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A novel method to rapidly assess the suitability of water treatment residual and crushed concrete for the mitigation of point and nonpoint source nutrient pollution

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Abstract

Freshwater ecosystems worldwide are at risk of becoming degraded as a result of excessive inputs of phosphorus (P) associated with terrestrial activities. This study describes a novel methodology to rapidly assess the potential of low-cost adsorbents which might be used to combat this issue. The ability of aluminum drinking water treatment residual (Al-WTR) and crushed concrete (CC) to remove P from dairy wastewater (DW) and forestry runoff (wastewaters representative of point and nonpoint P pollution sources, respectively) was assessed. In addition to predicting the longevity of these media in large-scale filters, potential risks associated with their use were also examined. The results indicate that both CC and Al-WTR show promise for use in removing P from forestry runoff, however the raised pH of effluent from CC filters may pose an environmental concern. Al-WTR showed greater promise than CC for the treatment of DW due to its higher adsorption capacity at high concentrations. Small releases of aluminum ($13.63\text{--}96.17\ \mu\text{g g}^{-1}$) and copper ($5.25\text{--}31.9\ \mu\text{g g}^{-1}$) were observed from both media when treating forestry runoff, and Al-WTR also released a small amount of nickel ($0.16\ \mu\text{g g}^{-1}$). Approximately 50% of total metal loss occurred during the first 25% of total filter loading, indicating that pre-washing of the media would help prevent metal release. These results indicate that field-scale tests are warranted for the treatment of both wastewaters with Al-WTR; CC is likely to be unsuitable for either forestry runoff or DW due to its effects on pH and its short lifespan.

Keywords: Low-cost adsorbents; adsorption; phosphorus; wastewater treatment

42 Nomenclature

a^{**}	Time constant in Eqn. 8
A	Constant of proportionality in Eqn. 12 ($\text{mg g}^{-1} \text{L}^{-(1/B)}$)
B	Constant of system heterogeneity in Eqn. 12
C	Sorbate concentration in bulk solution (mg L^{-1})
C_b	Breakthrough concentration (mg L^{-1})
C_e	Sorbate concentration of filter effluent (mg L^{-1})
C_o	Sorbate concentration of filter influent (mg L^{-1})
k_{BA}	Bohart-Adams rate constant ($\text{L mg}^{-1} \text{min}^{-1}$)
M	Mass of adsorbent (g)
N_t	Time dependent sorption capacity of bed (mg L^{-1})
q_t	Time dependent sorbate concentration per unit mass of adsorbent (mg g^{-1})
t	Empty bed contact time (min)
t_b	Service time/operating time of bed at breakthrough (i.e. when $C_e = C_b$) (min)
U	Flow velocity of solution past adsorbent (cm min^{-1})
V	Volume of solution filtered (L)
V_x	Volume of filter bed (L)
Z	Filter bed depth (cm)

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1. Introduction

Excessive nutrient enrichment of surface waters results in optimal conditions for the overgrowth of algae and many species of noxious aquatic plants. The proliferation of these nuisance species causes serious damage to aquatic ecosystems, both in terms of long-term losses of biodiversity, as well as the more immediate concern posed by the sudden influx of large volumes of biomass into aquatic ecosystems. Sources of nutrient pollution may be divided into two categories: point sources and nonpoint sources. Discreet, easily identifiable point sources such as outlets from municipal wastewater treatment plants and drains from livestock housing and farmyards are usually comparatively low-volume, high-concentration nutrient waste streams (Rodgers et al., 2005). By comparison, nonpoint sources such as runoff from pastures, arable lands, and forestry plantations represent high-volume, low-concentration nutrient pollution streams (Acreman, 2012). Nonpoint sources are particularly difficult to control for a number of reasons, though the primary challenge is simply that the pollution source is spread across such a large area, making it extremely challenging to implement effective runoff treatment strategies (Rao et al., 2009).

A multitude of technologies and management practices have been developed to curtail the loss of nutrients, primarily phosphorus (P) and nitrogen (N), from point and nonpoint sources, though the focus has been largely on P, as it is the limiting nutrient in freshwater environments (Blomqvist et al., 2004; Correll, 1999; Hilton et al., 2006; Schoumans et al., 2014). There is evidence to suggest that controlling N inputs alone can have a deleterious effect by favoring a shift in algal communities towards more objectionable nitrogen fixing cyanobacteria (blue-green algae) (Schindler et al., 2008), further supporting the assertion that P control is of primary importance to the prevention of eutrophication (Schindler et al., 2016; Sharpley et al., 2003).

In the case of point sources, P is usually removed at centralized wastewater treatment facilities using well advanced technologies such as metal precipitation and adsorption, enhanced biological P removal, and, more recently, struvite crystallization (de-Bashan and Bashan, 2004; Schoumans et al., 2015). Phosphorus losses from nonpoint sources are usually addressed at source through the implementation of sound management practices: balancing fertilizer application in relation to crop requirements, matching animal feed P inputs to the nutritional requirements of livestock, reducing particulate P losses by minimizing erosion, and, where P must be applied, timing applications to minimize losses in runoff. Many mitigation strategies targeting nonpoint source P losses take advantage of the fact that a large portion of total P is present as particulate bound P, and hence trapping P laden sediments in settling ponds, constructed wetlands, and riparian buffer zones is often an effective pollution control strategy.

There are still, however, many instances where conventional techniques and management practices such as these fail to produce desired results (i.e. mitigation of pollution), or where their implementation is not practicable (e.g. because of excessive costs). In the case of nonpoint source pollution, a problematic example is P losses from forestry harvesting on blanket peat soils. Riparian buffer zones are the recommended best management practice to control such P losses, but these have been shown to be largely ineffective at removing dissolved P released during clearfelling due to low P retention capacity of low-mineral soils and insufficient uptake by vegetation (Rodgers et al., 2010). Reducing inputs of P is not a feasible option either, given that much of the P lost during forest harvesting originates from the brash (tree harvesting residues) materials, and hence is already present on site (Finnegan et al., 2014). In the case of point source pollution, a potentially troublesome source of nutrients is improperly managed dairy wastewater (DW) (Dunne et al., 2005). Farms often lack the prohibitive amount of space required for treatment with a constructed wetland, and climatic/soil conditions often preclude

land spreading (Ruane et al., 2011), as to do so would simply transmute a point source problem to a nonpoint source problem.

In cases such as these, where source control is neither feasible nor effective and/or where traditional onsite treatment methods are not possible, alternative remedial strategies must be implemented in order to prevent unacceptable P losses. Phosphorus-sorbing materials may offer a solution, and there has been a great deal of recent interest in identifying low-cost sorbents suitable for use in on-site wastewater treatment systems (Cucarella and Renman, 2009; De Gisi et al., 2016). More recently, sorbents are also being used to remove dissolved P from surface and ground waters (Buda et al., 2012), and numerous technologies are being investigated, using sorbents (1) applied as soil amendments (Stout et al., 2000) (2) as substrates in constructed wetlands (Vohla et al., 2005), or (3) as filter media in permeable reactive barriers (Baker et al., 1997) and in-drain filters (Penn et al., 2007).

Once a prospective sorbent has been identified, its suitability for an in-field trial must be fully assessed. Commonly, this involves laboratory-based evaluation of the medium's adsorption capacity using batch tests, though there is a growing body of research which indicates that results of these tests are not suitable for the purposes of estimating a medium's lifespan (Drizo et al., 2002; Guo et al., 2017; Penn and McGrath, 2011; Pratt and Shilton, 2009; Seo et al., 2005; Søvik and Kløve, 2005). To determine filter lifespan, flow-through experiments are often performed (Ali and Gupta, 2007), and in conjunction with predictive modeling, these can give at least an indicative estimate of potential media longevity (Shiue et al., 2011). This is an obviously important first step before costly and time consuming field studies are performed, though many flow-through methodologies can be time consuming in their own right, lasting many weeks (Razali et al., 2007), months (Bowden et al., 2009; Heal et al., 2003), or even years (Baker et al., 1998).

The aim of this study was to assess the potential usefulness of two low-cost adsorbents, namely aluminum drinking water treatment residual (Al-WTR) and crushed concrete (CC), as filter media intended to remove P from DW and forestry runoff. These wastewaters are representative sources of point and nonpoint P losses, respectively, and the two low-cost media have shown past promise as P-sorbing materials (Babatunde et al., 2009; Callery et al., 2015; Egemose et al., 2012). A major concern with novel low-cost adsorbents is that they may be potential sources of metals (Velghe et al., 2012). To address this concern, the final effluent from both filter media were also analyzed for metals. The potential of the materials for use as filter media was assessed using a recently developed methodology which uses a combination of rapid small-scale filter experiments and modeling techniques to make predictive estimates as to the performance and longevity of hypothetical large-scale filters (Callery et al., 2016; Callery and Healy, 2017). This novel methodology assesses the media under flow-through conditions similar to those experienced in-field, but produces results in as little as 24 hours, similar to batch tests. These tests may serve as a useful precursor to large-scale, in-field tests which are required to assess the hydraulic performance of individual filter configurations, and to examine concerns including filter clogging and wash-out of reactive materials.

2. Materials and Methods

2.1 Sample collection and preparation

The two low-cost adsorbents investigated in this study were Al-WTR and CC. The Al-WTR, which had an initial dry solids content of approximately 20%, was first passed through a 1 mm mesh to remove any coarse particles. The strained sludge was then oven dried at 105°C for 24 hr, before being ground with a mortar and pestle and sieved; the fraction which was retained by a 0.5 mm sieve after passing a 1 mm sieve was stored in airtight, high-density polyethylene (HDPE) containers for use in the adsorption columns. The concrete was pulverized using a mortar and pestle, and dried in an oven at 105°C for 24 hr before being sieved; similarly, the fraction which was retained by a 0.5 mm sieve after passing a 1 mm sieve was stored in airtight HDPE containers prior to use in the adsorption columns.

2.2 Preparation of filter columns

For each filter medium, filter column sets, comprising four columns with lengths of 0.4 m, 0.3 m, 0.2 m, and 0.1 m, were prepared using low density polyethylene (LDPE) tubing with an internal diameter of 9.5 mm. The filter columns were packed with filter media, and syringe barrels (i.e. syringes with the plungers removed), packed with a small quantity of glass wool, were fastened to the top and bottom of each filter column. The columns were affixed to a stand to maintain a stable vertical orientation throughout the experiment, and silicone tubing with an internal diameter of 3.1 mm was attached to the syringe ends at the bottom and top of the filter columns to provide influent and effluent lines. A schematic of this experimental setup may be found as Figure S1 of the supplementary material.

2.3 Operation of filter columns

Coarse straining filters, comprising a syringe barrel packed with a small quantity of glass wool, were attached to the ends of the influent lines, and these were submerged in a feed tank filled with either forestry runoff or DW. A Masterflex peristaltic pump was used to supply influent the base of each filter column at flow rates of 105-205 mL hr⁻¹, corresponding to hydraulic loading rates (HLRs) of 1.47-2.88 m hr⁻¹, rates typical of activated carbon adsorption filters (Chowdhury, 2013) and tricking filters (Spellman, 2013), and HLRs that have been used in reactive filters for P removal (Erickson et al., 2012). The columns were mounted vertically and operated in “up-flow” mode (as shown in schematic included as Figure S1 of the supplementary material) to preclude any bypass flow. The effluent from each filter column was collected in 2 hr aliquots using an autosampler. The filter columns were operated in 12 hr on/off cycles to replicate the intermittent loading conditions that would be expected on site, thus allowing time for intra-particle diffusion of adsorbate molecules and associated rejuvenation of the sorbent surface. The collected aliquots were weighed to determine the volume of solution filtered, and subsamples of each aliquot were passed through a 0.45 µm filter before being analyzed for dissolved reactive phosphorus concentrations after APHA 4500-P E (Eaton et al., 1998). Subsamples of the aliquots were acidified to a pH<2 with nitric acid and metal concentrations were determined by ICP-MS after U.S. EPA method 6020A (U. S. Environmental Protection Agency, 2007). Metal analyses were only performed on effluent samples from the 0.4 m filter columns, as testing samples from all columns was cost-prohibitive.

2.4 Data collection and analyses

For each filter column, after any filter loading, V (L), the mass of P removed per gram of filter medium (mg g⁻¹), was calculated by:

$$q_t = \sum_{i=1}^n \frac{(C_o - C_e)V_i}{m} \quad (1)$$

Where q_t is the mass of P retained per gram of filter medium (dependent on the contact time between the solution and the filter medium) (mg g^{-1}), C_o is the P concentration of the influent (mg L^{-1}), C_e is the P concentration of the i^{th} aliquot of filter effluent (mg L^{-1}), V_i is the volume of the i^{th} aliquot (of a total number of aliquots, n , whose combined volume is V) (L), and m is the mass of sorbent in the adsorption column (g).

In a recent paper, Callery and Healy (2017) proposed that the performance of multiple adsorption columns could be described with one of two models. The first of these, which is best suited to the description of sigmoidal breakthrough curves, is based on a modification of the popular Bohart-Adams model (Bohart and Adams, 1920):

$$\ln \left(\frac{C_o}{C_b} - 1 \right) = k N_t \frac{Z}{U} - k C_o t_b \quad (2)$$

Where k is a model constant (with units of $\text{L mg}^{-1} \text{min}^{-1}$), Z is the filter-bed depth (m), U is the linear flow velocity (cm min^{-1}), t_b (min) is the filter-bed service time at which the concentration C_b occurs, and N_t is the time-dependent bed capacity (mg L^{-1}), defined as follows:

$$N_t = N_o \frac{t}{t + a^{**}} \quad (3)$$

Where t is the filter empty bed contact time (EBCT) (min), N_o is the maximum adsorption capacity of the filter bed per unit volume of filter medium (mg L^{-1}), and a^{**} is a model constant sometimes referred to as the ‘time of relaxation’, i.e. the time taken for the sorbent to reach half of its adsorption capacity.

Rearranging Eqn. 2, we get an expression for C_b at any filter loading, V :

$$C_b = \frac{C_o}{1 + e^{-k(C_o t_b - N_t \frac{Z}{U})}} \quad (4)$$

Eqn. 4 may also be rearranged to determine the time at which a given breakthrough concentration will occur:

$$t_b = \frac{N_t Z}{C_0 U} - \frac{1}{k C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (5)$$

Assuming that the influent concentration remains constant, the total mass of P loaded onto the adsorption column can be defined as follows:

$$\text{mass loading} = \int_0^V C_o dV \quad (6)$$

The total mass of P lost in filter effluent can be defined as the integral from 0 to t_b of Eqn. 4:

$$\int_0^{t_b} C_b dV = \frac{\ln \left(e^{C_o k t_b + e^{\frac{k N_t Z}{U}}} \right)}{k} - \frac{\ln \left(1 + e^{\frac{k N_t Z}{U}} \right)}{k} \quad (7)$$

Given that, at the time of breakthrough, the volume treated can be defined as $V = t_b * Q$ (where Q is the loading rate in $L \text{ hr}^{-1}$). The total mass retained by the filter medium, $q_t m$, can therefore be described by making this substitution and subtracting Eqn. 7 from Eqn. 6:

$$q_t m = C_o t_b Q - \frac{\ln \left(e^{C_o k t_b + e^{\frac{k N_t Z}{U}}} \right)}{k} + \frac{\ln \left(1 + e^{\frac{k N_t Z}{U}} \right)}{k} \quad (8)$$

q_t can be determined dividing both sides of Eqn. 8 by the filter medium mass, m , which after some simplification yields:

$$q_t = \frac{C_o t_b Q}{m} - \frac{\ln \left(\left(e^{C_o k t_b + e^{\frac{k N_t Z}{U}}} \right) \left(1 + e^{\frac{k N_t Z}{U}} \right) \right)}{m k} \quad (9)$$

214 The second model, proposed by Callery and Healy (2017), is best suited to the description of
 215 non-sigmoidal, convex to linear breakthrough curves of the type often observed in flow-
 216 through studies using low-cost adsorbents. This model is as follows:

$$217 \quad C_b = C_o - \frac{q_t m}{VB} \quad (10)$$

218 Where B is a model constant and q_t is an EBCT-dependent term for the mass of P adsorbed at
 219 a filter loading of V per unit mass of filter bed, described by:

$$220 \quad q_t = AV_b \left(\frac{1}{B}\right) \frac{t}{t+a^{**}} \quad (11)$$

221 Where A is a model constant of proportionality (with units $\text{mg g}^{-1} \text{L}^{-(1/B)}$) and V_b is the number
 222 of empty bed volumes filtered. As with Eqn. 9, Eqn. 11 may be rearranged to find the filter
 223 loading, V, at which any given breakthrough concentration occurs:

$$224 \quad V = \frac{q_t M}{B(C_o - C_t)} \quad (12)$$

225 Substituting Eqn. 11 for q_t in Eqn 12, we obtain the following:

$$226 \quad V = \left(\frac{B(C_o - C_e)(t+a^{**})}{V_x^{-\left(\frac{1}{B}\right)} AMt} \right)^{\frac{B}{1-B}} \quad (13)$$

227 Where V_x is the volume of the filter bed.

228 With experimental values for q_t determined from Eqn 1, an attempt was made to fit both Eqn.
 229 9 and Eqn. 11 to the data using nonlinear regression. Values for the model were obtained using
 230 the Solver tool in Microsoft Excel by minimizing the value obtained by the sum of the squared
 231 errors (ERRSQ) function:

$$232 \quad ERRSQ = \sum_{i=1}^n (q_{t,i,meas} - q_{t,i,calc})^2 \quad (14)$$

Where $q_{t,i,meas}$ is the measured value of q_t obtained using Eqn. 9, and $q_{t,i,calc}$ is the value of q_t predicted by either Eqn. 9 or Eqn. 11.

The mean percentage error (MPE), which can be negative or positive depending on whether the model over- or underestimated experimental values respectively, was also calculated by:

$$MPE = \frac{100\%}{n} \sum_{i=1}^n \frac{q_{e,i,meas} - q_{e,i,calc}}{q_{e,i,meas}} \quad (15)$$

The MPE provides a more an intuitive metric of goodness of model fit, providing information both on how closely a model fits experimental data, as well as whether modeled values over- or underestimate actual values. An Excel template is provided in the Supplementary Material.

Using the model coefficients obtained from the small-scale columns, the performance of full-scale pilot filters could be estimated with either Eqn. 5 or Eqn.13, depending on which of Eqn. 9 or Eqn. 11 best fit the small-scale data. If using Eqn. 5, the volume at which a given breakthrough concentration, C_b , occurs may be found by multiplying t_b by the volumetric flow through the large-scale filter. If using Eqn. 13, the volume at breakthrough is found by using the mass of adsorbent in the large-scale column in the place of 'M', and the volume of the large-scale column in the place of V_x .

3. Results and Discussion

3.1 Phosphorus retention

Graphs of P retention against filter column loading can be seen in Figure 1. When filtering forestry runoff, the maximum amount of P retained by Al-WTR and CC was 0.349 and 0.142 mg g⁻¹, respectively, and when filtering DW, the maximum amount of P removed by Al-WTR and crushed concrete was 3.673 and 1.333 mg g⁻¹, respectively. These values do not represent saturated adsorption capacities, and had the columns been loaded for longer, further adsorption would almost certainly have taken place; however, 24-36 hr of loading was sufficient to fit Eqns. 9 and 11 to experimental data (Callery et al., 2016). Though Al-WTR displayed a higher overall adsorption capacity when filtering forestry runoff, it also displayed a faster breakthrough (assuming breakthrough to be when the column effluent reaches 10% of the influent concentration (Ahmad and Hameed, 2010; Netpradit et al., 2004)). Crushed concrete's high performance upon initial loading of the filters would seem to suggest that processes other than only adsorption (e.g. precipitation of phosphate with metals) may be playing an important role early in the reaction, even though the material had a lesser adsorption capacity overall. Similar observations were made by Molle et al. (2003), who found that rapid dissolution of lime in CC and associated increases in pH and increased Ca²⁺ concentrations resulted in strong P precipitation in CC filters, followed by a sudden decrease in P removal rates once dissolution decreased. While P may bind to both Al and Ca surfaces in Al-WTR (with multiple sorption mechanisms possible even at low solution concentrations (Zohar et al., 2018)), at the observed pH range observed while treating both forestry runoff and DW (7.31±0.36 and 7.87±0.23 respectively), sorption onto amorphous Al hydroxides, which has previously been observed to be the dominant removal mechanism at a pH of ~7.5 (Massey et al., 2018), was likely responsible for the majority of P removal. The slightly alkaline pH of the solution may,

however, potentially have negatively affected the sorption capacity of these Al surfaces (Zohar et al., 2018).

The sorbent saturation, q_t , for each sorbent-wastewater combination was modeled using Eqn. 9 (the modified Bohart-Adams equation) and Eqn. 11 (the Callery-Healy model). When used to treat forestry runoff, it was found that crushed concrete's performance could be best modeled by Eqn. 9, which fit the experimental data with an MPE of 1.02% (Table 1). Eqn. 11 offered a better fit to experimental data from Al-WTR used to treat forestry runoff, concrete used to treat DW, and Al-WTR used to treat DW, with modeled values having MPEs of -4.03%, -0.27%, and -2.69%, respectively (Table 1). The negative MPEs obtained when fitting Eqn. 11 to experimental data indicate that model predictions were, on average, slightly higher than observed values, and the positive MPE obtained when fitting Eqn. 9 to experimental data indicated that model predictions were, on average, slightly higher; this indicates that both models tended to slightly under- or overestimate the adsorption capacity of each medium, though not significantly.

3.2 Metals release

In general, there was no significant release of metals from either media when filtering DW. However, both media released small amounts copper (Cu) and aluminum (Al) when filtering forestry runoff, and Al-WTR also released a very small amount of nickel ($0.16 \mu\text{g g}^{-1}$). Figure 2 shows the relationship between cumulative metals release from the 0.4 m columns and filter loading for each filter medium/wastewater combination studied. The total cumulative metal loss from 0.4 m filter columns of each filter medium/wastewater combination investigated is summarized in Table 2, and Table 3 shows metal concentrations in the influent to the filter

columns alongside maximum metal concentrations measured in the effluent from the 0.4 m filter columns. Of the metals tested, Mn, Cu and Fe were above the guide values for surface water intended for the abstraction of drinking water (S.L.549.21, 2002)

When CC was used to filter forestry runoff, there was an initial small release of chromium (Cr) and lead (Pb) - though there was subsequent uptake of these metals, resulting in net removal over the course of the experiment; manganese (Mn), zinc (Zn), and iron (Fe) were removed from the influent. There was a net removal of all metals tested when CC was used to filter DW, though there was an initial period where concentrations of Cu and Cr were slightly elevated. When filtering forestry water, Al-WTR released small amounts of Mn, though subsequent uptake resulted in net removal of Mn from the influent. Al-WTR also removed Cr, Zn, Pb, and Fe from the forestry runoff influent, and though Al was released initially, filter effluent concentrations quickly leveled off, indicating that a state of equilibrium had been reached, and further release was unlikely. Al-WTR removed all of the metals tested from DW, though there was an initial small release of nickel prior to this uptake.

A commonly observed phenomenon for all media was that there was a brief initial period of metal release for many metals. This was often followed either by a cessation in further release or often even subsequent uptake by the media, resulting in a net removal of metals over the duration of filter loading. This suggests that an initial washing of the filter media would be highly advisable to rinse off any loosely bound media particles and easily solubilized metals. This would likely help to prevent or significantly reduce any release of metals associated with extreme pH values and loss of particulate matter.

3.3 Filter effluent pH

Differences between filter influents and effluents were more pronounced for filters treating forestry runoff compared to filters treating DW (Figure 3). This was unsurprising, as the

forestry runoff was collected from a blanket peat catchment in an area which is known to have surface waters with low alkalinity and poor buffering capacities (Johnson et al., 2008). Crushed concrete initially raised the pH of the forestry runoff from an average of 6.62 ± 0.11 to a maximum value of 11.18. The magnitude of this increase in pH depended greatly on the contact time between the runoff and the CC, with shorter columns showing slightly higher changes and a quicker leveling off of pH values. After the full duration of filter loading had elapsed, the effluent from the 0.1 m, 0.2 m and 0.3 m filter columns had dropped below the upper recommended surface water environmental quality standard (EQS) for pH (EPA, 2001) of 9, and the pH of the effluent from the 0.4 m column was only slightly above this level. This indicates that approximately 240 bed volumes of wastewater had to pass through the crushed concrete filter medium prior to pH reaching acceptable levels ($\text{pH} \leq 9$); this requirement may preclude its use in the treatment of forestry runoff.

Al-WTR, by comparison, had a much smaller impact on the pH of the forestry runoff. Filter effluents showed an initial decrease in pH compared to that of the filter influent, with a minimum pH of 5.45 observed - slightly below the lower recommended surface water pH EQS of 6 (EPA, 2001). The contact time between the Al-WTR and the forestry runoff had a much less marked effect on observed changes in pH and, excluding the pH measurements from the first effluent aliquots, the effluent from all columns quickly stabilized to an average pH of 7.31 ± 0.36 .

When treating DW, effluent from both crushed concrete and Al-WTR stabilized very quickly at pHs of 8.00 ± 0.10 and 7.87 ± 0.23 , respectively (excluding the pH values from the first aliquot). All effluent from filters treating DW was within the recommended surface water EQS range of 6 to 9, though still raised compared to the influent pH of the DW which was measured to be 6.96 ± 0.04 .

3.4 Potential for use in full-scale filters

Figure 4 shows indicative lifespans of full-scale filters to a breakthrough concentration of 10% filter influent concentration; these were prepared using Eqns. 5 and 12, depending on which best modeled filter medium performance in the small-scale column tests. The charts show design curves for filters of bed depths ranging from 0.5 m to 2 m, although curves for intermediate bed depths may be interpolated, if desired. The purpose of these charts is to give the user the ability to roughly estimate filter medium longevity and filter performance over the course of a hypothetical filter's lifespan, thus aiding with the decision of proceeding to field-scale trials. As would be expected, the charts indicated that increases in filter depth could be expected to result in increases in filter life span. The high P adsorption affinity of CC led to greater adsorption at low concentrations, meaning CC filters would, in theory, have a longer lifespan when treating forestry runoff.

In general, lower loading rates could be expected to result in longer filter lifespans due to increased EBCTs, allowing for more complete treatment. The high adsorption affinity of CC led to rapid adsorption of P, implying that the HLR applied to CC filters was of less importance in determining filter lifespan. This is evidenced in the less pronounced curvature of the lifespan curves for CC in relation to HLR (Figure 4d). Similarly, the high concentration of DW drove more rapid adsorption of P by Al-WTR, as shown by the less pronounced curvature of the lifespan curves in Figure 4d.

As evident from comparison of Figure 4c and Figure 4d, the lifespans of filters utilizing Al-WTR to treat DW could be expected to be much greater than those of filters containing CC. This indicates that field-scale testing of Al-WTR could be expected to yield much better results than field-scale testing of CC.

Characterization methodologies like the one described in this paper are a critical first step in evaluating novel P-sorbing materials; however, subsequent full-scale in-field testing is still critical to investigate potential issues concomitant with in-field use, e.g. the formation of preferential flow pathways, surface clogging, effects of animal activity and vegetation etc. (Buda et al., 2012).

4. Conclusions

Crushed concrete and aluminum water treatment residual (Al-WTR) were investigated as potential filter media for use in filters intended to remove dissolved phosphorus from forestry runoff and dairy wastewater (DW). The primary study findings were as follows:

- The performance of small-scale adsorption columns could be described with great accuracy using two recently developed models.
- Model extrapolations to full-scale filters imply that, for a treatment standard of 90% phosphorus removal,
 - both crushed concrete and Al-WTR show promise for the treatment of forestry runoff, though crushed concrete may have slightly greater longevity as a filter medium due to its higher phosphorus adsorption affinity at low concentrations;
 - for the treatment of DW, filters containing Al-WTR would, due to its higher phosphorus adsorption capacity, likely have much greater longevity than filters containing crushed concrete.
- When utilized in small-scale filters, crushed concrete and Al-WTR both released small quantities of aluminum and copper when filtering forestry runoff; filters containing Al-WTR also released a small amount of nickel. There was no cumulative metal loss from either media when filtering DW.

393 • Effluent from small-scale filters utilizing crushed concrete to treat forestry runoff
394 was above recommended EPA environmental quality standards.

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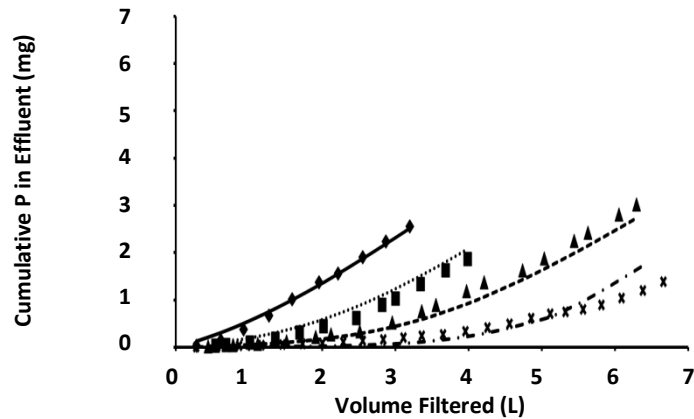
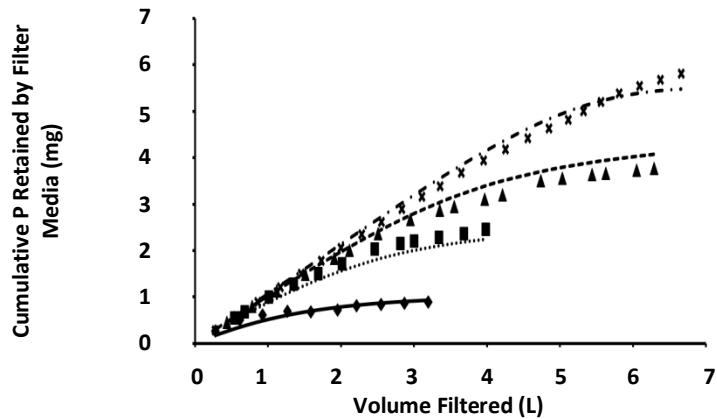
Figures

Figure 1. Phosphorus removal and cumulative phosphorus lost in filter column effluent for various filter depths and wastewater/filter media combinations.

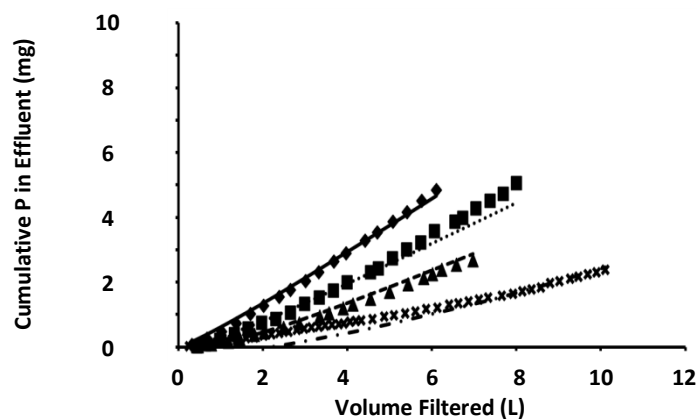
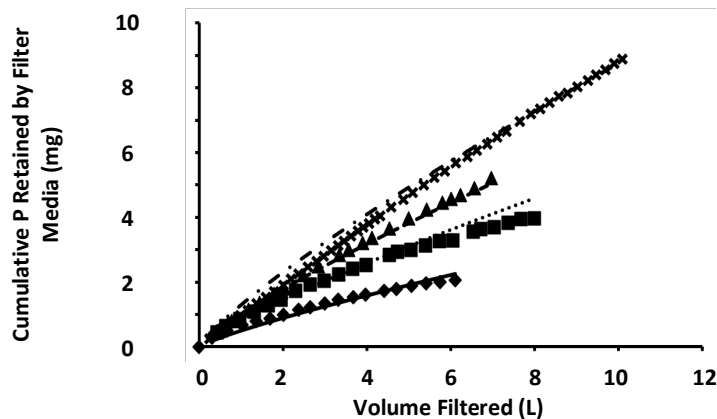
Figure 2. Cumulative metal release/uptake by 0.4 m filter columns.

Figure 3. Filter column influent and effluent pH and their relationship to EPA recommended environmental quality standards (EPA 2001).

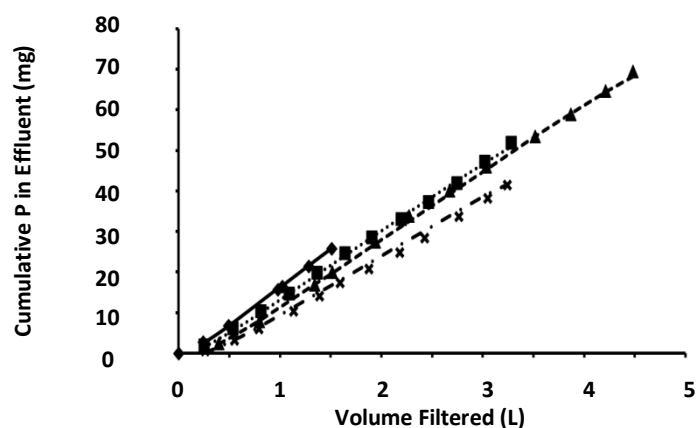
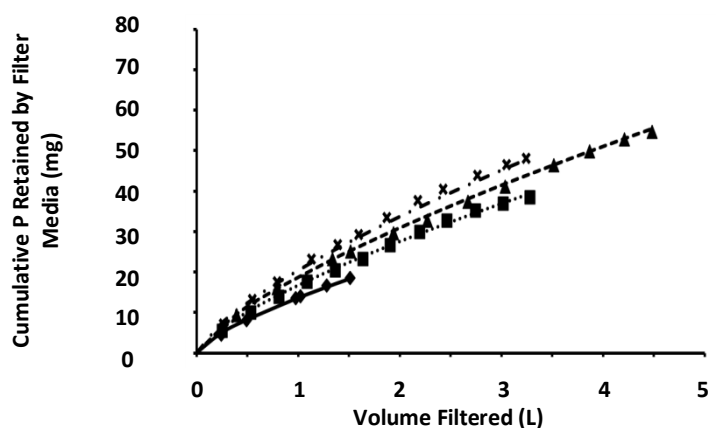
Figure 4. Indicative full-scale filter lifespan to effluent breakthrough concentration of 10% filter influent concentration for filter-beds of various depths subject to HLRs of 1-3 m hr⁻¹.



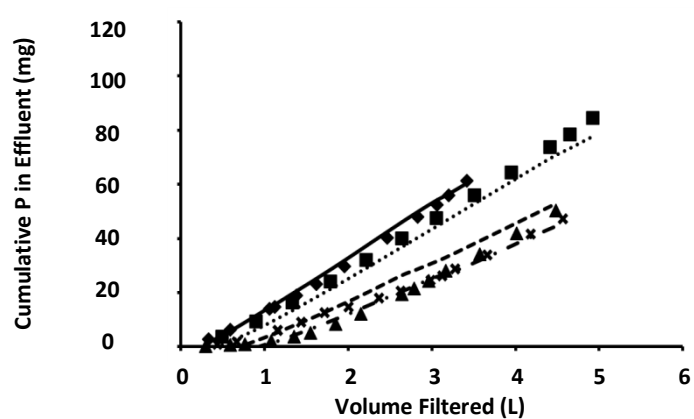
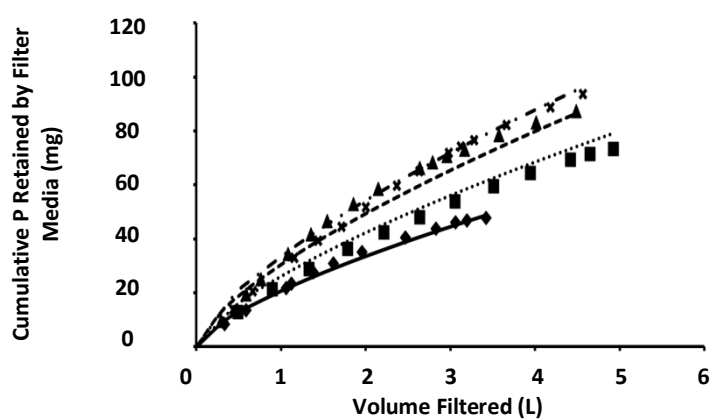
(b) AI-WTR treating Forestry Runoff



(c) Crushed Concrete treating DW



(d) AI-WTR treating DW



Filter depth:
Observed:
Modelled:

0.1m



0.2m



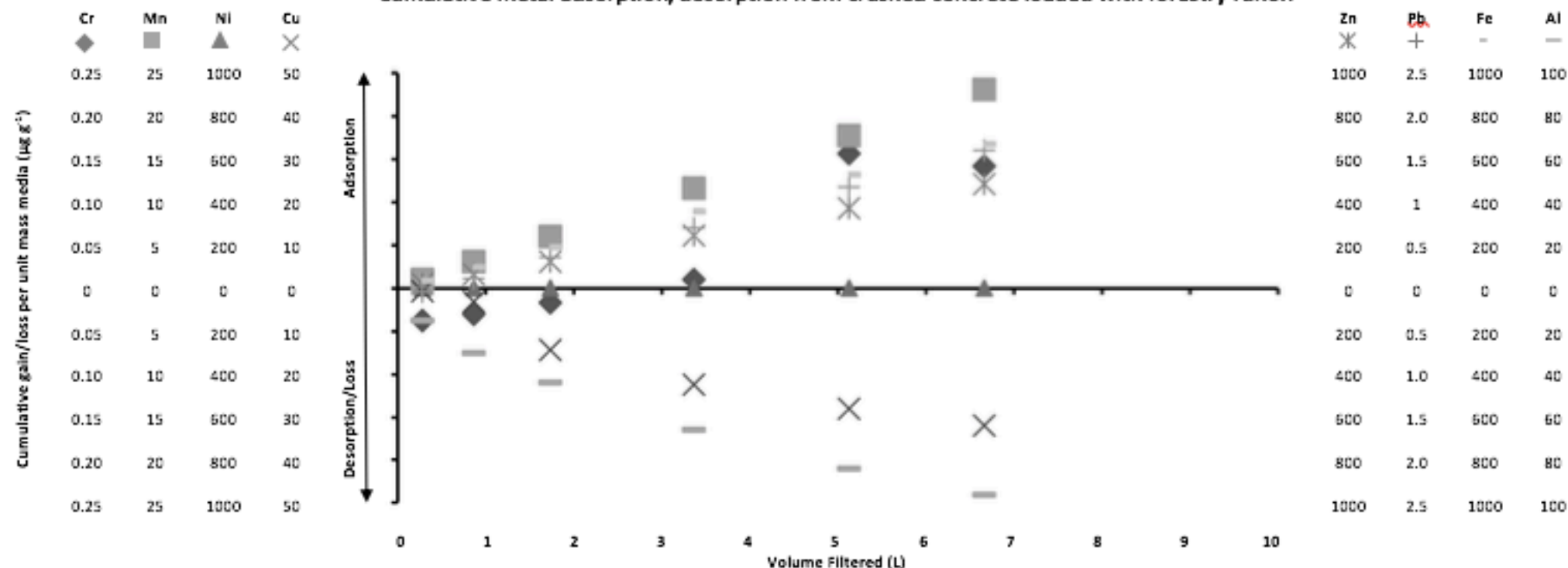
0.3m



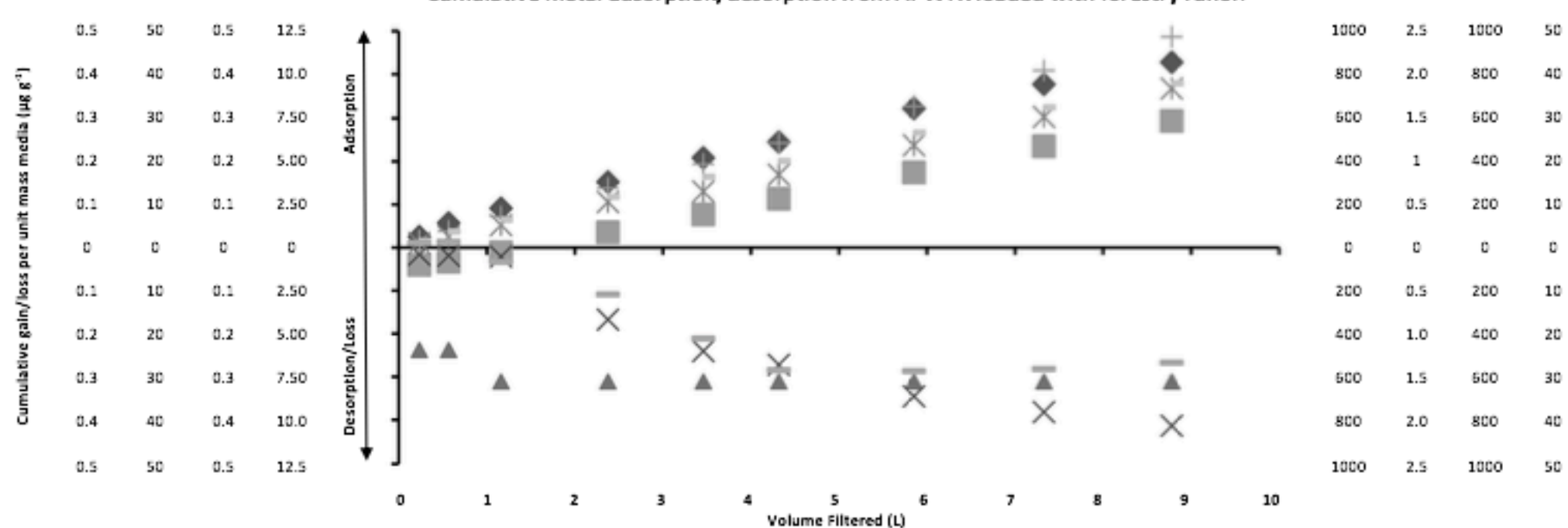
0.4m



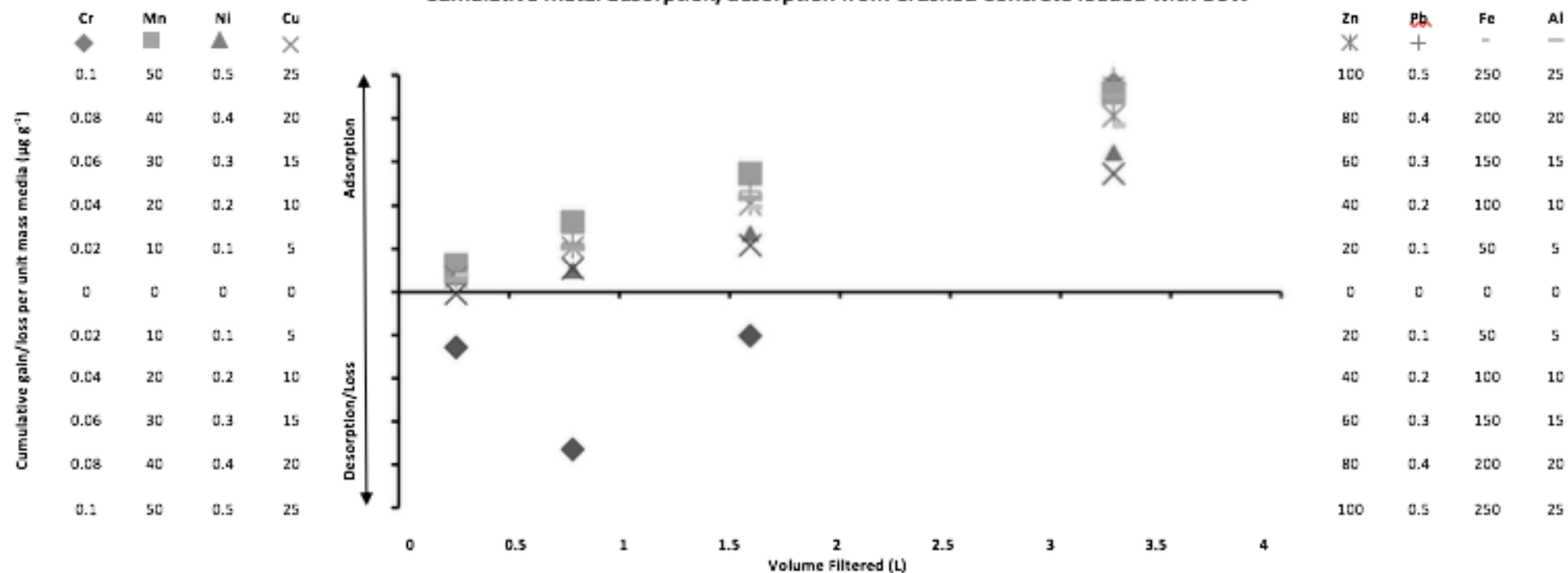
Cumulative metal adsorption/desorption from crushed concrete loaded with forestry runoff



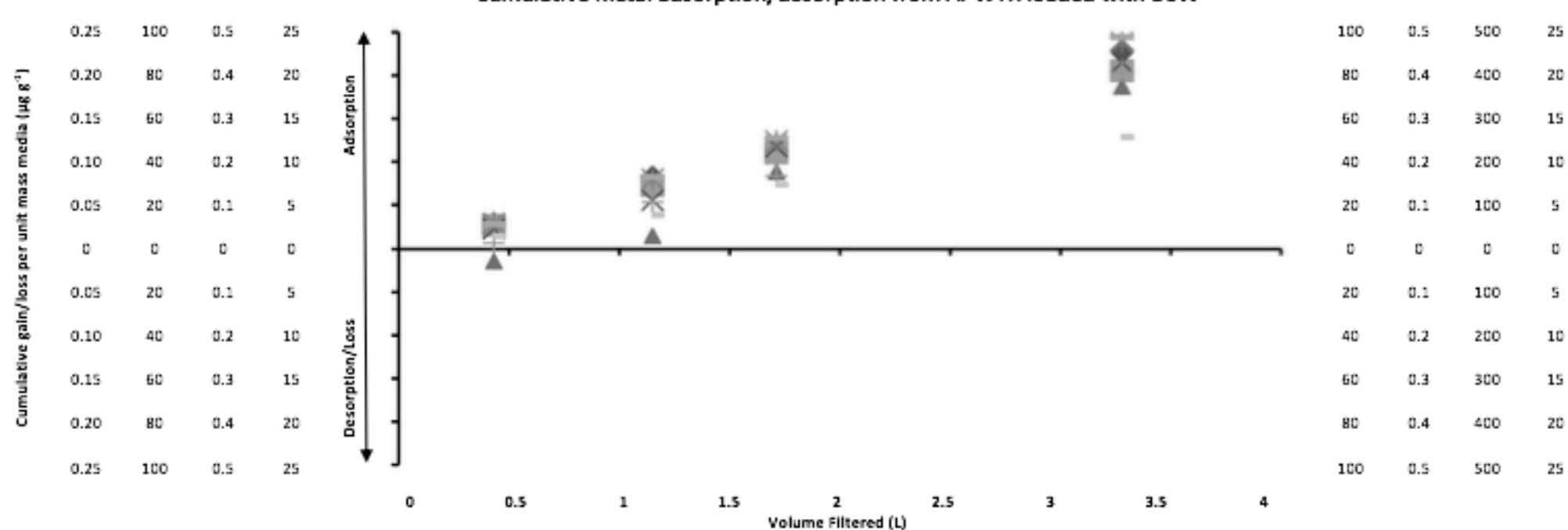
Cumulative metal adsorption/desorption from Al-WTR loaded with forestry runoff

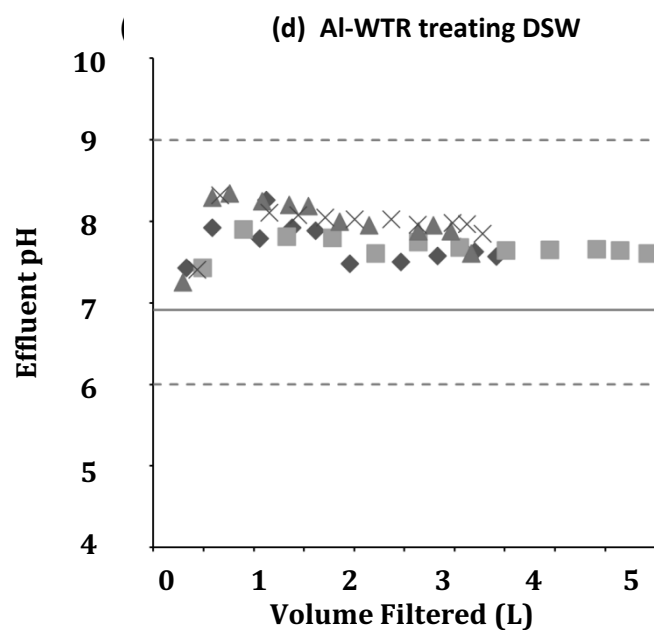
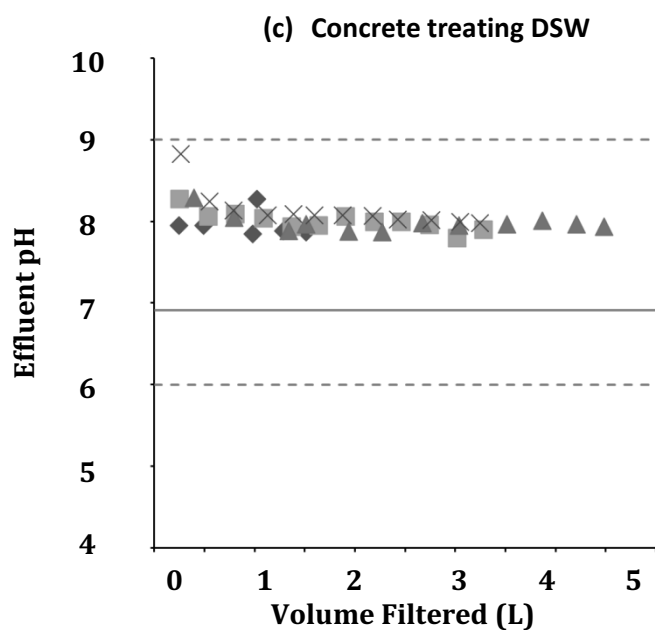
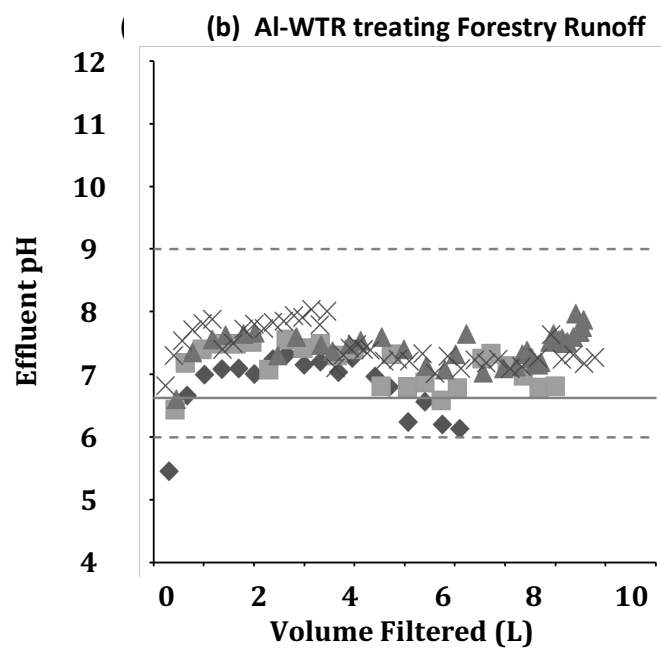
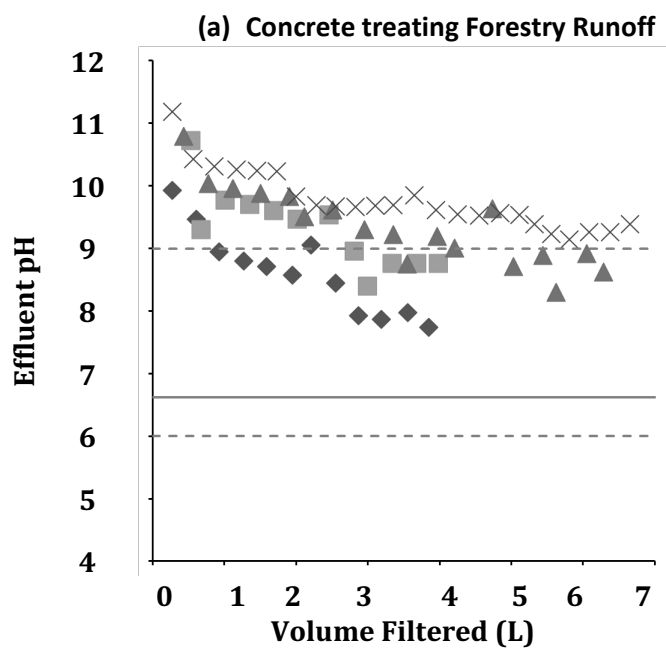


Cumulative metal adsorption/desorption from Crushed Concrete loaded with DSW



Cumulative metal adsorption/desorption from Al-WTR loaded with DSW





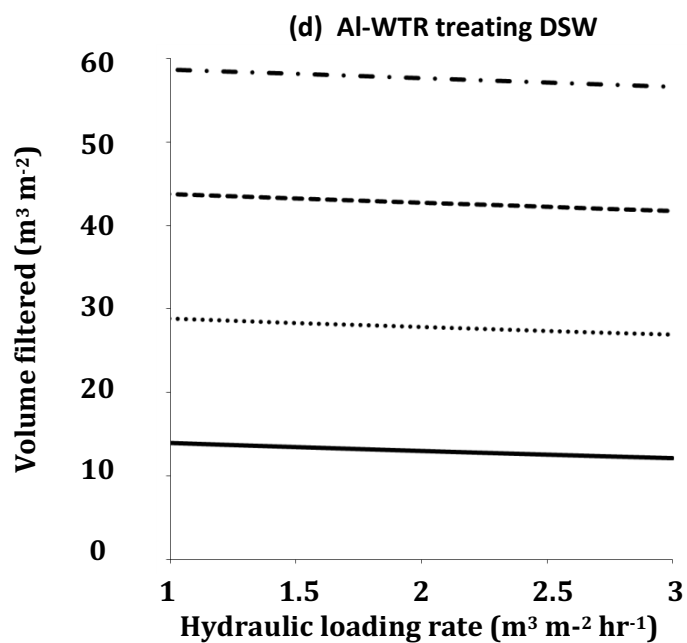
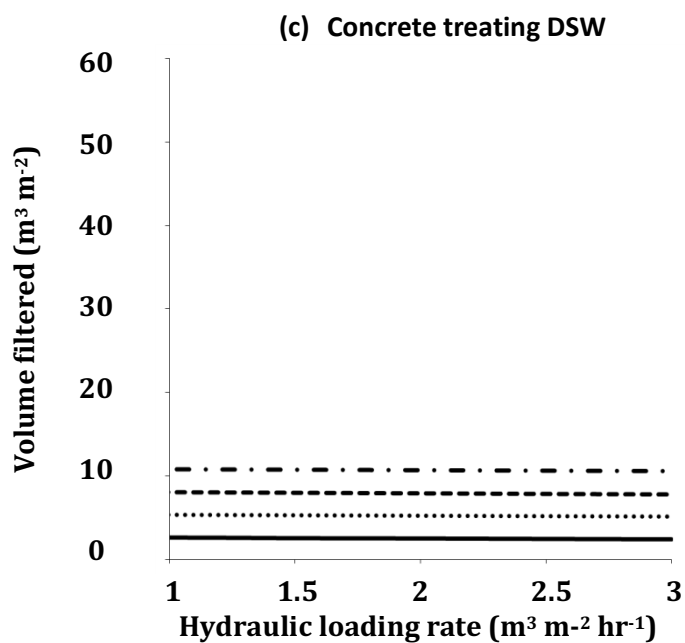
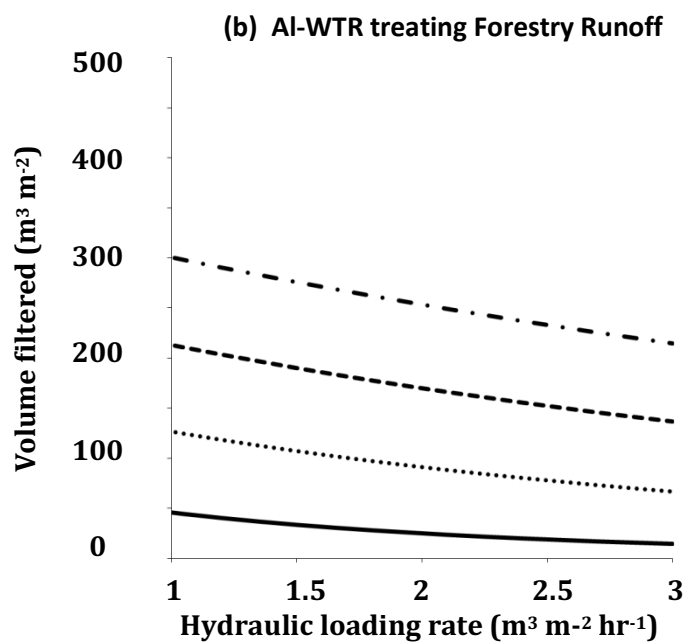
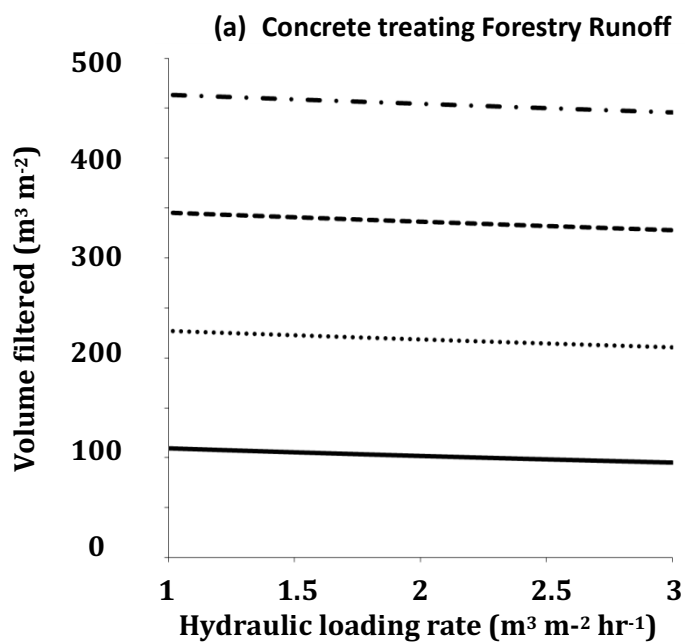
Filter depth: 0.1m

0.2m

0.3m

0.4m

EPA recommended EQS: -----
Influent pH: —————



Filter depth: 0.5m 1m

 —————

 1.5m 2m

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Tables

Table 1. Mean Percentage Errors (MPEs) obtained fitting q_t predictions obtained using Eqn. 9 and Eqn. 11 to small-scale adsorption column data using minimization of the ERRSQ function (Eqn. 14). Positive MPEs indicate that greater adsorption was predicted by the model than was observed experimentally, and negative MPEs indicate the converse.

Table 2. Cumulative release of metals from 0.4m filter columns.

Table 3. Maximum observed metal concentrations in filter effluents from 0.4m columns.

Table1

MPE of modelled vs. observed data				
	Forestry Runoff		DSW	
	Concrete	Al-WTR	Concrete	Al-WTR
Equation 9	1.02%	-14.77%	4.01%	-4.09%
Equation 11	-5.24%	-4.03%	-0.27%	-2.69%
Values in bold indicate lowest MPE				

Table 2

		Cumulative metals release ($\mu\text{g g}^{-1}$ filter media)								
		Cr	Mn	Ni	Cu	Zn	Cd	Pb	Fe	Al
Forestry	CC	-	-	-	31.90	-	-	-	-	96.17
Runoff	Al-WTR	-	-	0.16	5.25	-	-	-	-	13.63
DSW	CC	-	-	-	-	-	-	-	-	-
	Al-WTR	-	-	-	-	-	-	-	-	-

Table 3

		Maximum filter influent/effluent concentrations ($\mu\text{g L}^{-1}$)								
		Cr	Mn	Ni	Cu	Zn	Cd	Pb	Fe	Al
Forestry	Influent	2.1				1888.0	0.0			
		4	96.37	0.00	30.26	2	0	7.05	3230	194
	CC	5.6			356.8		0.0			
		0	9.72	0.00	4	43.76	0	10.96	829	1560
Runoff		1.4	432.1				0.0			
	Al-WTR	2	4	20.25	93.45	921.24	0	1.47	1630	389
	Influent	3.3	671.7		326.6		0.0			
		6	4	11	6	825.05	0	5.49	2690	241
DSW	CC	5.8	382.8		344.3		0.0			
		2	3	10.3	1	193.15	0	2.12	1220	109
		2.2	169.6		229.1		0.0			
	Al-WTR	6	9	12.35	9	242.58	0	4.89	1270	102

Values in bold indicate elevated metal concentrations in filter effluent