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Use of pilot-scale geomedia-amended biofiltration system for removal of polar trace organic and inorganic contaminants from stormwater runoff

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ABSTRACT

Stormwater runoff capture and groundwater recharge can provide a sustainable means of augmenting the local water resources in water-stressed cities while simultaneously mitigating flood risk, provided that these processes do not compromise groundwater quality. We developed and tested for one year an innovative pilot-scale stormwater treatment train that employs cost-effective engineered geomedia in a continuous-flow unit-process system to remove contaminants from urban runoff during aquifer recharge. The system consisted of an iron-enhanced sand filter for phosphate removal, a woodchip bioreactor for nitrate removal coupled to an aeration step, and columns packed with different configurations of biochar- and manganese oxide-containing sand to remove trace metals and persistent, mobile, and toxic trace organic contaminants. During conditioning with authentic stormwater runoff over an extended period (8 months), the woodchip bioreactor removed 98% of the influent nitrate (9 g-N m^{-3} d^{-1}), while phosphate broke through the iron-enhanced sand filter. During the challenge test (4 months), geomedia removed more than 80% of the mass of metals and trace organic compounds. Column hydraulic performance was stable during the entire study, and the weathered biochar and manganese oxide were effective at removing trace organic contaminants and metals, respectively. Under conditions likely encountered in the field, sustained nutrient removal is probable, but polar organic compounds such as 2,4-D could breakthrough after about a decade for conditions at the study site.

1. Introduction

Stormwater runoff is an underutilized resource that could help meet the demands of water-stressed cities through the use of managed aquifer recharge and recovery (Hamdan, 2009; Luthy et al., 2019). However, nutrients, toxic metals and polar trace organics are present in urban stormwater at concentrations that pose potential risks to drinking water supplies (Masoner et al., 2019; Page et al., 2014). Green stormwater infrastructure can reduce flood risks and remove numerous contaminants while simultaneously providing ecological and societal benefits (McFarland et al., 2019). Stormwater harvesting systems increase groundwater recharge, and typically include pre-treatment then retention basins to ensure saturated infiltration, and more recently, passive treatment systems (Fig. S1) (Hagekhalil et al., 2014; Martire, 2018). Biofilters treat captured urban stormwater by percolating it through porous media by gravity (i.e., biofiltration) prior to surface water discharge or use for aquifer recharge (Feng et al., 2012; Hatt et al., 2008). However, these systems are usually designed for hydraulic performance with contaminant removal as a secondary consideration (Edwards et al., 2016). The most commonly used biofiltration media (e.g., coarse sand amended with mulch), improves water quality, mostly through removal of suspended solids, particle-associated contaminants, and microbial transformation processes (Bester and Schäfer, 2009). Some contaminants of urban origin—particularly persistent, mobile and toxic (PMT) organic contaminants (Hale et al., 2020; Jin et al., 2020)—may not be adequately removed by such treatments (Reemtsma et al.,

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2016; Zhang et al., 2014).

Several types of engineered geomedia may more effectively remove contaminants during passive infiltration. Carbonaceous materials (e.g., biochar) adsorb trace organic and metal contaminants in stormwater (Mohanty et al., 2018). Some manganese oxide-coated sands oxidize electron-rich organic contaminants (Charbonnet et al., 2018; Grebel et al., 2016) and adsorb metals during stormwater infiltration (Charbonnet et al., 2020). Other cost-efficient geomedia, like woodchips and iron filings, can remove nitrate and phosphate from stormwater (Erickson et al., 2012; Halaburka et al., 2019, 2017). Thus, reconfigured green infrastructure systems with engineered geomedia could provide a means of contaminant removal by sorption and redox processes (Grebel et al., 2013).

Many types of geomedia perform well at the laboratory scale; however, little is known about how different weathered engineered geomedia perform when integrated into a series of continuous-flow unit operations subjected to authentic stormwater (Okaikue-Woodi et al., 2020). Field testing has demonstrated that geomedia performance can decline within a few months of operation (Robertson, 2010). In addition, combining different geomedia configurations (i.e., unit operations in series) or directly mixing geomedia (i.e., within the same unit operation) to assess their synergistic or antagonistic effects on contaminant removal is significantly under-developed (Spahr et al., 2019). For instance, biochar may adsorb natural organic matter and thus prolong the treatment capacity of manganese oxides (Charbonnet et al., 2020; Uchimiya et al., 2010). Conversely, reducing conditions stimulated by labile organic compounds in woodchip leachate may dissolve Fe(III) and Mn(IV) oxide geomedia, release adsorbed trace metals, and even promote trace metal removal through sulfide precipitation (Grebel et al., 2013). Similarly, microbial activity could enhance the transformation of some contaminants or could block sites for sorption or abiotic oxidation reactions (Hellauer et al., 2018; Portmann et al., 2022). Finally, physicochemical weathering and biofilm growth could lower the hydraulic conductivity of the infiltration system (Perujo et al., 2019). An improved understanding of these contaminant removal factors, including geomedia configuration, is essential to the design and sustained success of large-scale stormwater treatment trains.

In this study, we evaluated the efficacy of engineered geomedia for passive removal of stormwater contaminants over a 1-year period in a pilot-scale infiltration system. The objective of this research was to test a new approach for integrating stormwater treatment train unit operations for nutrient, metals, and trace organic contaminants under the saturated flow conditions that may be used for managed aquifer recharge (Fig. S1). This study uses a novel integration of coupled unit operations under continuous flow, weathered with authentic stormwater, and testing of multiple configurations of biochar and metal oxide geomedia for trace organic contaminant removal. Different unit-process configurations were evaluated during eight months of conditioning with stormwater. This was followed by a four month challenge test on 24 weathered geomedia-enhanced columns with stormwater spiked with representative contaminants. These results significantly expand upon our previous study evaluating the effect of different woodchip bioreactor configurations on the removal of trace metal and organic contaminants at the same site (Ashoori et al., 2019) by integrating multiple geomedia configurations. In the previous study, no contaminant breakthrough was observed in biochar-amended bioreactors, and a diffusion-limited sorption model predicted decades of service for trace organic removal. Understanding the effects of extended exposure to authentic stormwater on engineered geomedia, various configurations of geomedia unit operations, and chemical analysis of the geomedia after challenge testing provide novel insights into the biogeochemical processes relevant during stormwater infiltration and links laboratory studies to full-scale deployment of engineered infiltration systems.

2. Methods and reagents

2.1. Field site and water source

The pilot-scale treatment system was located inside a warehouse at Sonoma County Water Agency (SCWA) facilities in Sonoma, CA (Fig. S2). This structure moderated temperature (i.e., 18–25 °C) and provided a dark environment that limited algal growth on exposed tubing. Urban runoff and stormwater were collected from Fryer Creek (38°17′15″ N, 122°27′60″ W) for the eight month conditioning, which is fed primarily by stormwater runoff (during winter rainy season) and urban irrigation drainage (during dry summer season) from a mixed residential and commercial development (Table S1, Fig. S3). Every 2 to 4 weeks, stormwater was collected using a pump with a 300 μm polypropylene filter bag on the intake strainer and a 75 μm filter on the intake hose. Collected water was immediately transferred in a 1500 L polyethylene tank to the warehouse, where it was stored in a black 2500 L polyethylene tank. The tanks and collection equipment were rinsed with tap water and air dried after every use.

2.2. Geomedia-enhanced unit-process system

A pilot-scale unit-process treatment train was built to assess the different unit operations of the stormwater treatment system (Fig. 1). Collected stormwater ("Tank 0") was first pumped to an iron-enhanced sand filter designed to remove dissolved phosphorus (Erickson et al., 2012). The iron-enhanced sand filter was a down-flow PVC column (40 cm length × 10 cm inside diameter) filled with ASTM C33 grade sand and 5% iron filings (iron aggregate provided by Connelly-GPM Inc., Chicago, IL) by weight, for a designed hydraulic conductivity of 0.015 cm s^{-1}. This well-established technology served as a pre-treatment step for phosphate removal.

The iron-enhanced sand filter drained into a 40 L polyethylene tank ("Tank 1"). The flow from this tank was split into thirteen separate lines (not shown separately in the figure for clarity). One first line passed through a woodchip denitrifying bioreactor (50 cm length × 10 cm inside diameter) (Halaburka et al., 2019, 2017), prior to subsequent pumping through 12 geomedia columns (100 cm length × 5 cm inside diameter) consisting of sand (control), or manganese oxide-coated sand and sand amended with biochar (Fig. S4). Another 12 lines flowed directly to identical geomedia treatment columns (Fig. 1). Each column group (with and without the woodchip bioreactor nitrate pre-treatment) consisted of triplicates of three different biochar and manganese oxide-coated sand configurations and sand controls: mixed biochar/manganese oxide-coated sand (designated "MX"), 45-cm layers of biochar prior to manganese oxide-coated sand (designated "BM"), and 45-cm layers of manganese oxide-coated sand before biochar (designated "MB"). Columns in which the woodchip bioreactor was employed prior to geomedia treatment were designated with a "W" prefix.

A total of 24 geomedia-packed PVC columns (Fig. 1) were employed in this study. The columns exceeded the minimum ratio of column-to-particle diameter (i.e., 50:1) recommended to avoid preferential flow pathways due to wall effects (Lang et al., 1993). Geomedia columns were operated in continuous upflow mode to facilitate saturated conditions throughout the experiments, because saturated conditions are likely to be employed in large-scale treatment systems (Ashoori et al., 2019). The biochar was obtained from Mountain Crest Gardens (Etna, CA) and exhibited a N_2 B.E.T. surface area of 318 m^2 g^{-1} (Ulrich et al., 2015). It was sieved through a 20–30 mesh (0.6–0.85 mm), and mixed at 1 wt% with 20–30 mesh Ottawa sand. Manganese greensand was obtained from GreensandPlus™ (18–60 mesh, Clayton, NJ), and was sieved to remove <30 mesh fine particles prior to use. Further details on geomedia column characteristics, construction, and packing material preparation are included in the Supplementary Material.

Column porosities were calculated gravimetrically after saturation with deionized water (Table S2). Tracer tests with 4.86 mM NaBr were

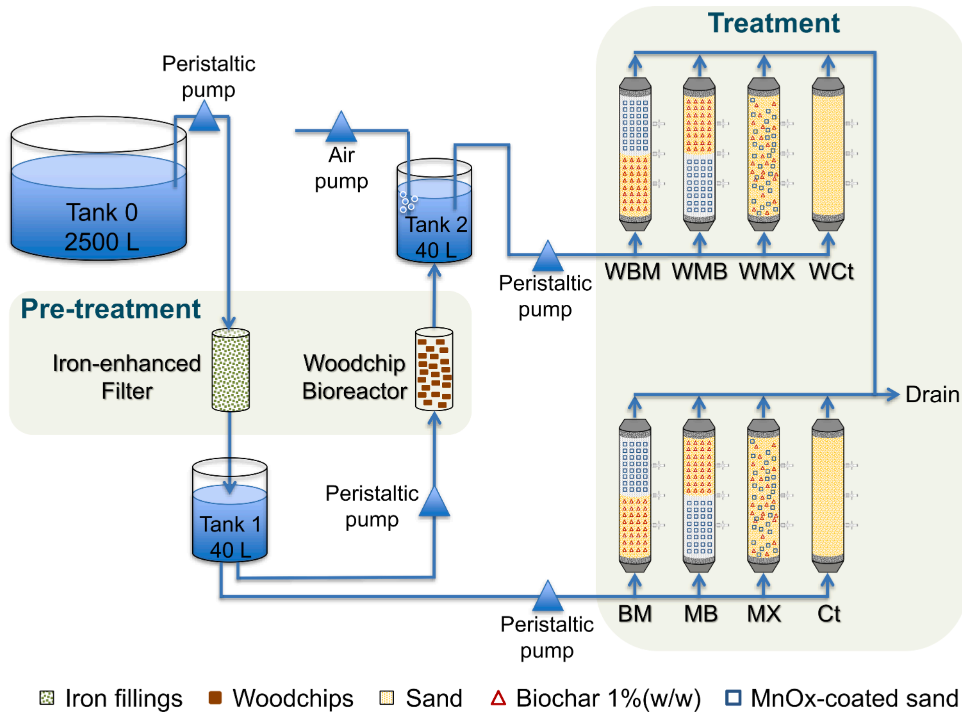

Fig. 1. Schematic representation of the pilot-scale stormwater treatment system. Two different influents were assessed: without and with ("W") pretreatment of woodchip bioreactor. Testing configurations include: biochar before Mn-Oxide ("BM"), Mn-Oxide before biochar ("MB"), mixed media of biochar/Mn-Oxide ("MX"), and control ("Ct"). A conditioning phase with authentic stormwater used this setup, but subsequent challenge testing was conducted without pretreatment and synthetic stormwater.

used to determine the hydraulic retention times at the end of the preconditioning stage (Table S3). Initial pore volumes were measured before challenge testing began and these values were used for reporting throughout the experiment. The saturated hydraulic conductivities (K_{sat}) of the columns were measured throughout the experiment (Eq. (S1), Fig. S5, Table S4) using the Constant Head Standard Method (ASTM, 2006). The Mn coating density of the manganese oxide-coated sand was quantified by dissolving the coating of a 0.5 g sample with 10 mL of 30 mM ascorbic acid and quantifying dissolved (i.e., passing through a 0.45 μm nylon filter) Mn by inductively coupled plasma-mass spectroscopy. The average Mn oxidation state was determined by iodometric titration (Murray et al., 1984).

Finally, a wireless sensor internet-of-things network enabled continuous system monitoring and remote control of the pilot-scale system (details in Supplementary Material, Fig. S6).

2.3. Field conditioning and challenge testing

Stormwater runoff was introduced into the treatment system during an eight month continuous conditioning period to develop a weathered geomedia (simulating one rainy and one dry season of use). The iron-enhanced sand filter and woodchip biofilter were operated at average volumetric flowrates of 90 and 18 mL min^{-1} (corresponding to a Darcy velocity of 68 and 14 cm h^{-1}), respectively. Geomedia columns were conditioned at a 0.85 mL min^{-1} volumetric flowrate (equivalent to a Darcy velocity of 2.5 cm h^{-1}). During the conditioning period, the top of the iron-enhanced sand filter was regularly scraped to avoid its hydraulic failure due to formation of a biologically active cake layer (i.e., schmutzdecke) (Huisman and Wood, 1974).

Following column conditioning, a four month challenge test was performed to assess the removal of trace organic compounds and metals. The challenge test was conducted using synthetic stormwater (see Table S5 for composition). The synthetic stormwater provided a consistent matrix throughout the test and represented typical stormwater conditions (Pitt et al., 2015). During the challenge test, to simulate the authentic stormwater used during the conditioning period, the synthetic stormwater used in geomedia-enhanced columns that had not received denitrifying woodchip bioreactor pretreatment (BM, MB, MX, and Ct) were enriched with nitrate, resulting in 2.6 ± 0.4 mg L^{-1} NO_3^-–N, whereas the synthetic stormwater used with columns that were conditioned with the woodchip bioreactor effluent ("W" columns) was prepared without supplemental nitrogen (Fig. S7).

To initiate the challenge test, the columns were acclimatized for 14 days (i.e., approximately 18 to 30 pore volumes) with synthetic stormwater. Then, 50 μg L^{-1} of each the following six persistent, mobile, and toxic trace organic contaminants were added to the synthetic stormwater: 2,4-dichlorophenoxy acetic acid (2,4-D), 1H-benzotriazole (1H-BT), tris(2-chloroethyl) phosphate (TCEP), atrazine (ATZ), diuron (DIU), fipronil (FIP). Additionally, 50 μg L^{-1} each of nickel, copper, zinc, cadmium, and lead were spiked as their chloride salts. The high concentrations of spiked contaminants (relative to concentrations typical of stormwater) were intended to induce breakthrough within the timeframe of the experiment. The actual concentrations of influent trace organic compounds and metals were measured immediately upstream of column inlets to control for any deviation from the nominal concentration due to losses in the storage tank. The true influent values were used to calculate removal efficiency for the contaminants (i.e., C/C_0). The chemical structure, physicochemical properties (e.g., partition coefficients), reported range and mean concentrations of contaminants in urban runoff, and typical urban runoff sources for the contaminants are listed in the Supplementary Materials (Table S6). The stormwater contaminants represented a broad range of physicochemical properties (e.g., octanol-water distribution coefficient, D_{OW}, values spanning four orders of magnitude) and reactivity towards the studied geomedia (Charbonnet et al., 2020; Grebel et al., 2016; Ulrich et al., 2015). The stock solutions of trace organic contaminants were prepared in methanol. The concentration of methanol in the synthetic stormwater (i.e., < 0.05%, around 100 mg C L^{-1}) is similar to amounts used in other studies, which mainly focused on abiotic removal processes of persistent chemicals (Ashoori et al., 2019; Cornelissen et al., 2005; Ulrich et al., 2017b). Although the additional methanol resulted in dissolved organic carbon (DOC) concentrations that were elevated relative to typical urban stormwater conditions (Pitt et al., 2015), there was no evidence of column hydraulic failure. Additionally, metal stock additions did not influence the pH of the synthetic stormwater stored in tanks during the challenge test (Tank 1 and 2; 7.7 ± 0.4 and 7.7 ± 0.1, respectively) and sulfidogenic conditions were avoided by constant aeration in both tanks (Fig. S7). Geochemical modeling with Visual MINTEQ indicated that no metals were present at concentrations above their solubility limits (further details in the Supplementary Materials). Every two months, all PTFE tubing connections were cleared scouring with a small plunger, washed with 1% HCl solution, and thoroughly rinsed with Milli-Q water to avoid biofilm accumulation and clogging. Feed solutions were homogenized by gentle aeration and were replaced weekly to minimize microbial activity.

2.4. Analytical methods, statistical analysis, and metal speciation analysis

Full details on analytical methods used for measuring water quality parameters, quantification of trace metals (by ICP-MS) and trace organics (by LC-MS/MS), together with QA/QC data are included in the Supplementary Materials (Fig. S8, Tables S7–S10).

3. Results and discussion

3.1. Field conditioning period

3.1.1. Pretreatment columns: iron-enhanced sand filter and woodchip bioreactor plus aeration

Both the iron-enhanced sand filter and woodchip bioreactor operated during the entire 8-month conditioning period without failure due to clogging. Although phosphate broke through the iron-enhanced sand filter, the woodchip bioreactor removed nitrate throughout the conditioning period (Fig. S9). The iron-enhanced sand filter removed 3.86 mg PO_4^{3-}–P per g iron filings, only about 16% of influent phosphate (Supplementary Materials, Eqs. (S2) and (S3)). The effluent remained oxic and the filter did not affect other water quality parameters (Figs. S10 to S12). The woodchip bioreactor consistently removed nitrate ($C/C_0 < 0.06$) throughout the eight months of conditioning (Figs. S9 to S11). On average, 98% of NO_3^- was removed, and effluent concentrations remained below 0.03 mg L^{-1} NO_3^-–N. Normalized for reactor volume, the removal rate was 9 ± 3.3 g-N m^{-3} d^{-1}, which was consistent with the performance of similar systems (Coleman et al., 2019; Schipper et al., 2010). Under the conditions tested, consistent nitrate removal from stormwater could achieve a decadal service lifetime (details in the Supplementary Materials section, Fig. S13). Denitrifying conditions were accompanied by the absence of dissolved O_2 in the woodchip bioreactor effluent (Figs. S10 and S11).

DOC concentrations in the effluent from the woodchip bioreactor ranged from 3 to 17 mg C L^{-1}, an increase from an average value of 4.4 $\pm$ 1.2 mg C L^{-1} in the influent (i.e., “Tank 1”). Approximately 18 g C d^{-1} was released per m^3 of woodchip bioreactor volume. The woodchip bioreactor also induced partial sulfate reduction (Figs. S10 and S11).

Based on our field observations, we hypothesize that the iron-enhanced filter failed hydraulically due to the continuous flow conditions; however, the 3.86 mg PO_4^{3-}–P removed per g iron filings falls within the reported ranges for similar systems at the end of their useful life (Erickson et al., 2017, 2012). We believe this failure was related to concurrent factors including: (i) physical clogging at the effluent spout (not removed by top filter maintenance); (ii) stratification of the thin (i.e., 5 cm) pea-gravel layer at the bottom of the unit; (iii) development of a rust-colored thin crust (probably iron ochre) on the columns at the end of the experiment (Fig. S14); and (iv) operating the system under continuous flow conditions at higher rates than tested in previous studies (Erickson et al., 2012). Similar issues have been observed in an iron-enhanced stormwater filtration system (Erickson et al., 2017).

3.1.2. Geomedia-amended biofilters

Geomedia-containing columns removed >90% of influent DOC from the stormwater runoff during the first 2–3 months of conditioning (i.e., up to 200 pore volumes), after which time breakthrough occurred (Fig. S15). In contrast, the sand control columns had higher effluent DOC concentrations during the first 2–3 months of the conditioning period ($p < 0.05$, Tables S11 and S12). These results suggest that DOC removal was mainly due to sorption on biochar or Mn-oxide, and breakthrough occurred after the geomedia surface became saturated. Microbial respiration likely accounted for a fraction of DOC removal during this period (largely originating from the woodchips or background stormwater organic carbon) and became a more important removal mechanism as the column aged, as evidenced by a decrease in effluent dissolved O_2 after the initial conditioning period (Fig. S16).

Influent dissolved O_2 concentrations to the geomedia-amended and the control sand columns were near saturation, though Tank 2 had significantly higher dissolved O_2 ($p < 0.05$) concentrations: the average values in Tanks 1 and 2 were 7.8 ± 1.3 and 9.0 ± 1.0 mg L^{-1}, respectively. Effluent O_2 concentrations were low for all geomedia-containing columns (typically < 4.5 mg L^{-1} throughout conditioning). Effluent O_2 concentrations were higher (i.e., 4–6 mg L^{-1}) for the sand controls (Fig. S16). The extent of microbial respiration increased during the first two months of conditioning, after which effluent O_2 concentration remained steady. A simplified mass balance for DOC removal and O_2 consumption indicated that, in the later stages of the challenge test, aerobic respiration by microbial communities greatly exceeded DOC removal by sorption (Fig. S17).

In all of the geomedia treatments, including the sand controls, the pH of the stormwater decreased by about 0.5 pH units (Fig. S18). The drop in pH in the geomedia columns was consistent with microbial respiration releasing CO_2. Geomedia-amended column effluents exhibited lower average pH values than their control counterparts (Fig. S18), though the differences were only statistically significant for layered geomedia columns with woodchip pretreatment (Tables S11 and S12).

Due to efficient pre-treatment by the woodchip bioreactor, geomedia columns that were fed by the woodchip bioreactor received influent nitrate at concentrations below the detection limit (i.e., <0.01 mg NO_3^-–N L^{-1}, Fig. S19), while the influent to the other columns contained an average of 1.4 ± 1.0 mg NO_3^-–N L^{-1}. Typically, about 30% of the nitrate was removed from those columns during conditioning period, suggesting that nitrate-reducing conditions were present. The incomplete nitrate removal in both control and geomedia-containing columns suggests that anaerobic conditions were limited to certain regions. No column configuration consistently removed phosphate or sulfate during the conditioning stage (Figs. S19 and S20).

3.2. Field challenge test

After eight months of field conditioning, the geomedia-amended columns exhibited sustained high removal of polar trace organic compounds over 200 pore volumes during the challenge testing (Figs. 2a, b and S21, and Table S13). Geomedia-containing columns attenuated contaminants significantly better than the sand control columns ($p < 0.05$; Tables S14 and S15). The removal of polar trace organic compounds (C/C_0 lower than 0.25) emphasizes the value of biochar for sorption, because results from previous studies indicate that widely-used woodchip and straw bioreactors alone cannot remove many of these compounds (Ashoori et al., 2019).

Concentrations of trace organic contaminants measured in samples collected from the column side-ports demonstrated that biochar removed trace organic contaminants more effectively than manganese oxide-coated sand (Figs. 2c-f and S22, Tables S16–17). Contaminant concentrations dropped most rapidly in the zones where biochar was abundant (i.e., in the front and back half of the BM- and MB-columns, respectively).

Depth concentration profiles also enabled predictions of contaminant breakthrough time. After 200 pore volumes, samples from the first side-port, (i.e., at 25 cm into the column), indicate that the sequence of contaminant breakthrough would be 2,4-D followed by atrazine, TCEP, fipronil, 1H-benzotriazole, and diuron (Fig. S23) regardless of woodchip

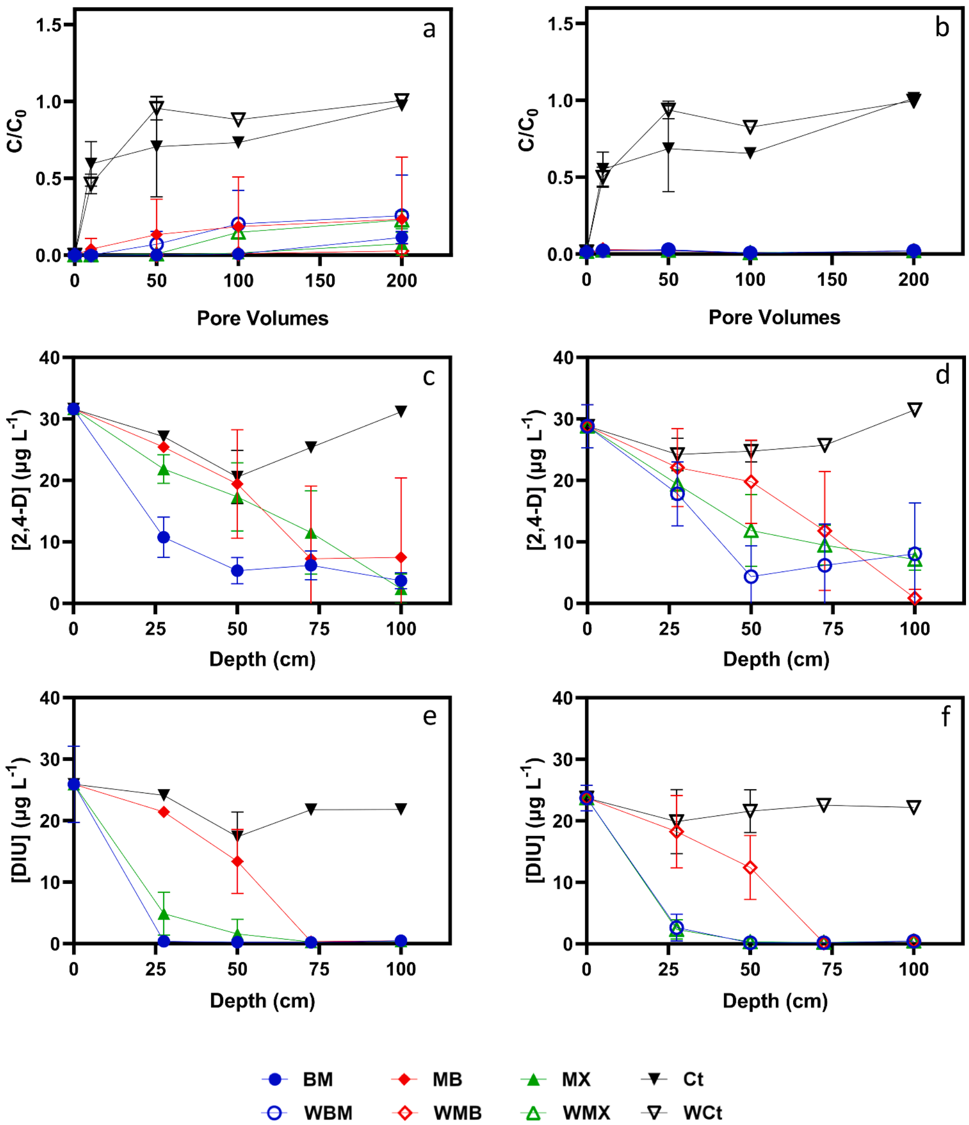

Fig. 2. (a, b) Breakthrough curves for 2,4-D (a) and diuron (b) spiked at 20–30 μg L^{-1} initial concentration in synthetic stormwater. (c-f) Depth profile for the concentration of 2,4-D and diuron following 200 pore volumes of synthetic stormwater. Testing configurations, without (closed symbols) and with ("W", open symbols) woodchip pretreatment, include: biochar before Mn-Oxide ("BM"), Mn-Oxide before biochar ("MB"), mixed media of biochar/Mn-Oxide ("MX"), and control ("Ct"). Error bars indicate ± standard deviation of the three replicate columns.

bioreactor pre-treatment. Diuron and 1H-benzotriazole are found in urban runoff (Arp et al., 2017; Neumann and Schliebner, 2019; Spahr et al., 2019), hydrophilic and mobile (i.e., log $K_{OC} < 4$ or log $D_{OW} < 4$), and persistent (i.e., half-lives > 40 days in groundwater) (Liu et al., 2011; Moncada, 2004) (Table S6). These two compounds are also known to persist during soil-aquifer treatments (Hermes et al., 2019). Therefore, the high removals achieved in this research demonstrate the value of engineered geomedia amendments in infiltration systems.

Measurements from the first side-port also highlighted the negative impact of the woodchip bioreactor leachate on biochar removal

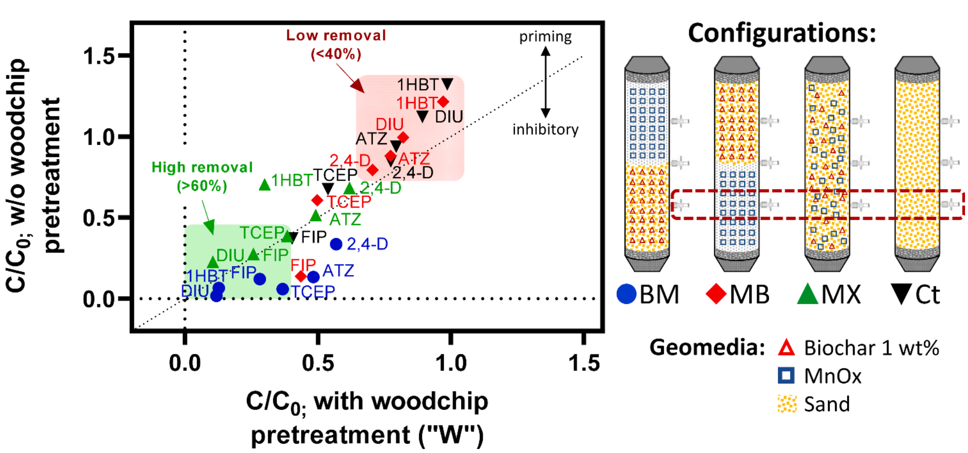

Fig. 3. Comparative plot of the removal (C/C_0) of trace organic contaminants at the first side-port (one quarter of the column depth, indicated by the red dashed line) after 200 pore volumes. X- and Y-axes measure removal with and without woodchip pretreatment. Sand (Ct and WCt) and MnOx (MB and WMB) showed low (< 40%) removals for most compounds. The mixed geomedia (MX and WMX) showed moderate removals, while the biochar (BM and WBM) showed high (> 60%) removals for most compounds. Compounds above and beneath the 1:1 dashed line were better (prime effect, upper triangular box) and less-well removed (inhibitory effect, lower triangular box) in columns with woodchip pretreatment, respectively.

performance (Fig. 3). Organic matter (measured as DOC) or microbial biofilm (not measured in this study, but inferred through changes in concentrations of terminal electron acceptors) accumulation on the biochar surface can compete for adsorption sites with the trace organics. Though precise mechanisms were outside the scope of this research, results of previous research demonstrate that organic matter can decrease site accessibility by blocking pore entrances, as observed during experiments with other carbonaceous materials (i.e., fouling effect) (Aschermann et al., 2018; Kwon and Pignatello, 2005; Teixidó et al., 2013). During the conditioning phase, WBM columns received nearly 40% more DOC than their BM counterparts, which inhibited trace organic removal. Results show from 15 to 60% lower removal depending on the trace organic contaminant during the challenge test (Fig. S23). The effect of woodchip bioreactor leachate was not that important in the other studied systems (i.e., WMB, WMx and WCt).

Abiotic removal of trace organic compounds (i.e., sorption onto biochar) occurs via pore-filling and sorption mechanisms that include coulombic forces, hydrogen-bonding, and π-orbital interactions (Ray et al., 2019; Spahr et al., 2019). Compound hydrophobicity, as measured by the octanol-water distribution coefficient (log D_{OW}, Table S6), or the organic carbon-water distribution coefficient (log K_{OC}, Table S6) –which is an important parameter to describe sorption-retarded mobility (Neumann and Schliebner, 2019)– is not the sole property governing removal of the polar compounds in the challenge test (Fig. S23). For instance, the retention of the most mobile compound, 2,4-D (log D_{OW}, −0.99; log K_{OC}, 2.13), confirmed that forces other than hydrophobic interactions played a role in abiotic compound removal. However, electrostatic repulsion between the ionized carboxylate group on 2,4-D (pk_a = 2.73) and the negatively charged surface of biochar and manganese oxides may have facilitated its partial breakthrough (Kah et al., 2017; Remucal and Ginder-Vogel, 2014).

Biotransformation also may have contributed to contaminant removal. Methanol from the trace organic carrier solution also may have influenced the development of microbial communities due to its role as a substrate (Ulrich et al., 2017b). Moreover, parts-per-million levels of labile organic carbon are not ideal for persistent trace organic biodegradation (Alidina et al., 2014; Onesios and Bouwer, 2012). Under this scenario, O_2 depletion demonstrated that aged columns were biologically active (Fig. S16), and biotransformation has been reported for several of the compounds studied here (Ulrich et al., 2017a; Wolfand et al., 2016). Although microbial activity (e.g., transformation pathways) was outside the scope of this research, fipronil biotransformation to fipronil sulfide has been documented under anaerobic conditions (Jones et al., 2007), or 2,4-D can undergo reductive dehalogenation (Robles-González et al., 2006).

Samples of column effluents indicated that geomedia enhanced the

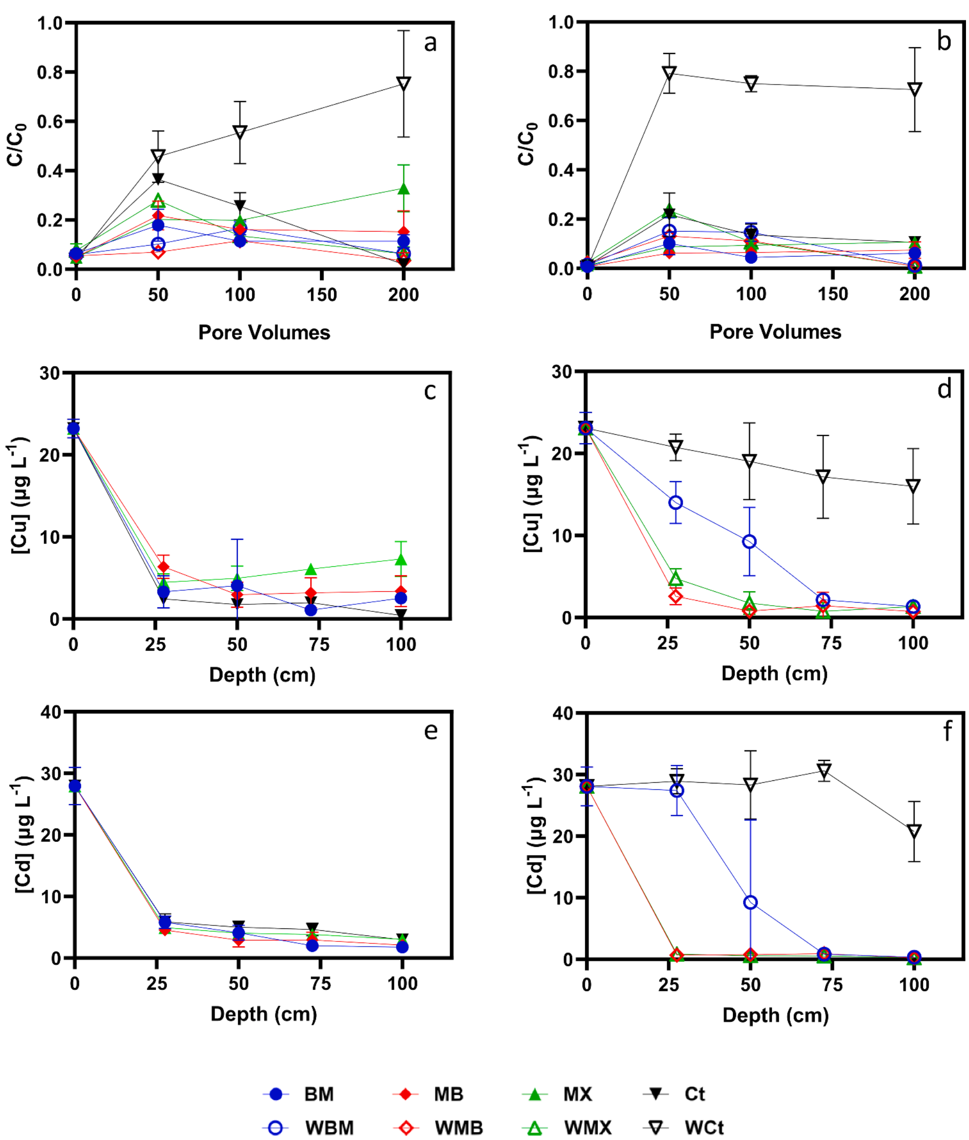

Fig. 4. (a, b) Breakthrough curves for Cu (a) and Cd (b) spiked at 20–30 µg L^{-1} initial concentration in synthetic stormwater. (c-f) Depth profile concentrations of Cu and Cd following 200 pore volumes of synthetic stormwater. Column configurations, without (closed symbols) and with ("W"; open symbols) woodchip pretreatment, include: biochar before Mn-Oxide ("BM"), Mn-Oxide before biochar ("MB"), mixed media of biochar/Mn-Oxide ("MX"), and control ("Ct"). Error bars indicate ± standard deviation of the three replicate columns.

removal of dissolved trace metals (Figs. 4a, b and S24, and Table S18). When columns were pre-treated by the woodchip bioreactor ("W" columns), the effect of the geomedia addition on trace metal removal was significant for all metals except Zn ($p < 0.05$, Tables S19 and S20).

The average metal removal in geomedia-amended columns followed the order: Pb > Cd >> Cu ~ Ni > Zn (Table S18). Results from previous laboratory-scale studies indicated that Cd(II) and Pb(II), which are poorly solvated due to larger ionic radii, were removed well by geomedia, while Zn was retained less extensively (Charbonnet et al., 2020; Liu et al., 2005). In the presence of multiple metals, Zn(II) was the most poorly retained trace element in biochar-amended woodchip bioreactors (Ashoori et al., 2019). Notably, when present as co-contaminants, Cd and Cu may outcompete Zn in biochar-amended columns (Park et al., 2015).

Samples from column side-ports after 200 pore volumes suggested that adsorption and/or (co)precipitation processes removed metal ions (Figs. 4c–f and S25). In the absence of sulfate reducing conditions (i.e., woodchip pre-treated "W" columns, Fig. S20), adsorption to weathered manganese oxides was likely the main mechanism responsible for metal removal (Charbonnet et al., 2020); aged biochar did not improve metal removal compared to the sand control for Ni, Zn and Cd, and low reactivity was observed for Cu (C/C_0, 0.7).

Metal removal generally increased during the final stages of the challenge tests for the columns that did not receive woodchip pre-treatment during the conditioning phase (BM, MB, MX, and Ct, which received lower DOC) (Figs. 4 and S24). Assuming that all the sulfate was reduced to H_2S and HS^- (as would be expected based on the removal of oxygen and nitrate and the disappearance of sulfate; Fig. S20), the stormwater may have been supersaturated with respect to metal sulfides for each of the trace metal species (see Supplementary Material 'Challenge test: trace metals' for further details). Under sulfate-reducing conditions, we presume sulfide mineral precipitation explains the decreases in dissolved Ni, Cu, Zn, and Pb observed at 200 pore volumes for all of the treatments (Ashoori et al., 2019; Jong and Parry, 2003). However, sulfidic conditions did not influence trace organic removal to the same extent as trace metals (Figs. 2 and 3). Nevertheless, the metal sulfide precipitates could re-dissolve after a shift in redox conditions (Schipper et al., 2010). As previously noted, sulfate-reducing conditions should be avoided as sulfide ion is potentially toxic and corrosive. In addition, such conditions could dissolve manganese and iron oxides (Fig. S26), contributing to turbidity or clogging (Kouzbour et al., 2020). Nonetheless, we did not observe clogging in our columns.

Chemical analysis of the geomedia after the challenge test indicated that the manganese oxide-coated sand lost much of its coating density and reactivity over the course of the experiment (Fig. 5). A regeneration experiment applying 0.04 M MnO_4^- on the exhausted manganese oxides showed that a decrease of the geomedia Mn-oxide coating density is permanent. However, the Mn oxidation state was almost completely restored to that of the virgin manganese oxide-coated sand. A preceding layer of biochar (i.e., arrangement "BM"), protected the manganese oxides from exposure to oxidizable organic carbon (e.g., in NOM) that reduced the Mn (IV) layer.

The use of equivalently-sized sand and biochar (0.6–0.85 mm) resulted in efficient trace organic contaminant removal without appreciable clogging during the experiment, overcoming the tradeoff between reactivity and particle size (Corwin and Summers, 2010; Kang et al., 2018). Although the saturated hydraulic conductivity (K_{sat}) in geomedia-amended columns was lower than that of the sand controls (Fig. S27), this reduction of K_{sat} was less than values observed by researchers who used smaller biochar particles (Ray et al., 2019; Trifunovic et al., 2018).

3.3. Environmental implications

It is essential to consider issues related to lifespan and maintenance if the pilot-scale system is to be employed in practice. To assess the potential for field-scale deployment of geomedia-enhanced stormwater treatment trains, we estimated treatment capacity using the data from our study; as detailed in the Supplementary Materials. Although the iron-enhanced filter clogged due to the continuous-flow conditions, this treatment unit is a well-established approach for removing P (Erickson et al., 2017, 2012), and could likely be adapted for the treatment train. Assuming that the clogging could be addressed (e.g., by operating under intermittent conditions and storing treated water in a pond), we used reported values of maximum adsorption capacity (Erickson et al., 2017) to estimate a 10-year service life before media exhaustion with routine anticlogging maintenance. An appropriately sized woodchip bioreactor would last for nearly two decades (see Supplementary Materials). The use of remote hydraulic retention time controls (Halaburka et al., 2019), or a small cascade aeration step between the denitrification unit and the geomedia-amended filters could be used to prevent sulfate reduction. However, if an aeration step is not present in a full-scale system, this could result in different bulk DOC, trace organic, and metal removal in the subsequent geomedia-amended biofilters (Regnery et al., 2015). We used data for the most mobile trace organic compound (2,4-D) collected from a side port after 200 pore volumes of challenge testing to estimate of geomedia exhaustion times (i.e., the time when C/C_0 equals 0.5). A stormwater treatment train system employing geomedia in configuration "BM" (the least effective configuration) is projected to treat 2,4-D (the most mobile trace organic compound) without breakthrough for 30 or 12 years, without or with woodchip pre-treatment, respectively (Table S21 and Fig. S28). However, these estimates should be

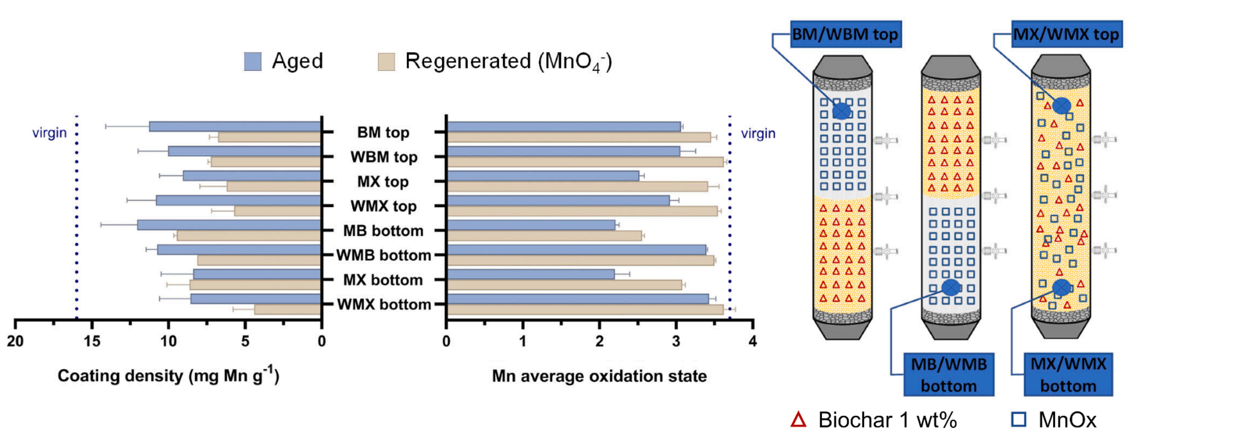

Fig. 5. Left: Evolution of Mn coating density and oxidation state for all geomedia-enhanced columns throughout the experiment (i.e., virgin, aged, and regenerated). Aged samples were collected at 10-cm layer depth (from top or bottom) at the end of challenge test and regenerated with 0.04 M MnO_4^- in the laboratory. Error bars indicate ± standard deviation of three replicate experiments. Right: postmortem sampling points.

interpreted with caution because they do not account for physical/biological clogging.

4. Conclusions

Trace metals, trace organic contaminants, and nutrients are not removed effectively in conventional stormwater infiltration systems. This research is, to our knowledge, the first long-term field validation of a stormwater unit-process treatment train that consistently removes toxic trace metals and persistent, mobile, and toxic organic contaminants. The main conclusions are:

(1) To meet the operational demand of a typical urban runoff/stormwater system, an iron-enhanced sand prefilter would benefit from inlet and outlet monthly maintenance (Erickson et al., 2017, 2013). Woodchip bioreactors can achieve consistent stormwater denitrification (> 98%, 9 g-N $m^{-3}d^{-1}$), and represent a viable long-term and cost-effective option for pre-treatment (nearly 20 years of service life). However, they leach labile organic carbon that can affect the performance of downstream processes. In addition, woodchip effluent would require a low-energy re-aeration step prior to infiltration to improve the DOC and trace organic removal, minimize reductive dissolution of redox-sensitive geomedia, and to avoid sulfate-reducing conditions that can yield hydrogen sulfide (along with a trace metal precipitation), methane, or methyl mercury (Easton et al., 2015; Hermes et al., 2019).

(2) The hydraulic performance of the system was stable, and target contaminants were removed well by geomedia that had been aged for 8 months in authentic urban stormwater runoff, suggesting greater effectiveness for passive stormwater treatment than conventional sand or gravel. The best removed metal was for Pb, followed by Cd, Cu, Ni and Zn. Metals were mainly removed via adsorption onto manganese oxides, while metal-sulfide precipitation likely contributed to metal removal under sulfate-reducing conditions. Counterintuitively, sulfate-reducing conditions were only observed in columns aged without a woodchip bioreactor pre-treatment (BM, MB, MX, and Ct), which had lower DOC loadings during the conditioning stage. Biochar amended columns removed polar trace organic contaminants with a retention order of 2,4-D < atrazine < TCEP < fipronil < 1H-benzotriazole < diuron. Under ideal hydraulic conditions, assuming no clogging, estimated breakthrough times for anionic 2,4-D were over 10 years.

(3) The commercial greensand tested in this study did not remove trace organic contaminants. However, the material tested was primarily designed for contaminant removal and operation under unsaturated applications (e.g., treatment of well water high in dissolved metals). Different Mn-containing geomedia may be preferable if reactivity towards polar trace organics is a design priority (Charbonnet et al., 2020).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119246.

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