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## **Fly ash amended pervious concrete: a laboratory study on removal potential for inorganic contaminants**

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**Abstract:** Pervious concrete is a recognised best management practice. This study investigated the removal efficiencies of various pervious concrete formulations when exposed to total suspended solids,  $\text{Pb}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  via simulated rainfall events. The results showed substantial total suspended solids,  $\text{Pb}^{2+}$ , and  $\text{PO}_4^{3-}$  removal. Removal rates as high as 72%, 36%, and 43% were observed for  $\text{PO}_4^{3-}$ ,  $\text{Pb}^{2+}$ , and total suspended solids, respectively. Removal efficiencies of total suspended solids,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  were not largely influenced by formulation. However, both  $\text{Pb}^{2+}$  and  $\text{PO}_4^{3-}$  removal were formulation dependent. Analysis of the void space in each individual pervious concrete cylinder was performed and compared to removal efficiency data. Surprisingly, no significant relationship existed between removal of potential contaminants and void space. Pervious concrete can aid in improving water quality of urban runoff.

**Keywords:** pervious concrete; fly ash concrete; inorganic contaminants; lead removal; suspended solids filtration; nitrate removal; phosphate adsorption; void space.

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## 1 Introduction

Between the years 1970 to 2000 there was a 58,000 km<sup>2</sup> increase in urban land use worldwide (Seto et al., 2011). Across all regions of the world during this time land use rates exceeded or equalled population growth rates. While North America experienced the greatest change in urban area, India, China, and Africa exhibited the highest rates of land development. Directly tied to this rapid land development has been the use of impervious surfaces, such as concrete or asphalt, which have the potential to increase stormwater volume, decrease groundwater recharge, and degrade water quality (Brabec et al., 2002; Kayhanian et al., 2007; Newman et al., 2004; Roberts and Prince, 2010; Steinke et al., 2007).

One structural best management practice recognised as a way to control rate and volume of runoff from stormwater (Fassman and Blackbourn, 2010; Gomez-Ullate et al., 2011; Jung et al., 2013), as well as provide pollutant reduction, is pervious concrete (Newman et al., 2004). Pervious concrete is a special form of concrete made with a higher porosity than conventional concrete (typically 15%–30%). However, with this increased porosity comes a decrease in strength, leading to pervious concrete being mainly used in lower loading and volume areas (e.g., parking lots, sidewalks, non-commercial roads). The construction and use of pervious concrete allows for stormwater (and its associated contaminants) to flow through concrete rather than flowing over the surface of the concrete, which occurs with impervious surfaces. With this redirection of water flow certain advantages not relevant to impervious surfaces, such as the potential to filter contaminants from stormwater, must be explored.

Previous research on the removal of inorganic contaminants via pervious surfaces (specifically pervious concrete) shows great potential (Drake et al., 2014; Haselbach et al., 2014; Legret et al., 1996; Luck et al., 2008, 2009; Pagotto et al., 2000; Park and Tia, 2004; Pratt et al., 1995). Brattebo and Booth (2003) directly compared water from a permeable pavement system to asphalt runoff and found lower concentrations of motor oil, copper, and zinc with the metals reaching state defined levels of toxicity in 97%

asphalt samples, but in only 14% of permeable pavement samples. Likewise, Bean (2005) compared the runoff from an impervious parking lot to the water collected from the bottom of permeable pavement and found a reduction of phosphorus, metals, and total suspended solids (TSS).

Multiple factors, such as fly ash amendments to pervious concrete and the amount of void space created during the fabrication may influence the removal rates of certain contaminants (Luck et al., 2008, 2009; Park and Tia, 2004). Fly ash, a material commonly added to pervious concrete as a cost-effective replacement for Portland cement, has very rarely been studied for its influence on contaminant removal, despite its high organic carbon content. Previous research has shown that in the presence of high carbon multiple contaminants, including metals, can be rendered non-bioavailable, therefore decreasing the potential for detrimental environmental effects (Calmano et al., 1993; Di Toro et al., 2001; Eggleton and Thomas, 2004).

Pervious concrete has the potential to reduce stormwater runoff and at the same time act as a filter for runoff associated contaminants. However, there is a lack of research investigating the influence of pervious concrete formulations on the removal of likely contaminants associated with pervious concrete. The objectives of this study were to

- 1 examine the removal efficiency of TSS,  $Pb^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $PO_4^{3-}$  in multiple concrete formulations with varying degrees of fly ash
- 2 examine the influence of concrete void space (porosity) on the removal efficiencies of TSS,  $Pb^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $PO_4^{3-}$
- 3 provide an in-depth experimental analysis of phosphate removal within pervious concrete.

## 2 Material and methods

### 2.1 Pervious concrete manufacturing

All the pervious concrete mixtures were proportioned using Type I Portland Cement (30% by weight) and limestone aggregates (70% by weight). The limestone aggregates used were defined by size, specifically being able to pass through a 12.5 mm sieve and retained on 9.5 mm sieve. The water-to-cement ratio or water-to-(cement+fly ash) ratio was maintained at 0.32 for all the mixtures. All mixtures were prepared using a laboratory mixer, and cast in 150 mm wide by 300 mm long cylindrical moulds. Mixtures were consolidated using a laboratory table vibrator and remained in the moulds for seven days. Immediately after removal from moulds each cylinder was cured for 21 days in a saturated lime bath. Following curing each cylinder was saw cut in half producing a final pervious concrete testing cylinder (150 mm diameter by 150 mm height).

Porosity of each cylinder was determined utilising ASTM D7063 (ASTM, 2001). Briefly, each cylinder was oven dried for 24 hours at 110°C, weighed to the nearest 0.1 g, then sealed in a vacuum bag, submerged in water and weighed again. A final weight measurement was then made after the vacuum bag was cut and water was allowed to fill the void space for eight minutes. The porosity of each cylinder was then calculated based on weight differences.

## 2.2 *Cylinder formulations*

Two factors, amount of fly ash and amount of organic carbon, were varied during the manufacturing of test cylinders to examine their influence on removal efficiency. Fly ash amounts examined were: 0%, 20%, and 30% (40% for leaching tests only). Two types of fly ash were utilised, both F-Class. Organic carbon amounts examined were fly ash with a 1%–2% loss on ignition (hereafter referred to as low carbon) and fly ash with 8%–13% loss on ignition (hereafter referred to as high carbon). The low carbon fly ash had 82% sum of oxides ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ) with 45%  $\text{SiO}_2$ , 18%  $\text{Al}_2\text{O}_3$ , 19%  $\text{Fe}_2\text{O}_3$ , and 9%  $\text{CaO}$ . The high carbon fly ash had 88% sum of oxides with 55%  $\text{SiO}_2$ , 25%  $\text{Al}_2\text{O}_3$ , 8%  $\text{Fe}_2\text{O}_3$ , and 5%  $\text{CaO}$ . Our own XRF analysis showed good agreement with the differences in elemental content between the two ashes. Ultimately, five manufactured cylinder formulations were used: 0% carbon, 20% fly ash-high carbon, 20% fly ash-low carbon, 30% fly ash-high carbon, 30% fly ash-low carbon. To help remove inherent error due to the manufacturing process, each cylinder, prior to experimental use was rinsed with tap water until the water flowing through the cylinder reached a consistent pH (typically between pH 8-9).

## 2.3 *Leaching experiments*

Individual pervious samples (all high carbon – 40%, 30%, 20%, 0% fly ash) were held on a wooden stand with a collection vessel below the block to collect the water that passed through the sample. An artificial rain simulator constructed of PVC piping with a 5-litre reservoir and stopcock was fixed above the wooden stand. Volumes of deionised water (DI) were delivered through perforated PVC piping and passed through the individual samples. After passing through the sample, the water was collected and acidified with nitric acid. Analysis of leachate for the concentrations of As, Ba, Cd, Cr, Pb, Se, Ag, Cu, Ni, Al, Sb, Be, Ca, Co, Fe, Mg, Mn, K, Na, Tl, V, Zn, Li, B, Mo, and Ti were performed using EPA SW-846 Method 6010 (USEPA, 2014a) with solid phase extraction and inductively coupled plasma atomic emission spectrometry (ICP-AES). Solid phase extraction disks used were 47 mm Cation-SR (3M Empore, St. Paul, MN, USA).

Three 20% low LOI testing cylindrical blocks were studied for anion leaching using the artificial rain simulator fitted with a shower head. Three 1-liter volumes of DI water were passed through each block, the water collected, filtered via 0.45  $\mu\text{m}$  filter and stored at 20°C. Within 48 hours of collection all samples were analysed for concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  using ion chromatography (Dionex ICS-2000).

## 2.4 *Removal efficiency experiments*

All removal efficiency studies were conducted using artificial rain simulators. Each simulator was constructed of a commercially available showerhead attached to polyvinyl chloride piping with a flow-controlling stopcock. Prior to first use, and between each experiment, artificial rain simulators were washed using soap, 0.05 molar Ethylenediaminetetraacetic acid, and deionised water.

#### 2.4.1 Total suspended solids

TSS efficiency removal experiments were conducted by evenly distributing a 2-litre treatment volume of 1,000 mg/L TSS over a pervious concrete testing cylinder, via artificial rain simulator, followed by 2-litre flush of deionised water. All water that passed through the cylinder was collected and analysed for TSS gravimetrically according to USEPA method 160.2 (USEPA, 2014b). Soil used for TSS experiments was collected from the same source and characterised for size. Only soil particles between 1,700–0.45  $\mu\text{m}$  were utilised. Three cylinders of each pervious concrete formulation were tested for TSS removal.

#### 2.4.2 Lead

Lead efficiency removal experiments were conducted by evenly distributing a 2-litre treatment volume of 1,000 mg/L  $\text{PbCl}_2$  over a pervious concrete testing cylinder, via artificial rain simulator, followed by 2-litre flush of deionised water. All water that passed through the cylinder was collected, acidified with nitric acid, and analysed via graphite furnace atomic absorption spectrophotometry (Schimadzu AA6600, Tokyo Japan). Three cylinders of each pervious concrete formulation were tested for  $\text{Pb}^{2+}$  removal.

#### 2.4.3 Anions

Anion removal efficiency experiments were conducted by evenly distributing a 1-litre cocktail treatment solution comprised of 25 mg/L of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , 50 mg/L  $\text{Cl}^-$ , and 100 mg/L  $\text{SO}_4^{2-}$  (all made from K and Na salts) over a pervious concrete testing cylinder, via artificial rain simulator, followed by 2-litre flush of deionised water. All water that passed through the cylinder was collected filtered (0.45  $\mu\text{m}$ ), stored, and analysed for concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  using ion chromatography (Dionex ICS-2000). Five cylinders of each pervious concrete formulation were tested for anion removal, except 20% fly ash-high carbon, which was tested with four cylinders.

#### 2.4.4 In-depth phosphate removal dynamics

In depth analysis of phosphate removal dynamics consisted of three separate experiments: sequential phosphate removal, phosphate sorption, and flow rate. In order to control variability all experiments were conducted using 20% fly ash-low carbon pervious concrete cylinders.

One pervious concrete cylinder was subjected to 41 sequential litres of 29 mg/L  $\text{PO}_4^{3-}$  via artificial rain simulator. Each liter that passed through the cylinder was collected individually, filtered (0.45  $\mu\text{m}$ ) and analysed for  $\text{PO}_4^{3-}$  using ion chromatography (Dionex ICS-2000).

Two pervious concrete cylinders were individually submerged into separate 15-litre plastic chambers containing 8 litres of either 25 mg/L or 750 mg/L  $\text{PO}_4^{3-}$ . A stir bar was added to each chamber and placed onto a stir plate to assure constant solution movement. The cylinder submerged in 25 mg/L  $\text{PO}_4^{3-}$  had 15 samples (3 ml each) taken at time points between 0.08–95.82 hours post experiment initiation. The cylinder submerged in 750 mg/L  $\text{PO}_4^{3-}$  had 18 samples (3 ml each) taken at time points between

1.18–338.6 hours post experiment initiation. All samples were filtered (0.45  $\mu\text{m}$ ) and analysed for  $\text{PO}_4^{3-}$  using ion chromatography (Dionex ICS-2000).

Flow rate experiments were conducted by evenly distributing 10 1-litre treatment volumes of 30 mg/l  $\text{PO}_4^{3-}$  through a single pervious concrete cylinder, via artificial rain simulator, at varying flow rates (1.72–14.49 ml/sec). All water that passed through the cylinder was collected, filtered (0.45  $\mu\text{m}$ ), and analysed for  $\text{PO}_4^{3-}$  using ion chromatography (Dionex ICS-2000).

#### 2.4.5 Statistics

Removal efficiency differences of TSS,  $\text{Pb}^{2+}$ , and anions were investigated using one-way ANOVAs with Tukey's post hoc tests. Linear regression modelling was performed to determine:

- 1 the influence of concrete cylinder porosity on TSS,  $\text{Pb}^{2+}$ , and anion removal and the relationship between flow rate and phosphate removal.

Phosphate sorption rate constants were determined using first order rate kinetics. Quadratic regression modelling was performed to determine the relationship between the cumulative phosphate removed as a function of total phosphate applied during the sequential phosphate removal experiment. Analysis of covariance (covariate of time and fixed factor of phosphate concentration) was performed to determine if significant differences in phosphate removal rates existed between treatments. All analyses were performed using JMP 11 software (Cary, NC, USA). Significant differences for all analyses were defined by having p-values < 0.05.

### 3 Results and discussion

#### 3.1 Leaching experiments

Before any removal experiments were conducted the pervious concrete was studied to quantify the contaminants released. This served two purposes. First, it allowed for more accurate quantification of any contaminants studied that were also found to leach from the blocks. Second, since fly ash is known to contain heavy metals (Harris and Silberman, 1983; Kim et al., 2003) it was important to ensure that the pervious concrete would not contribute significantly to pollutant loadings in the environment. While this is a common assumption, the authors are unaware of any research to support it.

ICP-AES analysis of 26 metals analysed over a 70-litre flushing experiment showed limited leaching of toxic heavy metals (< 10  $\mu\text{g/L}$ ) from pervious concrete. Seven metals (Cr, Pb, Se, Al, Ca, Fe, and Sn) were regularly detected above the detection limit (more than three total samples across all formulations). Calcium was detected most often and at the highest concentrations throughout the entire experiment. The highest level of lead detected was 9  $\mu\text{g/L}$ . Although not statistically significant, the samples with 40% fly ash often showed higher levels of metals leaching.

The levels detected for toxic heavy metals are not at environmentally relevant concentrations. The worst-case scenario would be these levels leaching directly into groundwater used for drinking wells. For example, the highest concentration of chromium found was 1.13  $\mu\text{g/L}$  and the USEPA drinking water standard for chromium is 100  $\mu\text{g/L}$  (USEPA, 2011). In fact all metals, with the exception of thallium, were below drinking water regulatory limits, in many cases, several orders of magnitude below. Thallium was detected at 3.0  $\mu\text{g/L}$  (regulatory limit 2.0  $\mu\text{g/L}$ ) in a single flush. Considering the total volume of water delivered (70.79 L) corresponds to about one year's worth of rain in middle Tennessee (USA), these are encouraging results. While Morar et al. (2012) found much higher levels of heavy metals such as chromium and arsenic, they looked at fly ash amended permeable reactive barriers. Presumably the long held assumption is valid, when the fly ash is incorporated into the concrete the metals are largely immobilised.

No leaching of  $\text{PO}_4^{3-}$  or  $\text{NO}_3^-$  was detected after three consecutive 1 litre flushes with DI water. Chloride showed minimal leaching ( $< 2.5$  mg/L) for each flush. However,  $\text{SO}_4^{2-}$  was consistently detected above the detection limit during each flush, with an average maximum concentration of  $54.9 \pm 14.8$  mg/L (standard deviation) being detected in the final two flushes. The USEPA does not have an MCL (maximum contaminant level) for sulphate. Its secondary drinking water regulation for sulphate is 250 mg/L. Again, this seems to be of no major environmental concern.

### 3.2 Removal efficiency

Removal of environmental inorganic pollutants commonly found on large surface structures, such as parking lots, before they enter waterways is an advantage of pervious surfaces (Legret et al., 1996; Pagotto et al., 2000; Bean, 2005). Overall, our findings are similar to other studies, in that the pervious surfaces tested demonstrated removal of metals (Bean, 2005; Brattebo and Booth, 2003; Legret et al., 1996; Pratt et al., 1995), nitrogen (Collins et al., 2010), suspended solids (Fassman and Blackbourn, 2011), and phosphorus (Bean et al., 2007; Luck et al., 2008, 2009). In a field study, Pagotto et al. (2000) found that water running through porous concrete reduced the concentration of TSS,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Pb}^{2+}$  in runoff by 81%, 69%, 7%, 23%, and 32%, respectively, compared to conventional concrete. In a laboratory study, Haselbach et al. (2014) found retention of zinc and copper to be no less than 83% and 88%, respectively, after ten consecutive simulated rain events through multiple pervious concrete cylinders. Removal efficiency experiments from the present study were similar to those observed in the literature by showing substantial removal of TSS,  $\text{Pb}^{2+}$ , and  $\text{PO}_4^{3-}$  (Table 1). Average TSS removal rates varied between 28.1%–43.1% between formulations. While TSS can clog porous pavements, Welker et al. (2013) demonstrated that when precautions are taken the amount of solids trapped in pores can be minimised and can actually serve as a benefit by sorbing pollutants. Lead and phosphate removal rates varied much more between formulations with removal as high as 36.6% and 72.1% respectively. The amount of  $\text{Pb}^{2+}$  leaching from the cylinders was insignificant compared to the concentrations studied in the removal experiments and could therefore be ignored. In some instances ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), the amount of leaching exceeded the amount sorbed and therefore negative numbers were observed in the removal experiments (Table 1).



**Table 1** Percentage removal efficiencies of anions, lead and TSS (mean  $\pm$  SE)

	Detection limit	Treatment volume	Treatment concentration	Flush volume	0% fly ash	20% fly ash high LOI	20% fly ash low LOI	30% fly ash high LOI	30% fly ash low LOI
Cl <sup>-</sup>	1.0 mg/L	1 litre	50 mg/L	2 litres	9.5 $\pm$ 3.9	-3.8 $\pm$ 1.3	-2.0 $\pm$ 3.1	6.8 $\pm$ 8.4	4.8 $\pm$ 4.4
SO <sub>4</sub> <sup>2-</sup>	1.0 mg/L	1 litre	100 mg/L	2 litres	6.2 $\pm$ 7.6	-11.4 $\pm$ 1.3	-5.9 $\pm$ 2.6	-1.1 $\pm$ 8.1	3.2 $\pm$ 6.2
NO <sub>3</sub> <sup>-</sup>	1.0 mg/L	1 litre	25 mg/L	2 litres	6.3 $\pm$ 2.5	1.9 $\pm$ 2.7	6.7 $\pm$ 5.5	13.0 $\pm$ 7.0	3.0 $\pm$ 5.3
PO <sub>4</sub> <sup>3-</sup>	0.74 mg/L	1 litre	25 mg/L	2 litres	27.6 $\pm$ 11.1	8.6 $\pm$ 5.1	72.1 $\pm$ 12.2	19.0 $\pm$ 4.7	41.7 $\pm$ 20.6
Lead	1.0 mg/L	2 litres	1,000 mg/L	2 litres	26.7 $\pm$ 6.7	31.6 $\pm$ 1.7	9.5 $\pm$ 5.4	36.6 $\pm$ 1.0	11.8 $\pm$ 4.0
Total suspended solids	1.0 mg/L	2 litres	1,000 mg/L	2 litres	32.5 $\pm$ 5.1	30.3 $\pm$ 3.8	30.0 $\pm$ 0.5	28.1 $\pm$ 8.1	43.1 $\pm$ 1.8

Note: TSS = total suspended solids; n = 3 for TSS and lead treatments; n = 5 for anions except for 20% high which was n = 4; negative values indicate greater leaching than removal.

### 3.3 Effect of concrete formulation

The American Concrete Institute (ACI, 2014) lists that percent of fly ash replacement allowed in concrete exposed to freeze thaw can be up to 35%. A typical range of fly ash replacement is between 15%–25% so two ratios were chosen for this study, 20% and 30%. 20% represents a large majority of fly ash amended projects and 30% represents fly ash amended projects in severe freeze thaw climates. To date, no published studies have focused on the impact of pervious concrete formulation on pollutant removal, specifically amount and type of fly ash incorporated during manufacturing. Results from the present study showed a significant effect of pervious concrete formulation on removal rates for  $\text{Pb}^{2+}$  ( $F_{(4,14)} = 7.65$ ;  $p = 0.0043$ ) and  $\text{PO}_4^{3-}$  ( $F_{(4,22)} = 3.6843$ ;  $p = 0.0232$ ), and no significant effect for TSS ( $F_{(4,14)} = 1.65$ ;  $p = 0.23$ ),  $\text{Cl}^-$  ( $F_{(4,22)} = 1.36$ ;  $p = 0.2867$ ),  $\text{SO}_4^{2-}$  ( $F_{(4,22)} = 1.55$ ;  $p = 0.2301$ ), or  $\text{NO}_3^-$  ( $F_{(4,22)} = 0.681$ ;  $p = 0.6136$ ). Post hoc analysis revealed both formulations made with high carbon (20% fly ash and 30% fly ash) removed a significantly greater amount of  $\text{Pb}^{2+}$  compared to cylinders made with low carbon. No significant differences were observed between high carbon cylinders and 0% fly ash formulations (30% fly ash-high carbon –  $p = 0.5258$ ; 20% fly ash-high carbon –  $p = 0.9272$ ). Compared to all other formulations, phosphate removal was the highest in 20% fly ash-low carbon, with an average removal of 72.1%. Post hoc analysis revealed this value to be statistically greater than the 20% fly ash-high carbon formulation and statistically similar to all other formulations, including the 0% fly ash formulation.

In summary, pervious concrete cylinders made with high carbon content fly ash, regardless of the amount of fly ash in the formulation (20% or 30%), removed more  $\text{Pb}^{2+}$  than formulations made with low carbon content fly ash. Phosphate removal showed an opposite trend, with more  $\text{PO}_4^{3-}$  being removed in low carbon formulations than high carbon formulations. Interestingly, in both the  $\text{Pb}^{2+}$  and phosphate removal experiments, the average removal rate of the 0% fly ash formulation was in between the averages observed for high and low carbon formulations.

While the two types of fly ash differ not only in carbon content but mineral composition, Kutchko and Kim (2006) showed that in several Class F fly ash samples from four different states, including Tennessee, the source of our fly ash, the primary mineral/morphological structures are fairly common. Although amorphous calcium aluminosilicates have a high potential for both cation exchange and adsorption, Kutchko and Kim (2006) demonstrated that Class F fly ash does not have its calcium associated with silicon and aluminium, but rather sulphur and phosphorus. Furthermore, carbon is known to influence the binding of multiple contaminants, including metals (Calmano et al., 1993; Eggleton and Thomas, 2004; Di Toro et al., 2001). In fact, Sipos et al. (2005) showed that organic matter is the single most important soil fraction for adsorbing lead. That is not to say the mineral fraction is unimportant. They also showed ion exchange to be the major mechanism. Since all the blocks in this study were equilibrated to a constant pH, the cation exchange capacities from variable charged sites should be normalised and differences should be due to the number of exchange sites. The high carbon fly ash would be expected to carry a greater cation exchange capacity than the low carbon. The differences seen here are not necessarily exclusively due to differences in carbon content and other factors not taken into account may play a role.

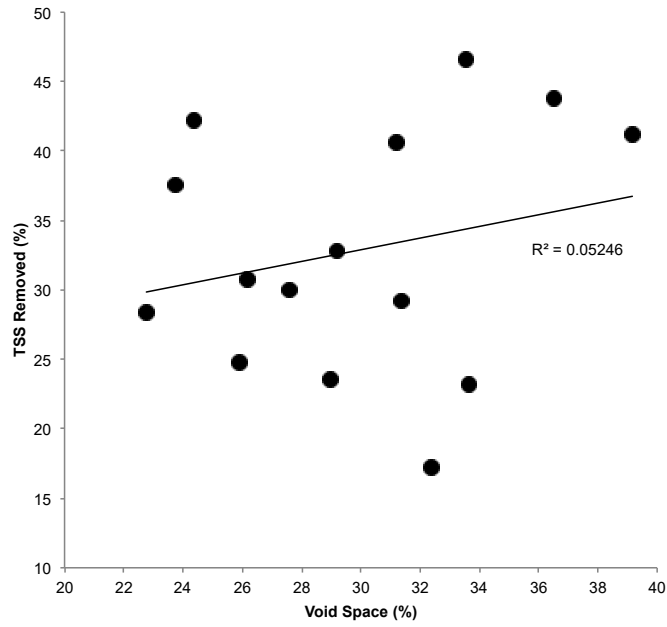
In the case of phosphate, the greater adsorption on the low carbon blocks is not surprising. Phosphate is known to adsorb by ligand exchange to mineral surfaces exchanging with  $\text{H}_2\text{O}$  and  $\text{OH}^-$  groups. These groups are more preferentially associated with hydrophilic mineral oxides as opposed to hydrophobic carbon. In fact, organic matter interferes with adsorption of phosphate to aluminium and iron oxides in soil (Borggaard et al., 1990). The additional mineral content ( $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ ) afforded by the fly ash appears to outweigh the small amount of added carbon.

While it is not possible to distinguish between the different fly ash components contribution to removal it is likely that the results of the present study were due to either fly ash's direct influence on contaminants as they pass through pervious concrete, it's influence on the formulation process, which cannot be understood by porosity measurements alone, or a combination of both. Previous research with nutrients and pervious concrete concluded that additives such as fly ash do not affect removal concentrations (Luck et al., 2008, 2009). These conclusions differ from the results of the present study and highlight the need for further investigations into the role of fly ash in pervious concrete.

### 3.4 *Role of porosity*

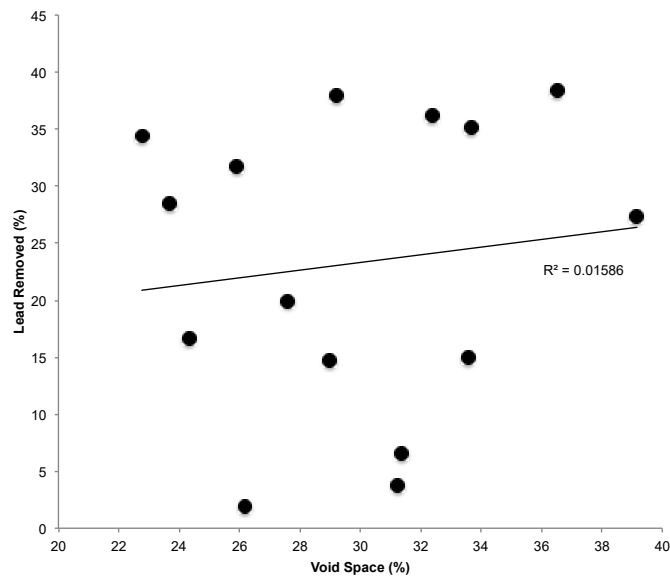
The connection between pervious concrete and contaminant removal has been established and intuitively, this removal has been linked to the amount of void space present within the concrete. Park and Tia (2004) showed in laboratory-controlled experiments that porous concrete with smaller aggregate size and higher void space were better at removing nitrogen and phosphorus than porous concrete with less void space. Overall, little published literature exists that investigates potential mechanisms for contaminant reductions within pervious concrete. In the present study, regression analysis was conducted to examine if the void space of the individual cylinders used would be a good predictor of contaminant removal. Surprisingly, no significant relationships existed between porosity and TSS ( $r^2_{(14)} = 0.0524$ ,  $p = 0.4116$ ),  $\text{Pb}^{2+}$  ( $r^2_{(14)} = 0.0158$ ,  $p = 0.6547$ ),  $\text{PO}_4^{3-}$  ( $r^2_{(22)} = 0.00469$ ,  $p = 0.7619$ ),  $\text{Cl}^-$  ( $r^2_{(22)} = 0.06371$ ,  $p = 0.2571$ ),  $\text{SO}_4^{2-}$  ( $r^2_{(22)} = 0.0483$ ,  $p = 0.3257$ ), or  $\text{NO}_3^-$  ( $r^2_{(22)} = 0.000384$ ,  $p = 0.9310$ ) (Figures 1, 2, 3, 4) meaning that void space alone cannot predict removal of these contaminants. While the treatments of fly ash and carbon vary within void space correlations, no significant trends were seen when the treatments were handled separately. However, the sample numbers for individual treatments are small and may mask any correlations. These results, combined with the results of the removal efficiency data, again highlight the need for further studies into contaminant removal and pervious concrete. One future direction that needs to be addressed and would shed light on this issue would be an analysis of the internal macro- and microstructure of different pervious concrete formulations in a controlled setting, so direct comparisons could be made.

**Figure 1** Relationships between total suspended solid removal (%) and void space (%) in pervious concrete



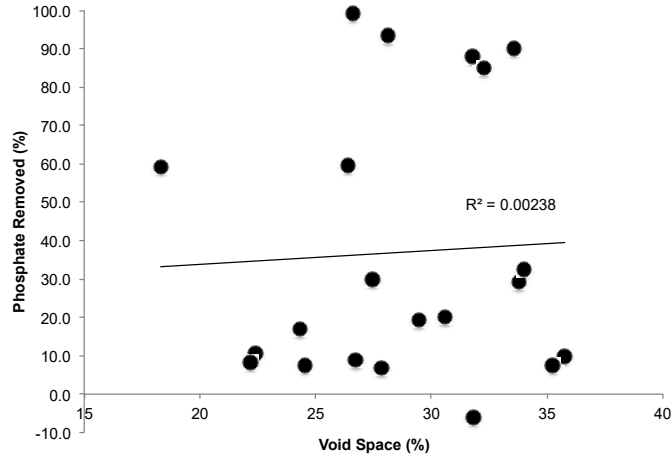
Note: Each data point is from an individual pervious concrete cylinder.

**Figure 2** Relationships between lead removal (%) and void space (%) in pervious concrete



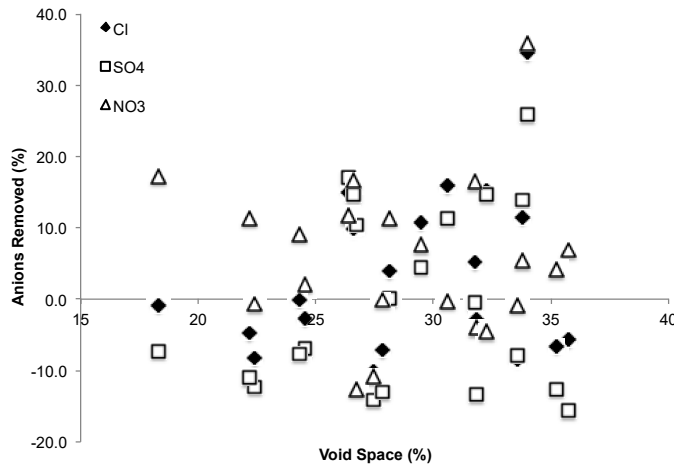
Each data point is from an individual pervious concrete cylinder.

**Figure 3** Relationships between phosphate removal (%) and void space (%) in pervious concrete



Note: Each data point is from an individual pervious concrete cylinder.

**Figure 4** Relationships between  $\text{Cl}^{-1}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^{-}$  removal (%) and void space (%) in pervious concrete



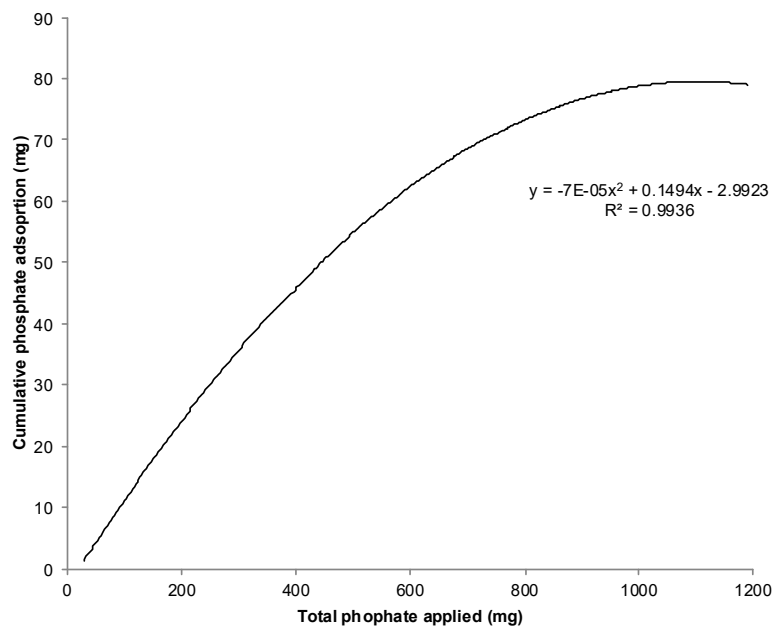
Note: Each data point is from an individual pervious concrete cylinder.

### 3.5 In depth phosphate removal dynamics

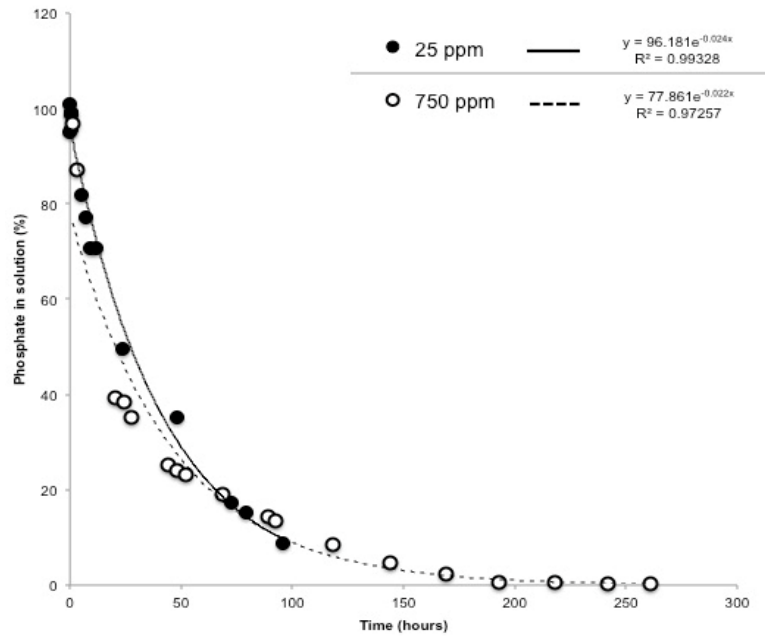
Research into factors controlling nutrient removal within pervious concrete has been limited. Park and Tia (2004) suggested microorganisms inhabiting the void space within pervious concrete might have contributed to the reduced phosphorus concentrations observed during their controlled laboratory analysis. In the present study, three different experiments were performed to better understand phosphate removal dynamics for one specific formulation (20% fly ash-low carbon) and from these experiments three major insights were gained. First, phosphate removal within pervious concrete has a saturation

limit (Figure 5). A saturation concentration of approximately 80 mg of phosphate was achieved after approximately 32 1-litre runs of 29 mg/L  $\text{PO}_4^{3-}$ , with the cylinder retaining approximately 80 mg of  $\text{PO}_4^{3-}$ . Second order quadratic modelling revealed a significant relationship, indicative of steady state dynamics, between cumulative phosphate adsorption and total amount of phosphate applied through the artificial rain simulator ( $r^2(41) = 0.9936$ ,  $p < 0.001$ ). Second, the rate of phosphate removal within pervious concrete will increase as the amount of phosphate being exposed to pervious concrete increases (Figure 6). This is supported by the sorption rate constants for phosphate removal not being different, despite the large difference between the concentrations tested (25 and 750 mg/l). First order kinetics analysis for 25 mg/L ( $r^2(15) = 0.9932$ ,  $p < 0.001$ ) and 750 mg/L ( $r^2(18) = 0.9725$ ,  $p < 0.001$ )  $\text{PO}_4^{3-}$  treatments were shown to be significant. ANCOVA analysis revealed that the slopes generated by the two treatment concentrations were not significantly different from one another ( $F_{(2,32)} = 1.3354$ ;  $p = 0.2573$ ). Third, flow rate through pervious concrete affects the removal rate of phosphate (Figure 7). Linear regression analysis revealed a significant relationship between the flow rate of the artificial rain simulator and  $\text{PO}_4^{3-}$  removal efficiency ( $r^2(10) = 0.7695$ ,  $p = 0.0009$ ) (Figure 7). Based on this relationship it is estimated that an average flow rate of 2.0 mL/sec would remove 44.1% of phosphate compared to 13.3% at an average flow rate of 14 mL/sec.

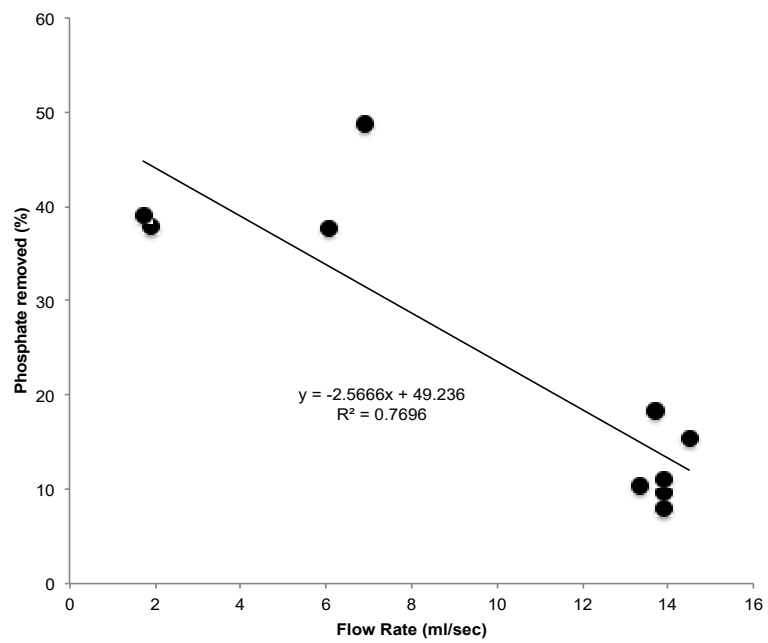
**Figure 5** Cumulative phosphate adsorption (mg) on a single 20% fly ash-low carbon pervious concrete cylinder



**Figure 6** Percentage of phosphate absorbed by a 20% fly ash-low carbon pervious concrete cylinder over time



**Figure 7** Relationships between phosphate removal (%) and flow rate (ml/sec) in pervious concrete



Note: All data is from a single 20% fly ash-low carbon pervious concrete cylinder.

Collectively these results reveal that the two most important factors involved in phosphate dynamics within pervious concrete are initial phosphate concentration and contact time within pervious concrete. It is important to note that these experiments were performed under controlled laboratory conditions with the goal of understanding removal dynamics and that the conditions used were not meant to mimic field conditions. For example, in the flow rate experiments, flow rates ranged from approximately 1–14 ml/sec, which would be the equivalent of 10–100 times faster than some of the heaviest rain events ever recorded (~13 in/hr), which suggests that pervious concrete could effectively remove phosphate from storm events even during extreme circumstances. However, the flow rates used in the present study agree very well with published field-test infiltration numbers (Bean et al., 2007). Future experiments investigating phosphate removal dynamics in a field setting are necessary to fully understand how to maximise the use of pervious concrete as a filtering mechanism for potential contaminants, such as  $\text{PO}_4^{3-}$ .

#### 4 Conclusions

Overall, results from the present study were similar to previous research that showed increased removal of TSS, metals and phosphorus in pervious concrete compared to impervious surfaces. Void space within the pervious concrete cylinders tested did not significantly correlate with removal. A more detailed analysis of phosphate removal dynamics revealed that the two most important factors controlling phosphate removal were initial phosphate concentration and time. Additionally, results demonstrated that different concentrations of fly ash and type of fly ash used in making pervious concrete might affect the removal efficiency of  $\text{Pb}^{2+}$  and phosphate. In conclusion, as land development continues to increase world wide, porous surfaces such as pervious concrete should be considered during development to aide in improving urban water quality.

#### Conflict of interest

The authors declare that they have no conflict of interest.

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