigated for both physical and chemical removal mechanisms. Physical filtering or a solute sieving effect of the hydrated ions in solution can occur in the tortuous microporosity of the cement paste. Scanning electron microscope (SEM) examination does indicate the existence of extensive networks of pores within cement paste of appropriate size to trap nitrate molecules. However, energy dispersive X-ray spectroscopy (EDX) is incapable of registering nitrogen at such low concentrations because the signal is overwhelmed by carbon and oxygen in the hydrated system. The data collected do not validate this hypothesis at this time, and further study investigating the potential plugging of pores is required. Mercury intrusion porosimetry before and after jar testing with nitrate can provide a qualitative measure of physical filtration removal capabilities but was outside the scope of this study.

Crystallographic alteration or simple ion exchange is also a potential removal mechanism. A variety of phases and hydration products exist that may serve as potential exchange sites. In order to test this theory, crushed cement rock fines and cement rock aggregate were prepared for smaller-scale batch reactor testing. Cement rock was proportioned using ASTM C150 Type I/II portland cement and DI water at a 0.2 w/c and 3.8% polycarboxylate high-range water reducer by mass of cement. The cement rock was prepared and cured in accordance with ASTM C192 [ASTM C192 (ASTM 2016)]. After a 7-day cure, specimens were crushed to obtain cement rock fine-aggregate between sieve 2.36 and 0.420 mm and cement rock fines below 0.420 mm diameter. The crushed cement rock was then stored in a 50% relative humidity, 23°C environmental chamber for at least 14 days to slowly dry before testing. Smaller batch reactor testing was then performed on the hydrated cement fines and cement aggregate batch reactors and compared control deionized water solutions with equivalent mass of materials immersed in a 16.1 $\mathrm{mg\,NO_3\text{-}N/L}$ solution. Batch reactor tests resulted in a similar percent removal to PC, 51% for the fine aggregate and 50% for the fines, respectively. Higher mass removal was observed per dose in the smaller batch reactor tests at 37.0 $\mu\mathrm{g\,NO_3\text{-}N}/(\mathrm{g}$ of cement rock fine aggregate) and 36.3 $\mu\mathrm{g\,NO_3\text{-}N}/(\mathrm{g}$ of cement rock fines) than the pervious reactive concrete specimens tested in the main study. The solid cement rock materials were separated from the supernatant solution, dried at 30° C, powdered, and examined for crystallographic alteration using powdered X-ray diffraction (XRD) (Figs. 7 and 8). No significant crystallographic alteration was noted, such as peaks shifting or bases widening when tested slowly. The XRD patterns of the material suggest that nitrate crystalline structures were not formed, or at least were not present in sufficient quantities to be detected at this time.

Other potential removal sinks include binding within hydration products, electrostatic attraction within the pores, the formation of calcium nitrate or hydro-nitrate within the solution and forming scale on the surface structures, surface attraction in the macropores, or physical absorption. No one single test can verify the location of the nitrogen at this time because nitrogen is difficult to detect in solid forms and is potentially masked by materials within the system. Further variables that may affect removal of pervious concrete mixture proportions include cement coating thickness, porosity, surface area, specimen age, storage conditions, water-to-cement ratios, and contact time.

Orthophosphate-Phosphorus

Jar-testing samples from the PC and DWTR25 phosphate series contained flocculants that would settle to the bottom of the jar when testing was completed. Flocs are presumed to be a reaction of dissolved phosphate with free calcium hydroxides, which formed calcium phosphate flocculants. Prior to testing the jar-testing effluent with the anion chromatography system, samples were titrated with 1N hydrochloric acid (HCl) and the flocculants dissolved in the PC and DWTR25 series effluents. Flocculants were not observed in the FA25 batch reactors phosphate series. However, after the FA25

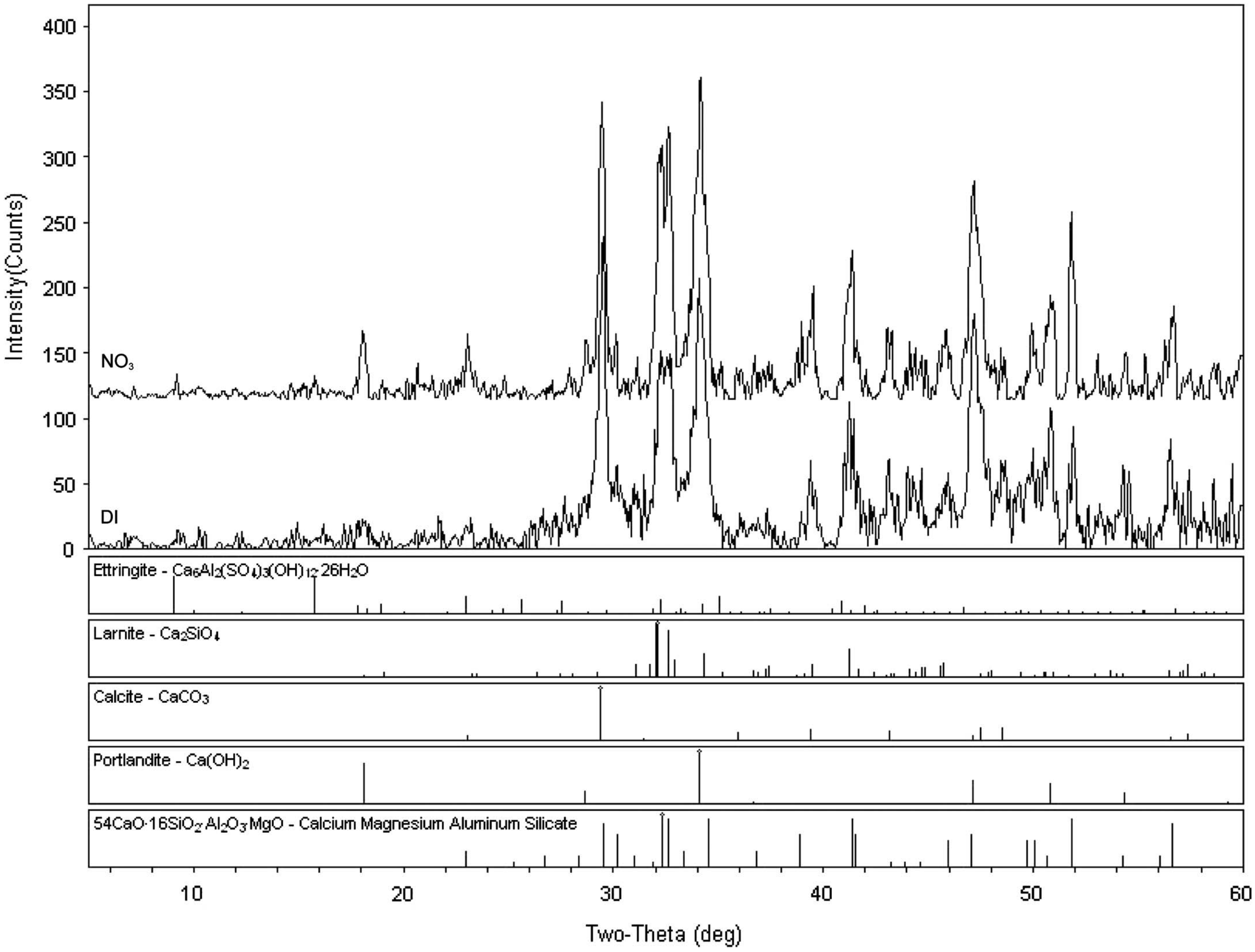

Fig. 7. Crushed cement rock fine aggregate XRD results

phosphate jar testing aliquots were titrated, flocculants began to appear. The mass removal and percent removal rates of PO_4-P for each mix design are shown in Fig. 9. Statistical analysis was performed comparing the sample mixture types and their capacities for removal. There is no statistical difference between the PC and DWTR25 noted in phosphorus removal. There is also no statistical difference between the 1 and 5 mg/L solutions, indicating similar removal rates at lower concentrations among the different mixture proportions. The FA25 mix design had higher mass removal rates for PO_4-P. For all designs, PO_4-P removal rates decreased with increasing concentration. Fig. 10 shows a linear adsorption isotherm for each mix design, whereas the coefficients for linear, Freundlich, and Langmuir isotherm constants are compared in Table 4. The range of values tested also resulted in a linear isotherm for phosphate concentrations, again resulting in insignificant differences between the isotherm types. No phosphate leached from the highest-concentration jar test specimen (3.3 PO_4-P mg/L), so the lower concentration specimens were not tested. The lack of PO_4-P in the leach testing effluent suggests little, if any, PO_4-P would leach from the specimens in the range of concentrations tested.

Soto-Pérez and Hwang (2016) found that the removal of phosphate reacting with OPC and fly ash in pervious concrete increased with increasing concentrations of phosphate in column testing. The column experiment had a relatively short contact time (~2 h) and higher concentrations (26.5 ± 11.6 mg PO_4-P) compared to the current experiment. The limited contact time in the experimental column set up by Soto-Pérez and Hwang (2016) resulted in a lower effluent pH (10.21 ± 0.20 for control and 9.95 ± 0.12 for 35% fly ash replacement) than observed presently. The difference in pH or contact time may have explained why the fly ash mixture proportions had lower phosphate removal rates in the study of Soto-Pérez and Hwang (2016). Furthermore, concrete was cured for 28 days in Soto-Pérez and Hwang (2016), which may have affected the removal of the fly ash mix design because of a reduction in available calcium hydroxide. The mass of fly ash replacement did not necessarily correlate to the percent removal of Soto-Pérez and Hwang (2016) because the mix design with 10% fly ash replacement resulted in lower removal percentages than the 35% replacement. Ugurlu and Salman (1998) found that the phosphate mass removal for fly ash decreased as the concentration of phosphate increased in 24-h batch testing of powdered material. Thus, the relationship between phosphorus removal rates and initial phosphorus concentration must be dependent on contact time or pore solution pH, as described by the formation of more complex phosphate calcium crystal structures with time as described by Sikdar (2007). By measuring dissolved analytes, the process for nutrient, at least phosphorus, removal in this case is primarily adsorption in this study and that of Ugurlu and Salman (1998). The sorption appears

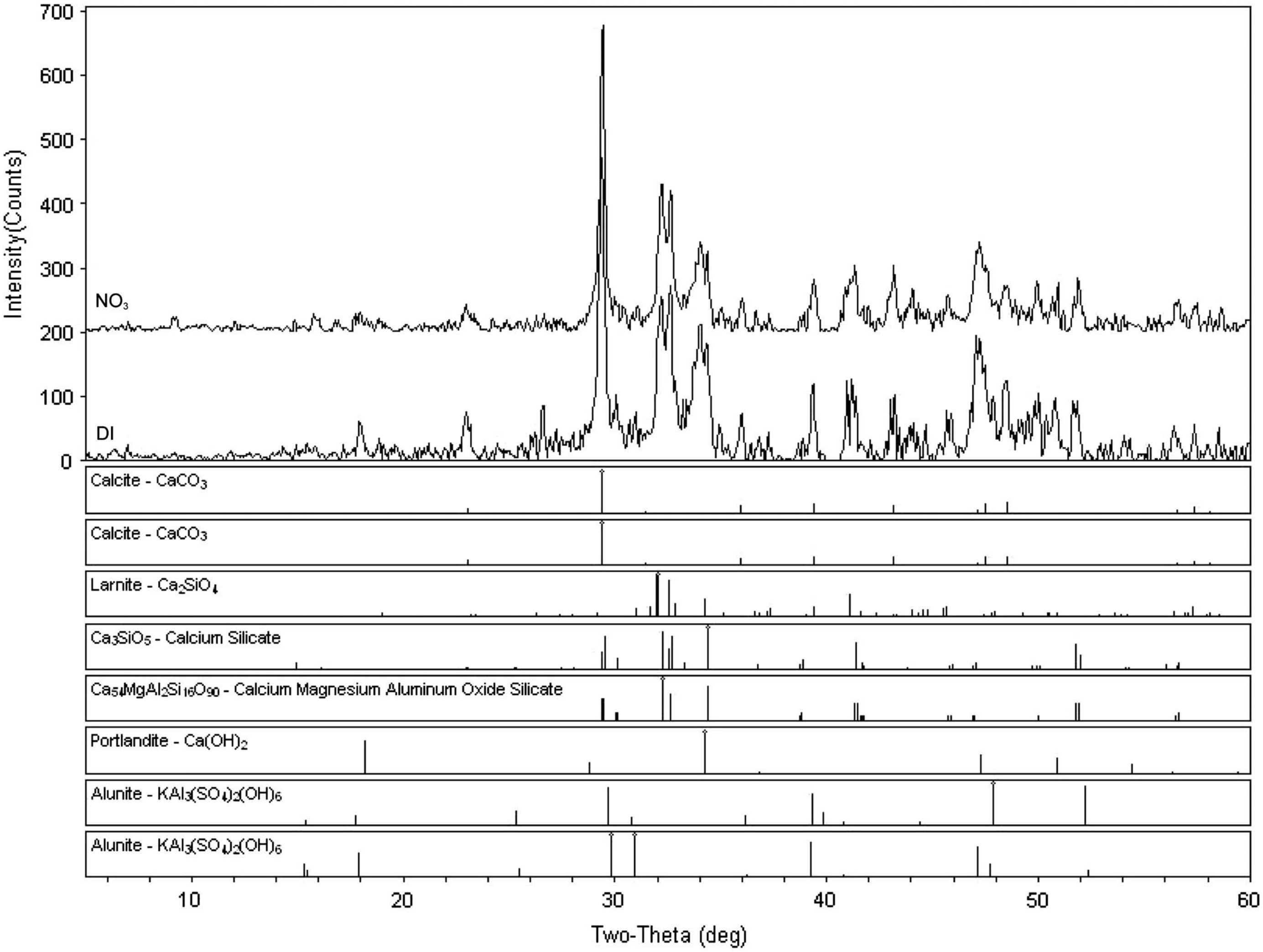

Fig. 8. Cement rock fines XRD results

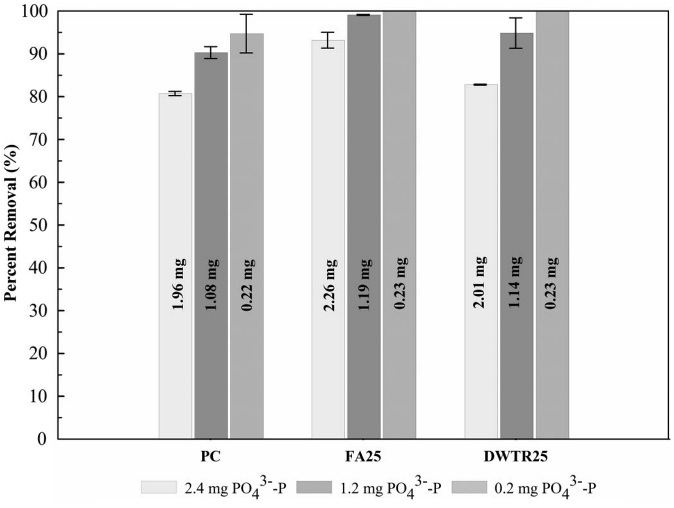

Fig. 9. Orthophosphate-phosphorus removal rates and mass removed (one standard deviation)

to be permanent in nature because no phosphate leached from the highest-concentration jar test specimen, so the lower-concentration specimens were not tested. This seems to be consistent with the recycled concrete tested by Molle et al. (2002).

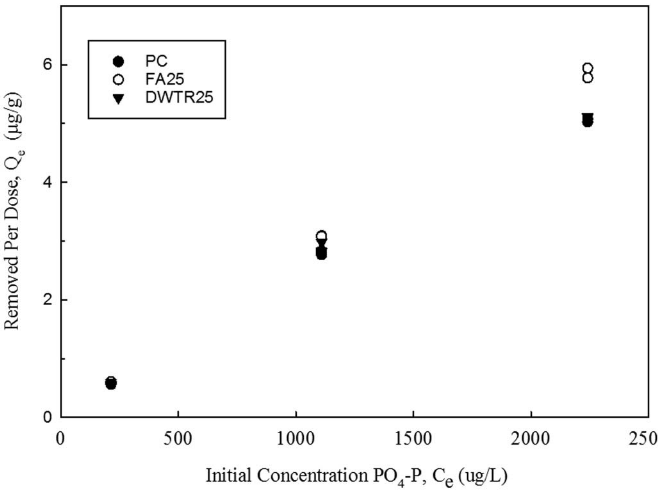

Fig. 10. Orthophosphate-phosphorus isotherm

Conclusion

The nutrient removal capacity of permeable pavements has been reported in the literature on a site-specific, system-level basis. The present study quantified the dissolved, inorganic nutrient removal capacity for three permeable reactive concrete mixtures while focusing on the effects of supplementary cementitious and filler materials. Concrete specimens were jar-tested and leach-tested for 72 h at three different concentrations of solution for either nitrogen in the form of potassium nitrate or phosphorus in the form of potassium phosphate. The capacity of PRC to remove nitrate-nitrogen and orthophosphate-phosphorus found in this study may represent an upper bound of removal because of constituents being tested individually. A more complex stock solution may result in competition for removal and lower removal rates. Of the two PRC mixtures tested, the mixture consisting of ordinary portland cement removed and retained NO_3-N better than the 25% fly ash replacement (FA25) mixture. The series including drinking water treatment waste (DWTR25) increased nitrate concentrations in the bench-scale testing. Therefore, the supplementation of fly ash and DWTR negatively affected NO_3-N removal and retention rates, and OPC would be preferred for maximum removal. The addition of fly ash increased the PO_4-P removal of the PRC, although this has not been replicated in column experiments. DWTR performed similarly to the PC series with respect to phosphate removal. The control mixture proportions removed 45–60% of NO_3-N and ≥80% of phosphorus, whereas the fly ash mixture removed 12–38% of NO_3-N and ≥91% of PO_4-P. The DWTR25 specimen removed ≥80% of PO_4-P, statistically the same as the PC mixture. The relatively longer testing period and higher PO_4-P percentage removals found in this study may indicate a contact time-controlled process. As much as 17–66% of the originally removed NO_3-N was leached from the FA25 specimen, whereas the PC specimen performed slightly better, with up to 13% of NO_3-N being leached. PO_4-P retention determined by leach testing was suggestive of long-term phosphate removal. The range of NO_3-N and PO_4-P concentrations tested resulted in linear isotherms. Further investigation is needed for higher NO_3-N and PO_4-P concentrations to better confirm linear, Freundlich, or Langmuir behavior and to confirm isotherm type. The results from this study indicate PRC has the potential to become one of the leading methods to remove nitrogen from surface waters and is as efficient as other methods for phosphorus removal.

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