



# Oxidation of organic contaminants by manganese oxide geomedia for passive urban stormwater treatment systems



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## ABSTRACT

To advance cost-effective strategies for removing trace organic contaminants from urban runoff, the feasibility of using manganese oxides as a geomedia amendment in engineered stormwater infiltration systems to oxidize organic contaminants was evaluated. Ten representative organic chemicals that have previously been detected in urban stormwater were evaluated for reactivity in batch experiments with birnessite. With respect to reactivity, contaminants could be classified as: highly reactive (e.g., bisphenol A), moderately reactive (e.g., diuron) and unreactive (e.g., tris(2-chloro-1-propyl)phosphate). Bisphenol A and diuron reacted with birnessite to produce a suite of products, including ring-cleavage products for bisphenol A and partially dechlorinated products for diuron. Columns packed with manganese oxide-coated sand were used evaluate design parameters for an engineered infiltration system, including necessary contact times for effective treatment, as well as the impacts of stormwater matrix variables, such as solution pH, concentration of natural organic matter and major anions and cations. The manganese oxide geomedia exhibited decreased reactivity when organic contaminants were oxidized, especially in the presence of divalent cations, bicarbonate, and natural organic matter. Under typical conditions, the manganese oxides are expected to retain their reactivity for 25 years.

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## 1. Introduction

Urban stormwater contains chemical contaminants that pose potential risks to drinking water supplies and aquatic ecosystems (USEPA, 1994; Marsalek et al., 1999; Burton et al., 2000). Organic contaminants of concern include compounds derived from paving materials (e.g., polycyclic aromatic hydrocarbons), automobile tires (e.g., benzothiazoles, alkylphenols), consumer products (e.g., organophosphate flame retardants, bisphenol A), and urban-use biocides (e.g., diuron, fipronil, triazines) (Makepeace et al., 1995; Stachel et al., 2010; Gan et al., 2012; Grebel et al., 2013). In many circumstances, protection of aquatic ecosystems requires removal of these compounds. Furthermore, the growing popularity of projects that use urban runoff to recharge drinking water aquifers may

necessitate additional treatment. For example, the Los Angeles Department of Water and Power is investing in centralized stormwater capture and infiltration sites in anticipation of increasing the share of incoming flow to the city originating from precipitation and run-off from 11% currently up to 33% by 2099 (LADWP, 2010).

Traditionally, the focus of stormwater management has been reduction of high peak flows during storm events. Popular stormwater management practices, such as bioinfiltration or bioretention cells, have been assessed with respect to their ability to remove certain regulated contaminants (e.g., nutrients and metals; Grebel et al., 2013); however, to date, the removal of trace organic contaminants has not been a major focus of system design. Bioinfiltration systems and other distributed treatment systems reduce stormwater peak flows by infiltrating runoff through permeable soil or sand prior to its release into surface waters via subsurface drains or its discharge to groundwater (Grebel et al., 2013). Centralized stormwater capture systems may also pass water through sand after a pretreatment step to remove coarse particles. Irrespective of scale or subsequent use of the water, stormwater infiltration systems should ideally be passive, require

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little maintenance and be relatively inexpensive. The addition of reactive geomedia to infiltration systems offers a potential means of improving performance of these systems with regard to removal of organic contaminants.

Manganese oxides, ubiquitous in soils, are capable of oxidizing a variety of aromatic Lewis bases, including phenols, aromatic amines and aromatic thiols (Stone and Morgan, 1984; Remucal and Ginder-Vogel, 2014). The oxidation of organic contaminants in these systems is typically attributed to sequential one electron-transfer reactions that result in reductive dissolution of the oxide and oxidation of the contaminant.

While certain types of manganese oxides have been used to remove cationic metals from drinking water and stormwater (Liu et al., 2005), their potential for removing organic contaminants from stormwater is unclear. Most previous research on the oxidation of organic chemicals by manganese oxide surfaces (Remucal and Ginder-Vogel, 2014 and references therein) has focused on naturally occurring minerals in soils and aquifer sediments. Often this research has employed batch experiments, though a few studies have employed column systems to investigate manganese oxides as a reactive media for the removal of organic contaminants from wastewater or drinking water, often in deionized water or buffered solutions (de Rudder et al., 2004; Huguet et al., 2014). As a result, it is uncertain if the introduction of a reactive manganese oxide media to an infiltration system can transform organic contaminants under the conditions encountered in urban stormwater or if the manganese oxides retain their activity in infiltration systems. Furthermore, among the organic chemicals frequently detected in urban stormwater, few have been evaluated with respect to their reactivity with manganese oxides under relevant conditions.

The objective of this research was to determine the feasibility of using manganese oxide geomedia amendments to transform organic contaminants in engineered infiltration systems for stormwater. To address this issue, the reactions of representative stormwater contaminants with several types of manganese oxides were studied under conditions relevant to stormwater infiltration. Column studies were used to evaluate design parameters, such as contact time, solution pH, and the concentrations of organic matter, divalent cations and carbonate species. In addition, long-term column studies were employed to assess the stability of manganese oxides and the likely mechanisms of failure.

## 2. Materials and methods

### 2.1. Reagents and manganese oxide preparation

All organic chemicals were used as received from Sigma Aldrich without further purification. Suwannee River natural organic matter (reverse osmosis isolate) was obtained from the International Humic Substances Society (St. Paul, MN). All experiments, unless otherwise noted, were conducted in a simulated stormwater matrix containing major anions and cations at concentrations representative of urban stormwater (Table 1).

Most experiments employed sodium bicarbonate as a buffer at pH 7.0. The pH of the simulated stormwater was adjusted with either 1 M HCl or 1 M NaOH. During pH adjustment, the simulated stormwater was mixed with a magnetic stir bar while acid or base was added dropwise to allow carbonic acid to equilibrate prior to initiation of the experiments.

To determine the role of ions present in stormwater, some experiments were performed in carbonate-free, pH 7.0, 4.6 mM buffered 3-(N-morpholino)-propanesulfonic acid (MOPS) or in pH 8.5, 4.6 mM carbonate-free borate buffer. The buffers were prepared from freshly generated Milli-Q water, while continuously

**Table 1**  
Simulated stormwater constituents.

Constituent	Concentration	Unit
Ca <sup>2+</sup>	0.75	mM
Mg <sup>2+</sup>	0.075	mM
Na <sup>+</sup>	1.75	mM
NH <sub>4</sub> <sup>+</sup>	0.072	mM
SO <sub>4</sub> <sup>2-</sup>	0.33	mM
HCO <sub>3</sub> <sup>-</sup>	1	mM
Cl <sup>-</sup>	1.7	mM
NO <sub>3</sub> <sup>-</sup>	0.072	mM
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	0.016	mM
Dissolved Organic Carbon (DOC) <sup>a</sup>	10	mg-C/L
Ionic Strength	4.6	mM
pH	7.0	

<sup>a</sup> Suwannee River RO Isolate. Only present in simulated stormwater recipe when specifically noted.

degassing with N<sub>2</sub> gas to remove any dissolved CO<sub>2</sub>. For the boric acid buffer, the pH was adjusted to a value of 8.5 with NaOH. Although this buffer was sometimes exposed to the atmosphere for up to two days prior to its passage through the columns, periodic monitoring of inorganic carbon indicated that the increase in dissolved inorganic carbon concentration was always less than 0.05 mM.

Authentic stormwater was collected from an urban runoff channel the morning following an overnight rain in Berkeley, CA in March 2013. The stormwater was filtered through a 0.7- $\mu$ m glass fiber filter and stored at 4 °C until use. The stormwater had a pH of 7.3, 120 mg L<sup>-1</sup> total hardness (as CaCO<sub>3</sub>), 253  $\mu$ S specific conductance, and an alkalinity of 1.1 mM. It contained 14.4 mg-C L<sup>-1</sup> of dissolved organic carbon and 20 mg-C L<sup>-1</sup> of dissolved inorganic carbon. A 2-L subsample of the authentic stormwater was exposed overnight to approximately 10 g of acid-washed granular activated carbon (GAC) (12–20 mesh, Sigma Aldrich) to lower the concentration of dissolved organic carbon. Following this GAC treatment, the stormwater had a pH of 6.2, <0.1 mg-C L<sup>-1</sup> organic carbon, 103 mg L<sup>-1</sup> total hardness (as CaCO<sub>3</sub>) and 253  $\mu$ S specific conductance. A nitrified wastewater effluent sample also was collected and filtered through a 0.7- $\mu$ m glass fiber filter and stored at 4 °C until use. The wastewater effluent sample had a pH of 8.0 and a dissolved organic carbon concentration of 5.8 mg-C L<sup>-1</sup>.

Powdered triclinic birnessite was synthesized according to the method of McKenzie (1981), which was based on the reduction of KMnO<sub>4</sub> with hydrochloric acid. Manganese solids were thoroughly rinsed with Milli-Q water and dried overnight at 100 °C. BET analysis indicated the surface area of the fine birnessite powder generated was 63.9 m<sup>2</sup> g<sup>-1</sup>. The average Mn oxidation state (as determined by the method of Murray, 1984) of the birnessite was 3.4. Birnessite-coated sand was synthesized in batch, under similar conditions to powdered birnessite, with the inclusion of 150 g of acid-washed Ottawa sand to the KMnO<sub>4</sub> solution. The average Mn oxidation state of the birnessite-coated sand was 3.75.

### 2.2. Batch experiments

Preliminary testing indicated that the presence or absence of oxygen during batch testing did not affect reaction rates. Therefore, all subsequent batch reactions were performed in sealed amber borosilicate vials with solutions that had been equilibrated with the atmosphere. Manganese oxide was added in molar excess relative to the organic compound to minimize changes in the oxide surface due to reductive dissolution. Batch experiments with mineral manganese oxides were performed in simulated stormwater (pH 7.0) in the presence of 150 nM organic compound and 6.0 g L<sup>-1</sup> of

birnessite. Batch experiments with manganese oxide-coated sand were performed in simulated stormwater (pH 7.0) in the presence of 5  $\mu\text{M}$  of an organic compound and 50.0  $\text{g L}^{-1}$  of birnessite-coated sand. To stop the reaction, samples were passed through a 0.7- $\mu\text{m}$  glass fiber filter to remove the majority of solids, followed by addition of ascorbic acid (–0.33  $\text{mM}$ ) to quench any remaining manganese oxide colloids prior to analysis.

### 2.3. Birnessite-coated sand columns

Column experiments were conducted in 2.5-cm inner diameter glass columns, with column lengths between 4.5 and 50 cm. Columns were operated in the up-flow mode using a peristaltic pump and 3.175 mm inner diameter PTFE tubing to deliver solutions. Columns were wet-packed with 35–450 g of birnessite-coated sand in Milli-Q water. Following packing, columns were mechanically vibrated to ensure consistent packing density. For most experiments, the volumetric flow rate was 0.44  $\text{mL min}^{-1}$ , equivalent to an infiltration rate of 5  $\text{cm h}^{-1}$ . Hydraulic residence times were determined using pulse injections of 1 mL of a 5  $\text{g L}^{-1}$  sodium bromide solution as a tracer. Reversible sorption of bisphenol A and diuron to birnessite-coated sand was negligible (see Fig. S1 and accompanying discussion).

### 2.4. Media failure testing

To minimize the time to failure, a modified column setup was used. The column inner diameter was 1.5 cm, with a packing depth of 6.5 cm. Columns were packed with 10 g birnessite-coated sand and run at a volumetric flow rate of 0.40  $\text{mL min}^{-1}$  (corresponding to an infiltration rate of 1.4  $\text{m h}^{-1}$ ) in the up-flow mode. To inhibit biological growth during longer failure tests, all columns and tubing, excluding the column media itself, were pre-sterilized before use by flowing 500 mL of a 1% HCl solution followed by MilliQ water through the system. Following preliminary testing indicating autoclaving of the stormwater did not impact behavior in failure testing, all solutions were autoclaved prior to use to further inhibit biological activity. Solutions were amended with bisphenol A after autoclaving, just prior to initiation of the failure experiments. Simulated stormwater solutions, containing different combinations of divalent cations, bicarbonate, NOM and pH were amended with 5  $\mu\text{M}$  bisphenol A and passed through columns for approximately 650 pore volumes or until failure. Simulated stormwater solutions at pH 5.1  $\pm$  0.4, 7.0  $\pm$  0.1 and 8.5  $\pm$  0.5 were also tested; the pH of the influent simulated stormwater varied at high and low pH values as the carbonate-buffered simulated stormwater equilibrated with the atmosphere, so influent stormwater solution was replaced at least every 48 h. Column eluent was sampled periodically. Total inorganic carbon concentrations of the column effluent did not differ significantly from the influent and pH typically varied by less than 0.1. Media failure experiments were not performed in replicate.

### 2.5. Chemical analyses

Most organic contaminants were quantified by high performance liquid chromatography tandem-mass spectrometry (HPLC/MS-MS) with electrospray ionization, using an Agilent 6460 system. Liquid chromatography was performed using an Agilent Zorbax SB-C18 column with the dimensions 2.1  $\text{mm} \times$  50  $\text{mm}$  and 3.5  $\mu\text{m}$  pore size. 100  $\mu\text{L}$  sample injection volumes were used with a mobile phase flow rate of 0.3  $\text{mL min}^{-1}$ . Further details of the LC/MS-MS method parameters are provided in Tables S2-A, S2-B and S2-C. Details of bisphenol and diuron transformation product identification by HPLC/MS-MS are provided in the supplementary material.

Fluoranthene was analyzed by gas chromatography-mass spectrometry (GC-MS) using an Agilent 6890N GC in conjunction with a Micromass Quattro Micro mass spectrometer. 4 mL of aqueous samples were amended with  $d_{10}$ -fluoranthene and were extracted with 500  $\mu\text{L}$  hexane. 1  $\mu\text{L}$  of solvent extract was injected into a splitless injector at 280  $^{\circ}\text{C}$ . The carrier gas used was helium, set at a flow rate of 1  $\text{mL min}^{-1}$ . The gas chromatographic column used was an Agilent DB-5ms, with dimensions of 30  $\text{m} \times$  0.25  $\text{mm}$ , 0.25  $\mu\text{m}$  film thickness. The oven program was as follows: an initial oven temperature of 120  $^{\circ}\text{C}$  was held for 1 min, followed by a ramp of 15  $^{\circ}\text{C min}^{-1}$  to 210  $^{\circ}\text{C}$ . The oven temperature was held for 6.5 min followed by a second ramp at 30  $^{\circ}\text{C min}^{-1}$  to 250  $^{\circ}\text{C}$ . This oven temperature was held for 1 min. The total run time was 15.83 min. The MS was used in the electron ionization mode. Quantification ions for fluoranthene were  $m/z = 101, 201, 203, 204$  and the ions used for quantification of  $d_{10}$ -fluoranthene were  $m/z = 106, 209, 211, 213$ .

Dissolved manganese was analyzed colorimetrically by the formaldoxime method (Goto et al., 1962; Burle and Kirby-Smith, 1979). Briefly, reagent A (0.575 M hydroxylamine HCl and 0.2 M formaldehyde) and reagent B (40%  $\text{NH}_4\text{OH}$ ) were mixed in a ratio of A:B of 5:4 immediately prior to analysis. 1.2 mL of this mixed reagent solution, which was prepared daily, was added to a 10 mL sample. The manganese-formaldoxime complex produced in the colorimetric reaction was detected at 450 nm ( $\epsilon_{450} = 1.49 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).

Dissolved carbon analysis was performed on a Shimadzu TOC- $V_{\text{CSH}}$ . Non-purgeable organic carbon (NPOC) analysis was performed using 1.5% acid addition followed by a 1.5 min air sparge. For tracer experiments, bromide ion was analyzed on a Dionex 120 ion chromatograph with a Dionex IonPac AS14A RFIC 4  $\times$  250 mm column. The mobile phase consisted of 4  $\text{mM Na}_2\text{CO}_3$  and 1.25  $\text{mM}$  of  $\text{NaHCO}_3$ .

## 3. Results and discussion

### 3.1. Reactivity of birnessite with organic contaminants

Reaction rates of stormwater contaminants were divided into three categories. Aromatic compounds containing Lewis base moieties and no deactivating (i.e. electron-withdrawing) functional groups (i.e., 2-mercaptobenzothiazole, N-octylphenol and bisphenol A) exhibited the fastest reaction rates, with first-order rate constants between 0.9 and  $58 \times 10^{-3} \text{ L g}^{-1} \text{ s}^{-1}$ . Compounds that contained ring-activating functionalities reacted more slowly if they also possessed electron-withdrawing groups (i.e., diuron) or exhibited steric hindrance at the most likely reaction site (i.e., prometon). Fluoranthene, a polycyclic aromatic hydrocarbon, also fell into this category of moderately-reactive compounds as its homogenous distribution of pi-electrons contains no easily substituted protons. Compounds in this category reacted with birnessite with first-order reaction rates ranging from 27 to  $130 \times 10^{-9} \text{ L g}^{-1} \text{ s}^{-1}$ . TCPP, benzotriazole, fipronil, and pendimethalin did not react with the manganese oxides under the tested conditions (i.e.,  $k \ll 10^{-9} \text{ L g}^{-1} \text{ s}^{-1}$ ).

To place these data into context and to facilitate predictions for other compounds, comparisons were made to prior studies on reactivity of organic compounds with birnessite (Table 2). To facilitate comparisons among studies conducted at widely varying oxide concentrations, reported initial reaction rates were converted to initial rate constants,  $k_{\text{initial}}$ . This approach minimized deviations from linearity that occur when the concentration of the organic compound is high with respect to that of  $\text{MnO}_{2(\text{s})}$  (e.g., 100–2000  $\mu\text{M}$  (Zhang and Huang, 2003; Rubert and Pedersen, 2006)).

**Table 2**  
Comparison of rate constants for reaction between various organic compounds and birnessite.

Chemical	Oxide conc. (g L <sup>-1</sup> )	pH	$k_{\text{initial}}$ (L g <sup>-1</sup> s <sup>-1</sup> )	Reference
<b>Fast-Reacting Compounds</b>				
2-Mercaptobenzothiazole	6	7.0	$9.17 \pm 0.75 \times 10^{-4}$	This study <sup>a</sup>
Aniline	0.435	4.0	$9.96 \times 10^{-4}$	Laha and Luthy, 1990 <sup>b</sup>
Bisphenol A	6	7.0	$1.84 \pm 0.34 \times 10^{-3}$	This study <sup>a</sup>
Bisphenol F	0.0087	5.5	$2.53 \times 10^{-3}$	Lu et al., 2011 <sup>b</sup>
Oxytetracycline	0.052	5.0	$5.21 \times 10^{-3}$	Zhang et al., 2008 <sup>b,c</sup>
2,4-Dichlorophenol	0.087	4.0	$6.29 \times 10^{-3}$	Zhang et al., 2008 <sup>b,c</sup>
Triclosan	0.087	4.0	$6.58 \times 10^{-3}$	Zhang et al., 2008 <sup>b,c</sup>
Tetracycline	0.052	5.0	$1.40 \times 10^{-2}$	Zhang et al., 2008 <sup>b,c</sup>
Phenol	0.087	4.0	$2.18 \times 10^{-2}$	Zhang et al., 2008 <sup>b,c</sup>
Aminobenzoic acid	0.435	4.0	$2.38 \times 10^{-2}$	Laha and Luthy, 1990 <sup>b</sup>
n-Octylphenol	6	7.0	$5.77 \pm 0.53 \times 10^{-2}$	This study <sup>a</sup>
Tetrabromobisphenol A	0.109	4.5	$7.82\text{--}8.69 \times 10^{-2}$	Lin et al., 2009b <sup>b</sup>
<b>Moderate-Reacting Compounds</b>				
Prometon	6	7.0	$2.69 \pm 0.16 \times 10^{-8}$	This study <sup>a</sup>
Atrazine	10	6.2	$4.38 \times 10^{-8}$	Shin and Cheney, 2004 <sup>a</sup>
Diuron	6	7.0	$66.7 \pm 0.48 \times 10^{-9}$	This study <sup>a</sup>
Fluoranthene	6	7.0	$1.29 \pm 0.18 \times 10^{-7}$	This study <sup>a</sup>
p-Nitroaniline	0.435	4.0	$7.66 \times 10^{-7}$	Laha and Luthy, 1990 <sup>b</sup>

<sup>a</sup> Birnessite used was synthesized according to the method of McKenzie, 1981.

<sup>b</sup> Birnessite used was synthesized according to the method of Murray, 1974.

<sup>c</sup> Additional compounds not shown here are reported in Zhang et al., 2008.

In general, the rate constants measured in this study agreed with data for compounds with similar structures. Using this approach, numerous fast-reacting compounds (i.e.,  $k > 10^{-4}$  L g<sup>-1</sup> s<sup>-1</sup>) were identified (e.g., phenol, triclosan, tetracycline, aniline) and two additional slower-reacting compounds ( $k < 10^{-6}$  L g<sup>-1</sup> s<sup>-1</sup>) were found (i.e., atrazine and *p*-nitroaniline). Additional research could employ the methods employed here to identify other compounds that are amenable to treatment with birnessite-coated sand.

### 3.2. Feasibility of employing manganese oxides in passive treatment systems

Saturated flow column experiments were conducted to assess the potential for using manganese oxides to remove contaminants under conditions expected in passive stormwater treatment systems. The fine powder generated when manganese oxides were formed by reduction of Mn [VII] proved to be unsuitable for use in a flow-through systems due to particulate Mn migration and clogging. To avoid these problems, birnessite-coated sand was used in column studies. Bisphenol A (BPA) ( $k_{\text{batch}} = 1.8 \pm 0.3 \times 10^{-3}$  L g<sup>-1</sup> s<sup>-1</sup>) and diuron ( $k_{\text{batch}} = 67 \pm 5 \times 10^{-9}$  L g<sup>-1</sup> s<sup>-1</sup>) were employed as representatives of the fast reacting and moderately reactive compounds.

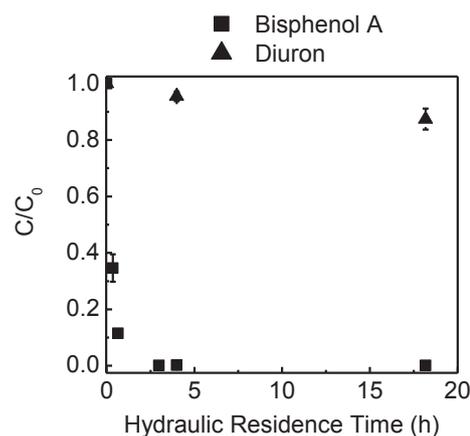
The efficacy of the columns was assessed as a function of hydraulic residence time (Fig. 1). Greater than 90% removal of bisphenol A was observed at hydraulic residence times above 0.6 h. This rate was considerably faster than the rate of biodegradation of bisphenol A reported in river water, which typically occurs with a half-life of 2–5 days (Kang and Kondo, 2002). In contrast, less than 5% of the diuron was removed at a hydraulic residence time of 4 h. Diuron removal increased to 13% at a hydraulic residence time of 18 h. Neither bisphenol A nor diuron exhibited significant reversible sorption to the column media (Fig. S1). This finding agreed with previous research with bisphenol A (Lin et al., 2012). Furthermore, the detection of oxidation products of both bisphenol A and diuron in the column effluent (Fig. 2), provided additional evidence that chemical transformation was the main removal mechanism.

On a mass basis, the manganese oxide-coated sand was much less reactive with bisphenol A than the powdered manganese oxide mineral phases, with a reaction rate with bisphenol A of

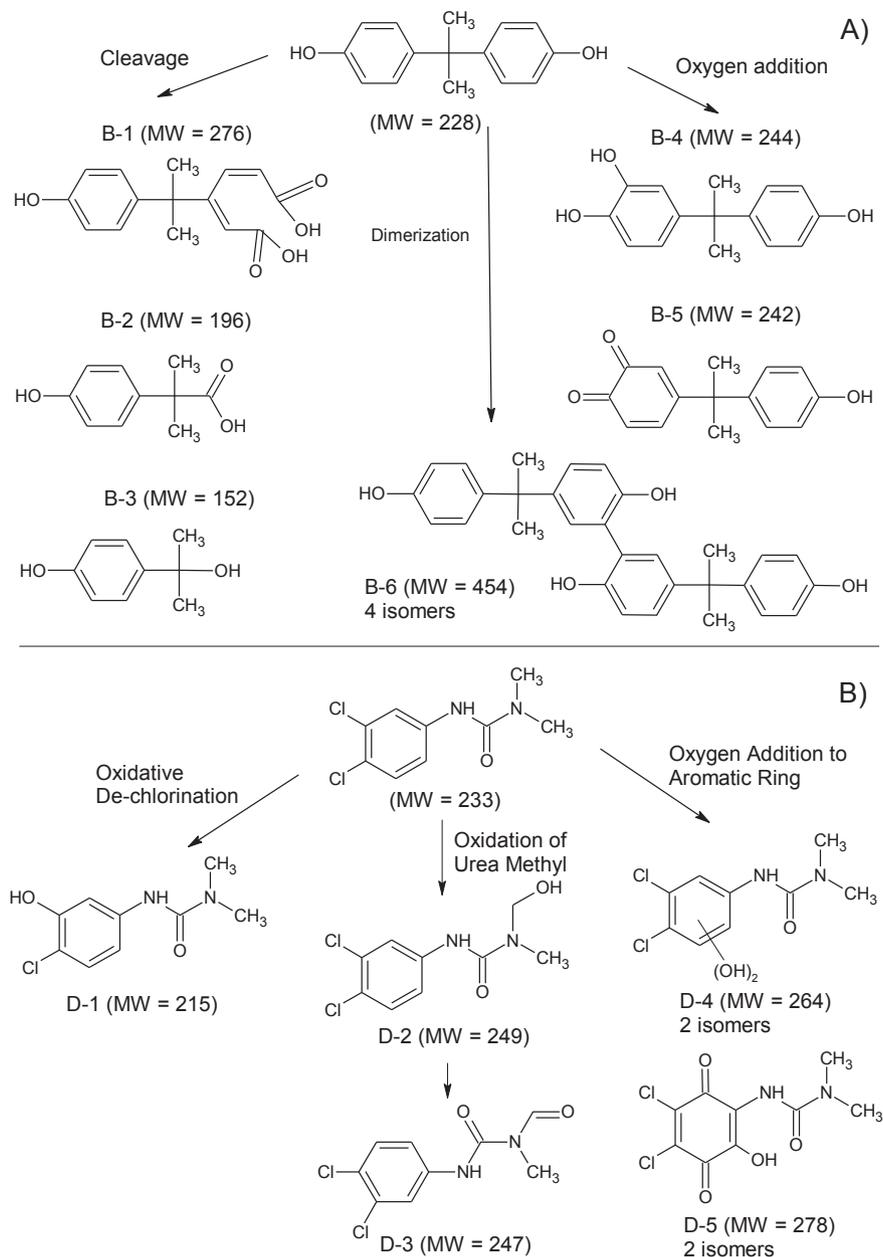
$k_{\text{initial}} = 1.72 \times 10^{-6}$  L g<sup>-1</sup> s<sup>-1</sup>, a full three orders of magnitude slower than rates observed for the powdered mineral phase. This is logical, as less than 1% of the mass of the coated-sand media was manganese oxides. This reaction rate was in good agreement with previously reported rates of bisphenol A degradation in 10 mM acetate buffer at circumneutral pH by manganese-oxide coated sands synthesized via a different method (Lin et al. 2012).

These data provided insight into the potential usefulness of manganese oxides in infiltration systems. Contaminants that reacted quickly with manganese oxides could be removed effectively in a manganese oxide treatment system with a hydraulic residence time as short as 0.4 h. To reduce the influent concentration of diuron or other moderately reactive compounds by more than 50%, some combination of increased media depth or reduced flow rate would be needed to achieve hydraulic residence times of more than 50 h.

To put these findings into perspective, bioinfiltration systems typically have areas ranging from 20 to 200 m<sup>2</sup> with total media depths of approximately 100 cm, of which about 50 cm may include



**Fig. 1.** Effect of residence time on removal of bisphenol A and diuron on birnessite-coated sand columns. All experiments performed using simulated stormwater (pH 7) containing 5 μM of each organic contaminant. Error bars represent standard deviation ( $n \geq 3$ ) of multiple samples collected over the first 10–100 pore volumes as well as replicate column experiments that were performed under the same conditions.



**Fig. 2.** Transformation products of (A) bisphenol A and (B) diuron detected in birnessite-coated sand column effluent. Conditions: 5 cm h<sup>-1</sup> loading rate, hydraulic residence time = 4 h. Simulated stormwater (no NOM) at pH 7.0 contained 5 μM of organic compound.

an amendment of some type (Hatt et al., 2009; Li et al., 2009). If a 50 m<sup>2</sup> system were constructed with birnessite-coated sand, a total of 25 m<sup>3</sup> of the geomedia would be needed. If the bioinfiltration system had a maximum drawdown time of 48 h, a rate typical of many systems (Hunt et al., 2010; Prince George's County, 1999), the maximum infiltration rate would be 2 cm h<sup>-1</sup>, which corresponds to a hydraulic residence time within the birnessite-coated sand media of 25 h. This simple calculation suggests that a typical stormwater infiltration system could remove over 99% of the fast reacting compounds, but less than 25% of the moderately reactive compounds. Managed aquifer recharge projects and permeable reactive barriers more suitable for centralized stormwater treatment, however, frequently achieve hydraulic residence times on the order of several days to weeks—timescales over which manganese oxide-coated sands could remove substantial amounts of moderately reactive compounds like diuron (Bartlett and Morrison,

2009; Laws et al. 2011).

### 3.3. Transformation of bisphenol A and diuron

The initial steps in the oxidation of electron-rich aromatic compounds by manganese oxides often result in addition of a hydroxyl group (Zhang and Huang, 2003). These transformation products often undergo further oxidation to ring cleavage products. However, complete mineralization is unlikely because many of the ring cleavage products do not react with manganese oxides at an appreciable rate.

Concentrations of non-purgeable organic carbon (NPOC) and transformation products were monitored to assess the extent of transformation in the column studies. At hydraulic residence times ranging from 0.6 h up to 18 h, the concentration of bisphenol A decreased by over 99% and the NPOC detected in the column

effluent decreased by 60%. No further reduction in NPOC was observed at longer contact times. The organic carbon loss was attributable to partial mineralization of the compounds or through the formation of purgeable low molecular weight compounds, such as short chain aldehydes (Sunda and Kieber, 1994). No significant loss of phenol, oxalic acid or acetic acid was observed during NPOC analysis, suggesting that formation of phenols or organic acids were not responsible for the observed loss.

Oxidation products detected in the effluent of the birnessite-coated sand columns included a number of compounds previously reported in batch experiments with manganese oxides (Lin et al., 2009a and Zhang et al., 2013). These products (Fig. 2A) included compounds resulting from cleavage of aromatic rings, dimerization products, and oxygen addition products. Due to the absence of analytical standards, the relative concentration of the oxidation products could not be determined. It is noteworthy that the bisphenol A concentrations used in these experiments (5  $\mu\text{M}$  or  $\sim 1000 \mu\text{g/L}$ ) were several orders of magnitude greater than those likely to be present in stormwater (Grebel et al., 2013). Therefore the dimers and other radical–radical recombination products are unlikely to account for a significant fraction of the stable transformation products under realistic operating conditions.

With respect to human health effects or ecological risks, it is known that the estrogenicity of bisphenol A decreases upon oxidation (Alum et al., 2004; Chen et al., 2006). Assuming a similar trend in estrogenicity as bisphenol A is oxidized by manganese oxides, a passive treatment system with birnessite-coated sand would substantially reduce the estrogenicity contributed by bisphenol A. Additional research would be needed to assess changes in estrogenicity and other endpoints for the bisphenol A transformation products.

For diuron, the concentration of non-purgeable organic carbon did not decrease appreciably during passage of water through the column, but five oxidation products were detected in the column effluent (HRT = 4 h; 4% diuron transformation): one monodechlorinated product, and four oxidation products with both chlorine atoms remaining (see Fig. 2, Table S3 and corresponding text). Due to the low extent of diuron transformation under these experimental conditions, a series of batch experiments was conducted to identify transformation products that might be expected in systems with longer hydraulic retention times. These experiments indicated the formation of fully dechlorinated products (see supplementary material). All of the chlorine-containing products detected in positive ionization mode (see Table S3) in column and batch experiments contained the daughter ion  $m/z = 72$ , which is characteristic of methylphenylureas (corresponding to the fragment  $\text{O}=\text{C}=\text{N}^+(\text{CH}_3)_2$ ) (Kanawati et al., 2009).

To our knowledge, this is the first time that oxidation of diuron by manganese oxides has been reported. The suite of products produced from the reaction of diuron with birnessite were distinct from products of hydrolysis (Salvestrini et al., 2002) or biotransformation (Giacomazzi and Cochet, 2004); pathways that result in formation of the toxic intermediate, 3,4-dichloroaniline (Tixier et al., 2001). No de-methylated products or 3,4-dichloroaniline were detected during diuron oxidation by manganese oxides in either column or batch experiments.

#### 3.4. Effect of the stormwater matrix on contaminant removal

The performance of manganese oxide geomedia will be affected by solution composition. Due to the highly variable nature of stormwater (Gobel et al., 2007; Grebel et al., 2013), understanding the sensitivity of Mn-oxide treatment to the composition of the matrix is important to predicting the conditions under which the

treatment systems may fail.

The reaction between Mn-oxides and organic compounds involves the adsorption of the organic compound on the manganese reaction site, followed by electron transfer and release of the oxidized organic compound. Under certain conditions, the reduced manganese can dissolve into solution (e.g., as  $\text{Mn}^{2+}$ ). The reaction rate can be described as follows:

$$\text{Reaction Rate} = R = k [N_{\text{Rxn}}^{\text{Mn}}] [C_{\text{Organic}}] \quad (1)$$

The reaction rate,  $R$ , depends on the number of available manganese reaction sites,  $[N_{\text{Rxn}}^{\text{Mn}}]$ . In the presence of elevated concentrations of divalent cations, the adsorption of trace organic compounds can decrease (Barrett and McBride, 2005). For example, high concentrations (e.g.,  $2000 \text{ mg L}^{-1} \text{ Ca}^{2+}$ ; Lin et al., 2009a) of divalent cations slowed the rate of transformation of bisphenol A in batch experiments by over 90%. In stormwater, concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  rarely exceed  $100 \text{ mg L}^{-1}$  (Makepeace et al., 1995; Gobel et al., 2007). Therefore, the concentration of bisphenol A in the effluent of the column was measured at  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations up to  $100 \text{ mg L}^{-1}$  (Fig. S3A). At the highest concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , columns of birnessite-coated sand still removed >90% of BPA from stormwater.

The presence of organic matter (e.g., humic substances) also could affect system performance. The concentration and composition of organic matter present in stormwater varies considerably with the season and among locations. For instance, samples of highway runoff collected in California exhibited dissolved organic carbon concentration ranging from 1 to  $70 \text{ mg-C L}^{-1}$  (Caltrans, 2003). To assess the potential effects of organic matter on the performance of manganese oxide-coated sand treatment systems, three types of dissolved organic matter were tested: Suwannee River natural organic matter, a  $0.7 \mu\text{m}$ -filtered authentic urban stormwater runoff sample, and filtered municipal wastewater effluent.

Increasing organic matter concentration resulted in a modest decline in bisphenol A removal (Fig. 3). This low sensitivity of the manganese oxides to organic matter was particularly notable in comparison to passive treatment systems that employ Fe- and Al-oxides, where significant drops in the removal of bacteria and metals (Mohanty et al., 2013; Rangsvik and Jekel, 2005) have been observed in the presence of organic matter. The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) of Fe-oxide media ranges from 7.5 to 8.5 (Liu et al., 2005) while that of Al-oxide media ranges from 8.3 to 9.1 (Genc-Fuhrman

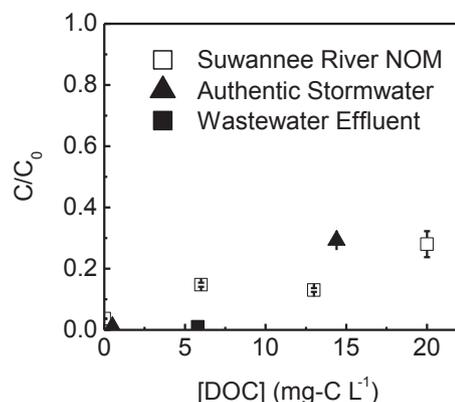


Fig. 3. Effect of organic matter on initial bisphenol A treatment efficiency. Conditions: 5  $\mu\text{M}$  bisphenol A, 8.2 cm-deep birnessite-coated sand column, flow rate =  $0.44 \text{ mL min}^{-1}$ , HRT = 0.6 h. Error bars represent standard deviation of three or more effluent samples collected during replicate column experiments.

et al., 2007). The  $\text{pH}_{\text{pzc}}$  for various kinds of manganese oxide media ranges from 1.5 to 6 (Murray, 1974; McKenzie, 1981; Stone and Morgan, 1984; Liu et al., 2005). Because natural organic matter tends to be negatively charged at circumneutral pH values, electrostatic forces will repel organic matter from the negatively charged Mn-oxide surface and inhibit fouling of the oxide surface.

Manganese oxides could also oxidize electron-rich moieties in natural organic matter. For example, manganese oxides can oxidize Suwannee River fulvic acid, producing low molecular weight carbonyl compounds, including pyruvate and aldehydes (Sunda and Kieber, 1994).

The organic matter in the secondary wastewater effluent sample had less of an impact on bisphenol A removal by birnessite-coated sand than the authentic stormwater or the Suwannee River NOM. Manganese oxide media has been proposed as a technology for wastewater effluent polishing (de Rudder et al., 2004; Forrez et al., 2010). These data suggest that it may be quite resistant to fouling by organic matter in this application.

Experiments investigated the effect of matrix pH on system performance. The pH of stormwater typically ranges from 4 to 9 (Wiley et al., 2000; Caltrans, 2003). Protons are consumed during the oxidation of organic compounds by manganese oxides and the redox potentials of manganese oxides decrease as pH increases (Remucal and Ginder-Vogel, 2014). Therefore, it is expected that increasing pH will lead to decreased rates of oxidation of organic contaminants by manganese oxides.

Batch experiments conducted with birnessite and birnessite-coated sand exhibited similar trends for bisphenol A transformation: pseudo-first order rate constants decreased as pH

increased from 3 to 5 and increased from pH 6 to 11 (Fig. 4A). This behavior was consistent with previous investigations of bisphenol A reactivity with manganese oxides (Lin et al., 2009a; Zhang et al., 2006). The increased reactivity at high pH values has been attributed to deprotonation of bisphenol A ( $\text{pK}_{\text{a}}^{\text{BPA}} = 9.6$ ; Lin et al., 2009a). In contrast to the batch experiments, concentrations of bisphenol A remained constant (within experimental error) in column effluents at pH values ranging from 6.0 to 10.0. As both batch and column experiments were performed with the same stormwater matrix, one possible explanation of this differing behavior involves local non-steady state conditions within the birnessite-coated sand column. For instance, pores in the columns that were hydraulically isolated or near regions of high reactivity likely had very different solute activity than the bulk solution. Such regions may have locally elevated concentrations of dissolved Mn or higher pH values due to the consumption of protons. These regions may slow the reactivity in regions of the column that otherwise would oxidize large amounts of the contaminant. The differing behavior exhibited in batch and column experiments is yet another example of the difficulty of predicting the behavior of a flow-through manganese oxide engineered system from studies that employed equilibrium batch reactions.

### 3.5. Behavior of reduced manganese

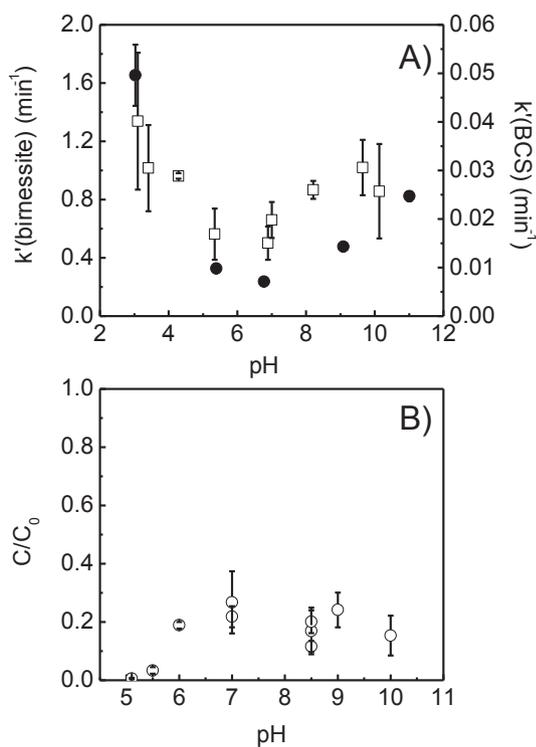
Acidic conditions (pH 5) resulted in appreciable, but low, concentrations of dissolved Mn in column effluents (i.e.,  $[\text{Mn}_{\text{dissolved}}] \cong 500 \mu\text{g L}^{-1}$ ). Excessive Mn exiting a treatment system is undesirable, due to health and esthetic concerns. The US Environmental Protection Agency (USEPA) has established a drinking water maximum contaminant level for manganese of  $50 \mu\text{g L}^{-1}$  based on esthetic concerns. For health effects, the US EPA lifetime health advisory level is  $300 \mu\text{g L}^{-1}$  (USEPA, 2004). At circumneutral pH values in the presence of 1 mM total inorganic carbon, dissolved Mn was always less than  $220 \mu\text{g L}^{-1}$ , and in many cases dissolved Mn in the effluent was much lower. Lower concentrations of dissolved Mn in columns were likely due to adsorption of reduced Mn on the mineral surface (Table S1) as well as the formation of Mn precipitates.

### 3.6. Estimated system operating lifetime and mechanisms of failure

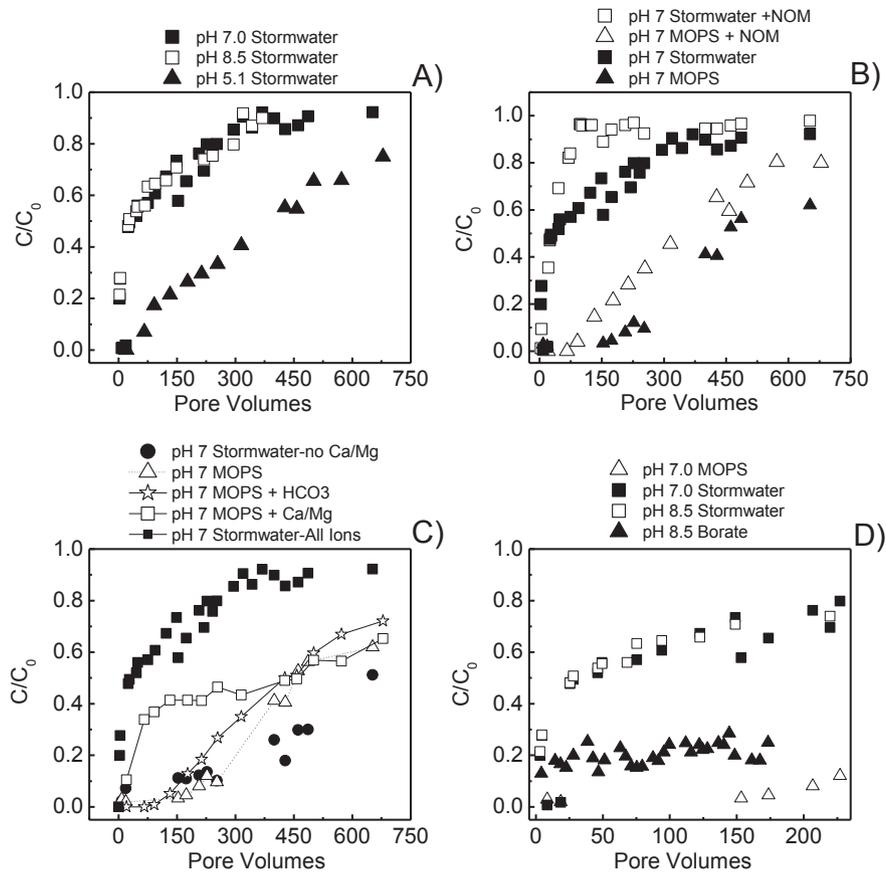
A passive treatment system will require replacement or regenerative maintenance after Mn-oxides lose their reactivity. To assess media longevity, a series of failure tests were conducted with bisphenol A. Through systematic variation in pH and concentrations of divalent cations, carbonate and natural organic matter it was possible to gain insight into the factors controlling long-term system performance.

To determine if exposure to the simulated stormwater matrix would result in system failure in the absence of contaminants, control experiments were performed using simulated stormwater containing no added trace organic contaminants. After 650 pore volumes, 5  $\mu\text{M}$  bisphenol A was introduced to the influent simulated stormwater. The effluent concentration initially observed after the addition of bisphenol A was approximately 1  $\mu\text{M}$ . In contrast, for columns in which bisphenol A was continuously present in the influent, bisphenol A concentration in the effluent was approximately 4.0  $\mu\text{M}$  after 650 pore volumes (Fig. 5). Therefore, the presence of an oxidizable organic compound played an important role in loss of reactivity of the birnessite-coated sand.

To investigate the impact of pH on long-term system performance, simulated stormwater amended with 5  $\mu\text{M}$  bisphenol A was tested at pH 5.1, 7.0 and 8.5 (Fig. 5A). A total of 3.6  $\mu\text{moles}$  of bisphenol A were oxidized at pH 5.1 and 0.75  $\mu\text{moles}$  of bisphenol A



**Fig. 4.** Effect of stormwater pH on bisphenol A removal in A) batch and B) column conditions. 4A: Pseudo-first order rate constant of bisphenol A removal on birnessite (squares: 6 g L<sup>-1</sup> of birnessite; closed circles: 100 g L<sup>-1</sup> birnessite-coated sand) 4B: Normalized bisphenol A concentration in effluent of birnessite-coated sand columns. Bisphenol A column experiments were performed in simulated stormwater containing 1  $\mu\text{M}$  bisphenol A, column diameter = 1 cm, column length = 6.5 cm, flow rate = 0.40 mL min<sup>-1</sup>. Error bars represent the standard deviation of replicate ( $n \geq 3$ ) effluent samples collected between  $10 < \text{PV} < 100$ .



**Fig. 5.** Effect of A) stormwater pH, B) natural organic matter, C) calcium and magnesium and D) dissolved inorganic carbon on birnessite-coated sand column failure behavior. Bisphenol A column experiments were performed in sterilized simulated stormwater or sterilized MOPS buffer containing 5  $\mu\text{M}$  bisphenol A, column diameter = 1 cm, column length = 3.5 cm, flow rate = 0.40  $\text{mL min}^{-1}$  ( $n = 1$ ).

were oxidized at pH 7 (and hence more manganese oxide was reduced at pH 5.1). Nonetheless, the birnessite-coated sand failed faster at pH 7 (Fig. 5A). Therefore, even though the presence of an oxidizable organic was required for failure, the loss of reactive capacity was not exclusively related to the total amount of the organic oxidized. Some constituent of the stormwater matrix was also involved. The stormwater pH could also have influenced the availability of reactive sites at the manganese oxide surface, contributing to passivation. This effect, however, would be expected to influence initial reaction rates and have a constant impact for the duration of the experiment. Because initial bisphenol A removal rates were similar at the pH values tested and the removal rates declined faster at the higher pH values, other matrix effects likely played an important role in the observed declines in long-term performance.

To assess the effect of dissolved organic matter on treatment efficiencies, column experiments were conducted in the presence and absence of 10  $\text{mg-C/L}$  of natural organic matter (NOM) (Fig. 5B). In experiments with organic matter in both a simulated stormwater matrix and a matrix buffered by MOPS at pH 7, NOM caused failure faster than in the organic matter-free systems. The impacts of NOM on treatment efficiency and system longevity, however, were small compared with the impacts of the presence or absence of the stormwater matrix.

A series of failure experiments were performed to evaluate the long-term impact of the divalent cations,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , and dissolved inorganic carbon on birnessite-coated sand failure (Fig. 5C and D). Simulated stormwater, containing no  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  but all other ions at pH 7, was run through birnessite-coated sand columns

until failure was observed. Removal of divalent cations from the matrix had a profound effect on failure behavior. Failure of the birnessite-coated sand column exposed to the simulated stormwater was significantly faster than stormwater containing no divalent cations. Similarly, a MOPS-buffered solution (pH 7) containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions at the same concentration as in the simulated stormwater caused failure of the birnessite-coated sands in column tests much faster than a MOPS-buffered solution without any added ions. In fact, the failure trends for the stormwater solution with no divalent cations and MOPS-buffered solution were similar, suggesting that the presence of divalent cations was important to the failure mechanism observed.

The slight decrease in operating lifetime of birnessite-coated sand exposed to MOPS buffer or MOPS buffer along with 1 mM dissolved inorganic carbon as compared to simulated stormwater containing 1 mM dissolved inorganic carbon but no divalent cations was consistent with the slight inhibiting effect of MOPS on organic-manganese oxide reactions previously observed by Huguet et al. (2013).

A column test with pH 8.5, 4.6 mM carbonate-free borate buffer was performed to further investigate the impacts of pH and inorganic carbon on the trend of decreasing long-term performance of the media (Fig. 5D). The results indicate that even at pH 8.5, in the absence of inorganic carbon the manganese-oxide media sustained bisphenol A removal better than in simulated stormwater at pH 7.0. Such a result suggests that carbonate ion may be important to the observed failure mechanism, as it was present at significantly higher concentrations in the simulated stormwater at pH 7.0 and 8.5, than at pH 5.1 or in the MOPS- or borate-buffered solutions at

pH 7.0 and 8.5.

Such results regarding the impacts of  $\text{Ca}^{2+}$  and inorganic carbon suggest that calcite precipitation on the geomedia surface may have played a role in passivation of birnessite-coated sand in the column tests. Indeed, in the simulated stormwater solution, the saturation indices (S.I. =  $\log(\text{IAP}/K_{\text{sp}})$ ) of calcite were  $-4.40$ ,  $-1.32$ , and  $0.26$  at pH 5.1, 7.0, and 8.5, respectively. Oxidation of organic contaminants resulted in the release of Mn(II), which could adsorb or precipitate onto the birnessite surface. Rhodochrosite ( $\text{MnCO}_3(\text{s})$ ) is sparingly soluble ( $\log K_{\text{sp}} = -10.39$ ). At typical  $\text{Mn}^{2+}$  concentrations in the column effluent (i.e.  $10 \mu\text{M}$ ), the saturation indices of rhodochrosite in the simulated stormwater solutions are  $-3.76$ ,  $-1.03$ , and  $0.55$  at pH 5.1, 7.0, and 8.5, respectively. These results indicate that at pH 8.5 calcite or rhodochrosite could have formed on the surface of the birnessite-coated sands, playing a role in passivation, but not at pH 7.0 or 5.1.

On the basis of these results, we infer that failure of the columns was likely caused by a combination of mechanisms, as experiments verified that birnessite-coated sand columns experienced a gradual decline in treatment efficiency for all tested failure conditions (Fig. 5). Likely mechanisms include the inhibitory effect of  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on oxidation reactions (Lin et al. 2009a). This inhibition may have been caused by the cations occupying the reactive surface sites on the birnessite, or by the cations complexing with dissolved or sorbed BPA (Barrett and McBride, 2005). Precipitation of carbonate minerals on the surface of birnessite-coated sand also likely contributed to passivation in this system. At sufficiently high pH values,  $\text{CaCO}_3$  and  $\text{MnCO}_3$  precipitates could form, with the composition of such a system ranging between calcite and rhodochrosite depending on the concentration of  $\text{Mn}^{2+}$  ions present. Another possible cause of system failure in the absence of divalent cations or carbonate was the reductive dissolution of reactive sites on the birnessite surface. For instance, studies have found that certain birnessite morphologies demonstrate higher reactivities in chemical reactions with aromatic hydrocarbons (Hou et al., 2014; Villalobos et al., 2014). Reductive dissolution of these more reactive sites on the birnessite surface over the course of the chemical reactions may have diminished the system's reactivity with time. Each of these mechanisms likely contributed to a decrease in reactivity and eventual passivation of the geomedia with time, though their relative importance varies with the specific stormwater matrix.

The combination of neutral to alkaline pH and the presence of  $0.75 \text{ mM Ca}$ ,  $0.075 \text{ mM Mg}$ ,  $1 \text{ mM}$  dissolved inorganic carbon and  $10 \text{ mg-C/L NOM}$  resulted in the fastest failure of the columns. As most stormwater is likely to contain divalent cations and carbonate, these conditions represent the most likely mode of geomedia failure in stormwater infiltration systems. The total mass of bisphenol A removed prior to exhaustion of the media (i.e., a decrease in removal exceeding 90%) was  $0.21 \mu\text{Mole per g}$  birnessite-coated sand under these conditions (i.e.,  $0.75 \text{ mM Ca}$ ,  $0.075 \text{ mM Mg}$ ,  $1 \text{ mM}$  dissolved inorganic carbon and  $10 \text{ mg-C/L NOM}$ ). The generation of a passivated layer as a result of oxidation of the organic compounds suggests that total Mn present in the system (e.g., Mn-coating density) is not a good gauge of system lifetime. Instead, the load of oxidizable organic compounds on the media is a better proxy for progress towards failure.

The failure experiments described above considered a situation that exaggerated the rate of failure due to the elevated concentrations of oxidizable organic compounds. To provide a better estimate of failure under more realistic field conditions, it is necessary to approximate the anticipated loading of oxidizable organic compounds. A typical stormwater infiltration system (a  $50 \text{ m}^2$  bio-infiltration system with  $50 \text{ cm}$  geomedia depth; Hatt et al., 2009) treating an area with average annual rainfall of  $50 \text{ cm year}^{-1}$  with a

capture efficiency of 100% and an area of  $0.405 \text{ ha}$  ( $\sim 4000 \text{ m}^2$ ) of impervious surface would capture approximately  $2 \text{ million L year}^{-1}$  of stormwater. Assuming that stormwater contained  $50 \mu\text{g/L}$  of oxidizable organic compounds (i.e., organic compounds and reactive functional groups in natural organic matter) with pH 7 stormwater containing NOM, divalent cations and carbonates at the concentrations in Table 1, the passive treatment system could be expected to operate for approximately 25 years before failure due to the mechanism observed in this study. This estimate is based on the total mass of bisphenol A removed prior to failure reported above, assuming a linear relationship between the concentration of reactive organic and birnessite-coated sand failure rate. Under more optimal conditions (e.g., a stormwater matrix with lower hardness or lower pH), the system could operate for more than 200 years before failure. Although this is only a crude estimate, these calculations suggest that manganese oxides may provide a suitable geomedia amendment for removal of certain classes of contaminants from stormwater infiltration systems. Additional research on this media under actual field conditions is needed to evaluate these assumptions.

#### 4. Conclusions

Manganese oxides exhibited varying reactivity with stormwater contaminants in a stormwater matrix. Activated aromatic compounds with no electron-withdrawing groups reacted quickly with manganese oxides, while similar compounds with electron-withdrawing groups or steric hindrance at the most likely reaction site reacted considerably slower. Compounds without electron-donating groups were unreactive under these conditions. Column tests with birnessite-coated sands under conditions encountered in stormwater suggested the potential for using geomedia in passive infiltration systems to treat organic stormwater contaminants with electron-donating moieties. This media could also be effective in treating a wider variety of organic contaminants in applications with longer hydraulic residence times such as permeable reactive barriers, river bank filtration and managed aquifer recharge.

Transformation products of bisphenol A, a fast-reacting compound, were identified. Birnessite-coated sand could partially mineralize the compounds under the conditions expected in infiltration systems. Transformation products of diuron, a moderately-reacting compound, included fully dechlorinated products.

The matrix in which these reactions occurred greatly affected the rates of transformation of bisphenol A. The presence of divalent cations, NOM, and elevated pH values decreased initial removal rates of bisphenol A from stormwater. Additional research is needed to clarify the exact mechanism of passivation of birnessite-coated sand columns. Such studies should elucidate the precise roles of  $\text{Mn}^{2+}$  ions, divalent cations such as  $\text{Ca}^{2+}$ , and carbonate species in the failure of the geomedia columns. Under typical conditions, however, this media could remain an effective treatment for organic contaminants for 25 years.

These bench-scale tests, while confirming the plausibility of this treatment technology, did not account for several complicating factors that could arise in field-scale applications and merit further research. Paramount among these factors is the role of biological activity. Biofilms could foul the reactive surface or prevent organic contaminants from reaching reactive sites. In prolonged saturated conditions, respiration could cause anaerobic conditions in the column, leading to reduction of the Mn-oxides. Conversely, biological activity could also help to degrade contaminants in stormwater and manganese-oxidizing bacteria could regenerate reactive Mn-oxides, helping to prolong the lifetime of the system.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2015.10.019>.

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