Environmental Science
Water Research & Technology

The Use of Manganese Oxide-Coated Sand for the Removal of Trace Metal Ions from Stormwater

Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-09-2019-000781.R1
Article Type:	Paper

Water Impact

This research evaluated the capacity of manganese oxide-coated sand to remove metals during stormwater infiltration and assessed the potential for regeneration of geomedia. Results suggest that this geomedia can remove toxic metals from stormwater for years before regeneration with a mild acid. This geomedia removes metals and other contaminants during aquifer recharge, facilitating the use of stormwater as an inexpensive, local water supply.

The Use of Manganese Oxide-Coated Sand for the Removal of Trace Metal Ions from Stormwater

Joseph A. Charbonnet, Yanghua Duan and David L. Sedlak*

Department of Civil & Environmental Engineering, University of California,
Berkeley, CA, USA
and
National Science Foundation Engineering Research Center for
Reinventing the Nation's Urban Water Infrastructure (ReNUWIt)

*Corresponding Author: Department of Civil & Environmental Engineering, University of California, Berkeley, CA, 94720; phone: (510)643-0256; e-mail: sedlak@berkeley.edu

Abstract

The large-scale, systematic introduction of urban stormwater into the subsurface could contaminate groundwater with metals including cadmium, copper, lead and zinc. To assess the potential for using manganese oxide-coated sand to remove metal ions during stormwater infiltration, batch and column tests were used to simulate conditions encountered in treatment systems. The geomedia exhibited a relatively high affinity for Zn, Cd and Pb at environmentally relevant conditions in batch tests. In column tests conducted in the absence of natural organic matter (NOM), dissolved Cu and Pb were removed for over 2000 pore volumes, whereas Zn and Cd were removed for several hundred pore volumes. In the presence of NOM, Cu and Pb removal diminished, but the adsorption of Zn and Cd decreased only slightly. Treating manganese oxide-coated sands with pH 3 hydrochloric acid after column tests recovered over 90% of the adsorbed Cd, Cu and Zn. It also restored the adsorptive capacity of the geomedia with minimal loss of the surface coating. Neither acids nor organic ligands removed significant amounts of adsorbed Pb from the geomedia. The results of this study imply that manganese oxide-coated sand can remove metal ions from stormwater, and that saturated geomedia can be regenerated with a mild acid solution.

Introduction

Urban stormwater runoff is a plentiful resource that is increasingly used for aquifer recharge.[1,2] However, stormwater often contains elevated concentrations of chemical contaminants, which can limit its use to augment municipal water supplies.[3–5] In particular, toxic metals in urban runoff can threaten human health and aquatic ecosystems (Table S1).[6,7] As managed aquifer recharge systems that exploit stormwater become more popular, and as regulations for stormwater discharge become more stringent, it will be necessary to remove metal ions from urban runoff.[3,8]

During managed aquifer recharge, water is typically infiltrated through porous media.[9,10] Manganese oxide-coated sand is an inexpensive geomedia that can improve water quality during infiltration. Due to its redox properties, it can oxidize certain electron-rich organic contaminants during infiltration.[11] Manganese oxides also exhibit high affinities for metal cations, and therefore may be able to remove metals during stormwater infiltration.[12–15] Manganese oxide-coated sand is better suited for this application than pure manganese oxide minerals because of its higher hydraulic conductivity and lower propensity for displacement from treatment systems.[16]

Manganese oxides adsorb metal ions through several mechanisms. Structural vacancies and isomorphic substitution give manganese oxides pH_{pznpc} values ranging from 1.5 to 6.0, resulting in a negative surface charge at environmentally relevant pH values. Hence they can remove metal cations through electrostatic interactions.[17,18] Some metal ions also adsorb to manganese oxides via specific mechanisms.[19–21] Soft metal ions (e.g., Pb^{2+}) and transition metal ions with labile, polarizable electron configurations (e.g., Cu^{2+}) tend to form strong complexes with surficial MnOOH, MnOH and $Mn(OH)_2$

groups.[14,22–24] In particular, Pb has a high adsorption affinity for manganese oxides, likely due to its penetration into the interlayer and tunnels of manganese oxides and where it forms both double- and triple-corner-sharing complexes.[12,20] Other metal ions, such as Zn, form triple-corner-sharing complexes over vacancies, though these interactions are weaker than those of Pb.[19,21,25] Manganese oxide selectively adsorbs some metal ions. Pb can displace adsorbed Cu, Zn and Cd.[26,27] Cu, Zn or Cd may also be mutually competitive adsorbates.[27,28]

Manganese oxide-coated sand may lose treatment capacity after adsorption sites saturate.[13,14] However, a chemical treatment that removes metal ions without stripping away the adsorbing sites could restore the adsorptive capacity of the geomedia. Such a treatment would enable inexpensive regeneration *in situ*, without having to excavate the geomedia. Metal contaminants could be recovered via valved underdrains for offsite disposal. Periodic recovery of adsorbed metal ions would also limit the potential for release of metal contaminants if changing water chemistry favors desorption, which could occur during intermittent flow conditions[29–31] or through fluctuations in pH or ionic strength (e.g., from stormwater contaminated with deicing salts).[32,33]

To gain insight into the performance of manganese oxide-coated sand in stormwater treatment systems and to assess its potential for regeneration, we evaluated affinity of manganese oxide-coated sand for Cd, Cu, Pb and Zn in batch and column experiments in simulated stormwater. Experiments were conducted in the presence and absence of natural organic matter (NOM) to assess the role of organic complexation on metal ion removal. We tested acids and metal-complexing ligands for their potential to release adsorbed metal ions and assessed the performance of the regenerated geomedia.

Materials and Methods

Reagents and Simulated Stormwater

All chemicals used for simulated stormwater and in the synthesis of manganese oxide-coated sand were used as received from Fisher Chemical without further purification. Ultrapure water from a Milli-Q system (R = 18.2 MΩ) was used for all dilutions and for geomedia synthesis. All experiments were performed at room temperature (21 ± 2 °C).

Simulated stormwater solution contained major anions and cations typically detected in urban stormwater (Table S2), as previously described.[34] The pH of the solution was adjusted to either 5.0 ± 0.1 or 7.0 ± 0.1 with 1 N HCl and 1 N NaOH. To prevent the precipitation of Pb-phosphate species, phosphate was omitted from Pb adsorption experiments and the ionic strength of the solution was maintained at 4.6 mM with 0.016 mM NaCl. In several batch tests, Suwannee River NOM (reverse osmosis isolation IHSS #2R101N) was added at 8.0 mg-C/L. In column tests, Sigma humic acid was added at 6.3 mg-C/L because the 3 g mass of NOM required precluded the use of Suwanee River NOM (cost > $300/g). To compare the effect of the two types of NOM on metal ion adsorption, 6.3 mg-C/L Sigma humic acid was used in several batch experiments. Dissolved organic carbon was analyzed using a Shimadzu TOC-V_{CSH}.

Concentrated solutions of metal cations were made from dichloride salts obtained from Sigma Aldrich (> 98% purity). Regenerant solutions were made from trace metals grade HCl, disodium ethylenediaminetetraacetic acid (EDTA) dihydrate, and crystalline anhydrous citric acid obtained from Fisher Chemical. All containers were washed in 2.5 N HNO_3 and repeatedly rinsed with deionized water prior to use.

Manganese Oxide-Coated Sand

Manganese oxide-coated sand was synthesized using a previously described method.[11] Briefly, in a 1 L beaker, 100 g of acid-washed 20-30 mesh (595-841 μm) Ottawa sand obtained from Fisher Chemical was added to 250 mL of 2 N acetic acid containing 0.5 M $MnSO_4$. The sand was stirred as 200 mL of 0.43 M potassium permanganate solution was added. The coated sand settled before air drying at 30 °C, after which it was sieved with 40 mesh, rinsed with Milli-Q water and re-dried. The sand had a coating density of 1.17 ± 0.30 mg Mn/g geomedia. All geomedia was stored in amber glass bottles under N_2 until use, which occurred within 35 days.

Batch Adsorption

Triplicate batch adsorption experiments were conducted in polystyrene bottles containing 50 mL of simulated stormwater at pH 5.0 and 7.0 without NOM and at pH 7.0 with 8.0 mg-C/L Suwannee River NOM or 6.3 mg-C/L Sigma humic acid. Initial metal ion concentrations ranged from 0.050 - 440 μM Cu, 0.20 - 460 μM Zn, 0.010 - 270 μM Cd or 0.010 - 1.0 μM Pb. 500 mg manganese oxide-coated sand was added to the bottles prior to placing them on a shaking table. Control experiments were conducted with uncoated, acid-washed sand. Negligible particulate manganese (i.e., < 1 nM detection limit) was released during the batch experiments.

Total and dissolved Cu, Zn, Cd, Pb and Mn were measured in unfiltered samples and in samples filtered with 0.22-μm polyethersulfone filters. Samples were immediately acidified with a 1% HCl/0.5% HNO_3 solution.

Samples were collected before and 24 hours after geomedia addition. Preliminary kinetic experiments (data not shown) indicated that equilibrium was reached within 24 hours. The quantity of metal ion (Me) adsorbed per unit mass of manganese oxide, q (mol Me/mg MnO_x), was calculated according to the relationship:

$$q = \frac{(C_i - C_e)V}{m} \quad \text{(Eq. 1)}$$

where C_i is the initial metal ion concentration, C_e is the equilibrium metal ion concentration, V is the solution volume and m is the mass of manganese oxide.

Metal ions were quantified in triplicate on an Agilent 7700 Series Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). A full description of sample acquisition and quantification parameters is presented in the supplementary information (Table S3).

Geomedia Longevity Tests

We packed 16 mm inner-diameter glass columns with polyethylene fittings with 10 g of manganese oxide-coated sand to a height of 36 mm. The geomedia porosity was 0.33. Columns were operated in saturated upwards flow at 0.4 mL/min, which is equivalent to a 9.5 cm/h infiltration rate typical of stormwater infiltration systems.[10] All columns and Tygon and PTFE tubing were washed with 250 mL of 1% HCl solution followed by 250 mL of Milli-Q water before use and covered with foil during the experiments. Simulated stormwater solutions were autoclaved and continuously stirred in 2 L aluminum foil-wrapped glass containers.

The average influent concentrations of dissolved metal ions immediately upstream of the columns were: $Cu_0 = 2.5 \pm 0.7$ μM, $Zn_0 = 27 \pm 4$ μM, $Cd_0 = 3.9 \pm 0.5$ μM and $Pb_0 = 0.59 \pm 0.08$ μM. These concentrations (3 to 125 times higher than typical in urban stormwater) were needed to obtain breakthrough from columns within the timeframe of the experiment. Column effluent was collected and immediately filtered and acidified approximately every 240 pore volumes. Dissolved Cd, Cu, Pb, Zn and Mn were measured by ICP-MS. Flow was stopped after C/C_0 for the metal ion consistently exceeded 0.9, or after 2200 pore volumes. Porewater was drained and column ends capped before geomedia analysis or regeneration within 24 hours.

Equilibrium speciation of metals was modeled using Visual MINTEQ software.[35] The model temperature was fixed at 25 °C and solid precipitation was prohibited. Total metal concentrations were fixed at $Cu(II)_{tot} = 3.14$ μM, $Zn(II)_{tot} = 30.6$ μM, $Cd(II)_{tot} = 4.45$ μM and $Pb(II)_{tot} =0.724$ μM. The native DOC-SHM model was used for NOM.

Geomedia Regeneration

Chemical regenerants were tested in batch to assess their recovery of metal ions by lowering pH (i.e., HCl), complexing adsorbates (i.e., EDTA) or both (i.e., citric acid). Following longevity tests, triplicate 1g samples of manganese oxide-coated sand from each column were added to polystyrene containers with 50 mL of regenerant solution and shaken for 3.5 hours. HCl solutions were applied at 100 mM and 1 mM (i.e., pH 1 and pH 3). The EDTA and citric acid were each applied at a 1:1 and 2:1 stoichiometric ratio of ligand to mass of adsorbed metal ion (Table S4). Regenerant solutions were unbuffered. Metal speciation was modeled in Visual MINTEQ with the parameters noted above and the concentrations of ligands shown in Table S4.

Regenerant solution was sampled every 60-120 minutes and analyzed by ICP-MS to determine the amount of metal ion desorbed from the manganese oxide surface.

The pH 3 HCl solution was evaluated as a regenerant in columns for 150 pore volumes (50 hours) at a flow rate of 0.4 mL/min. Column regeneration effluent was sampled approximately every 20 pore volumes for analysis by ICP-MS. Geomedia was analyzed no more than 24 hours after regeneration.

Geomedia Characterization

The geomedia from the front and back halves of the columns were individually collected, homogenized, and air dried at 30 °C prior to quantifying Mn coating density and total adsorbed metal ion concentration. The coatings of triplicate geomedia samples were dissolved with ascorbic acid. The dissolved metals were quantified by ICP-MS.

Scanning electron microscopy (SEM) was performed with a Zeiss EVO MA10 scanning electron microscope at 20 kV and a 1 nA current. Energy dispersive X-ray spectroscopy (EDS) was performed with an EDAX Genesis Imaging/Mapping analyzer.

The pH_{pnpzc} of the manganese oxide-coated sand was determined by sonicating the geomedia and diluting the coating material suspension with HCl to produce various pH conditions. The zeta potential was measured using a Malvern Zetasizer Nano. The pH_{pznpc} was approximated using a linear fit of zeta potential vs. pH within 0.5 pH units of the pH_{IEP}.

Results and Discussion

Batch Adsorption Experiments

Each metal was tested individually in batch experiments in NOM-free simulated stormwater at pH 5 and pH 7, and at pH 7 in the presence of NOM. At pH 7 in the absence of NOM, over 95% of Cu, Cd and Pb and 50% of Zn were removed from solutions at metal ion concentrations typical of stormwater (Table 1). Under the same conditions with 8.0 mg-C/L Suwannee River NOM present, only about 50% and 70% of Cu and Zn were adsorbed, respectively, but over 90% of the Cd and Pb were adsorbed.

In the absence of NOM, Pb was the most strongly adsorbed metal ion, followed by Cu, Cd and Zn, respectively (Figures S1 and S2). These relative affinities are consistent with previous findings of manganese oxide selectivity.[22,26–28,36–38] The Ca in solution may have competed with Zn and Cd (e.g., due to similar valence electron configuration), but it has a smaller effect on Cu or Pb adsorption.[14,26]

Langmuir and Freundlich models were applied to the adsorption isotherm data (Figures S1, S2 and S3). The Freundlich model was expressed by the relationship:

$$q = K_F {C_e}^{1/n} \qquad \text{(Eq. 2)}$$

where q [mol Me/mg MnOx] is the concentration of the adsorbate on the adsorbent, C_e is the equilibrium activity of the adsorbate, and K_F and n are constants (Table 2).

Freundlich models fit the results better than Langmuir models for all metal ions tested (data not shown). Freundlich models consistently fit the data well ($R^2 > 0.97$ for the linear regression of log(q) vs. log(C_e)), except for Cu and Pb in NOM-free pH 7 simulated stormwater, where dissolved metal ion concentrations were often below the detection limit (i.e., 0.4 nM).

Values of n in the Freundlich model near 1 indicate nearly linear adsorption of Pb in all conditions and of Cu in the presence of NOM. Linear adsorption implies uniform site strength in the concentrations range tested (i.e., many strong sites for Pb adsorption and sites that compete weakly for Cu relative to NOM). In the Freundlich model—which represents a multi-site Langmuir model in which site abundance decreases geometrically with increasing affinity[39,40]—the moderate values of n for Zn, Cd, and NOM-free Cu are consistent with adsorption involving multiple sites or mechanisms with different adsorption energies.[28,41] Differences in apparent equilibrium binding constants depending on manganese oxide fractional surface coverage and contribute to site heterogeneity.[26] The Freundlich equation is consistent with the prevailing mechanistic models of specific adsorption to manganese oxides[26,27] and other research fits adsorption to manganese oxide with Freundlich or multi-component Langmuir models.[25,28,36,41,42]

These experiments did not account for competition among metal ions. Notably, Pb-impacted stormwater may reduce the adsorption capacity for Cu, Zn and Cd.[26,27]

Metal ion removal decreased when NOM was present, although adsorption isotherms still fit a Freundlich model (Figure S3).[43] Cu adsorption was the most diminished by the presence of NOM, followed by Pb. This result was consistent with the relative magnitudes of the stability constants for metal-NOM complexes: $Cu^{2+} > Pb^{2+} >> Zn^{2+} \approx Cd^{2+}$.[44–48] Dissolved metal-NOM complexes compete with the mineral surface.[49–51] Reductive dissolution of the manganese oxide by NOM also may have slightly diminished adsorption. This reaction produces Mn^{2+}, which can compete with the metal ion contaminants.[49]

The NOM concentration in these experiments is similar to typical urban stormwater.[34,52] However, dissolved organic matter concentrations as high as 73 mg-C/L have been observed in stormwater.[6,52] Sigma humic acid is well-characterized and practical for tests using large volumes of water, but it is not representative of NOM with respect to metal ion complexing functional groups, particularly in comparison to

Suwannee River reverse osmosis isolate.[53,54] However, the two types of NOM had similar effects on metal ion adsorption in this system (Figure S3, Table 2). Therefore, we concluded that Sigma humic acid is a reasonable, reproducible surrogate NOM for assessing the performance of the manganese oxide-coated sand.

The geomedia adsorbed all metal ions more strongly at pH 7 than at pH 5. The linearity of the adsorption isotherm and relative strength of adsorption between metal ions (i.e., Pb followed by Cu, Cd and Zn) remained consistent between the two pH conditions. Stronger adsorption is expected at higher pH conditions because the formation of surface-metal complexes (e.g., $>MnO\text{-}Me^{+}$) or hydrolysis species (e.g., $>MnO\text{-}MeOH$) displaces surface-associated protons.[22,55] The more electronegative surface charge at the higher pH may have contributed to greater adsorption.[36,56] Furthermore, metal hydrolysis species are more abundant at high pH values. Hydrolysis species have lower hydration energies than unhydrolyzed cations, and typically are the dominant surface species above pH 6.[26,28,56,57]

Stormwater may have pH values near 5 prior to its interaction with soil minerals (i.e., when its composition is similar to rainwater) or as a result of anthropogenic acidification.[6,52] The batch results at pH 5 demonstrate that manganese oxide-coated sand is a viable treatment technology in a “worst-case” pH condition in which this geomedia might be deployed.

Column Longevity Tests

Columns of manganese oxide-coated sand removed more than 80% of each metal ion for the first 240 pore volumes in NOM-free stormwater (Figure 1). The relative removal of metal ions followed the same trends observed in the batch experiments. Copper and Pb removal remained high throughout 2200 pore volumes. Zinc breakthrough occurred after 970 pore volumes, with incomplete removal prior to breakthrough. Complete breakthrough of Cd occurred after 1420 pore volumes.

The manganese oxide coating was responsible for the removal of metal ions. Acid-washed sand columns exhibited rapid breakthrough (i.e., $C/C_0 \approx 1$ after 240 pore volumes for Cu, Zn and Cd and after 720 pore volumes for Pb; Figure S4). SEM/EDS showed co-location of the adsorbed metal ion and Mn coating on the geomedia (e.g., Cd; Figure S5).

Copper and Pb, the two metal ions that did not exhibit breakthrough in these experiments, had considerably higher masses of adsorbed metal ions on the front half of geomedia compared to the back half of geomedia (Table S5). Little Pb may have reached the back half of the column due to the low mass applied relative to the high adsorption capacity of manganese oxide: adsorbed Pb on the geomedia in the front half of the column remained two orders of magnitude below the reported saturation capacity.[14,58] Copper concentrations on the front half of the geomedia were likely near saturation by the end of the column experiment,[58] but the low Cu concentration on the back half of geomedia implies that significant capacity remained in the columns after 2200 pore volumes had been applied. These results suggest that equilibrium was reached quickly within the columns with little mass transfer limitation.

For columns in which breakthrough occurred (i.e., Zn and Cd), the geomedia in the front and back halves adsorbed similar concentrations of metal ions (Table S5). We assume that these concentrations correspond to the adsorption capacity of the manganese oxide-coated sand in the absence of competing metal ion contaminants. The geomedia adsorption capacity was approximately 0.8 mmol Cd/g manganese oxide. This value is approximately half of a previously reported capacity, possibly due to competition by Ca^{2+} or differences between the manganese oxide coating and pure minerals.[14,28,58,59] The adsorption capacity for Zn was approximately 3 mmol Zn/g manganese oxide, which is consistent with previously reported capacities.[28]

Copper and Pb removal in columns decreased markedly in the presence of natural organic matter (Figure 1). The impact of NOM was closely related to the abundance of metal ions complexed by NOM, as predicted by equilibrium models (Table 3). Over 96% of Cu and Pb in this system were predicted to be complexed by NOM. Surface complexation models suggest that the free metal ion and its first two hydrolysis species are important for adsorption on manganese oxides.[26,28,41] The large decline in the abundance of these species in the presence of NOM may explain the incomplete removal of the Cu and Pb.

Zinc and Cd removal were less strongly affected, consistent with their weaker complexation by NOM.[44,47] Equilibrium models indicate that less than 25% of Zn and Cd were complexed by NOM in the simulated stormwater.

Other mechanisms may have had only small impacts on metal ion adsorption in the presence of NOM. For example, NOM is unlikely to block a large number of adsorptive sites because manganese oxides repulse negatively charged NOM by electrostatics.[49] (The pH_{pznpc} of the coating of the geomedia was approximately 3.3.)[11]

The manganese oxide-coated sand initially had a coating density of 1.17 ± 0.30 mg Mn/g geomedia. Over the experiment, approximately 1% of the manganese oxide coating (i.e., approximately 100 μg Mn) was lost in the effluent, likely due to reduction by the phenolic groups (approximately 100 μeq) in the NOM.[18,60,61] Average effluent Mn concentrations (approximately 0.6 μM), were much lower than concentrations of the metal ion contaminants (Figure S6).

Dissolved Mn can be an aesthetic concern in drinking water at concentrations as low as 1.4 μM;[62] the US EPA secondary standard for maximum total dissolved Mn is 0.91 μM.[63] The concentrations observed in this experiment suggest the Mn released by columns is unlikely to be a water quality concern, especially if the water is diluted in the aquifer or if dissolved Mn adsorbs onto surfaces as it travels through the aquifer.

In conjunction with other geomedia, manganese oxide-coated sand could be deployed for metals treatment in high NOM stormwater. Operators could use carbonaceous geomedia (e.g., biochar) prior to manganese oxide-coated sand to remove organic matter and enhance the geomedia performance.[64]

Geomedia Regeneration

Three different chemical treatments were evaluated in batch to determine the most effective regenerant of the manganese oxide-coated sand (Figure 2). HCl was the most effective regenerant. Metal ion desorption occurred rapidly at pH 1 and pH 3: Nearly all adsorbed Cu, Zn and Cd were released after 3.5 hours.

EDTA applied at 1:1 and 2:1 stoichiometric ratios relative to the mass of adsorbed metal yielded > 70 % recovery of Zn, but less removal of the adsorbed of Cu, Cd, and Pb. Equilibrium models indicated that virtually all of the dissolved metal ions were complexed by EDTA.

Citric acid, applied at 1:1 and 2:1 ratios relative to the mass of adsorbed metal, removed Zn well, but less than 50% of the Cu, Cd, and Pb. The equilibrium model indicated that over 90% of dissolved Cu was complexed by citrate, but only about 50% of dissolved Zn and less than 5% of dissolved Cd and Pb were complexed by citrate. These results indicate that complexation was more important for release of adsorbed metal ions by organic ligands than their effect on solution pH (3.9 to 6.5; Tables S6 and S7).

No batch regeneration treatment removed more than 25% of the adsorbed Pb. Similar results have been reported previously: A 2.5% acetic acid solution did not release Pb from manganese oxide,[22] and 0.5 M HCl was required to desorb Pb from manganese oxide-coated tea waste.[14] Lead forms strong triple-corner-sharing complexes over internal vacancies in phyllomangate interlayers as a result of its electronic properties.[14,20,38] Pb ions also enter the interlayer and tunnels of manganese oxides.[12] Substitution reactions facilitating the formation of Pb-Mn minerals such as coronadite are unlikely, even at high Pb surface concentrations.[22] Adsorbed Pb ions were probably not further oxidized. The oxidation potential of Pb^{2+} (+1.46 V) implies oxidation is only thermodynamically possible by forms of manganese oxide—Mn_2O_3 (+1.48 V) and Mn_3O_4 (+1.81 V)—that were unlikely to be present.[11,65] Investigations of Pb^{2+} oxidation by manganese oxide have found no evidence of such a reaction, likely due to slow kinetics.[12,22]

These results suggest that Pb adsorption on manganese oxide-coated geomedia is practically irreversible under the conditions likely to be encountered in infiltration systems. The strong adsorption is not problematic for this application because of the very high capacity of the manganese oxides for Pb. Lead concentrations in stormwater are low relative to the geomedia adsorption capacity, so saturation and breakthrough are very unlikely during treatment system lifetime. Further, environmental perturbations are unlikely to release Pb from a manganese oxide-coated sand.

All regeneration treatments released some Mn (Figure 3). Approximately 5% and 2% of the manganese oxide coating was released during batch treatment with pH 1 HCl and pH 3, respectively, which is consistent with the solubility of birnessite ($k_{sp} = 10^{-15.62}$).[35] EDTA and citric acid treatments also released some Mn: 11% of the Mn coating was lost during treatment with 146 μM EDTA and 9% was lost with 146 μM citric acid.

These data suggest that both lowering pH and adding ligands release adsorbed metal ions, but that lowering pH is a more efficient regeneration technique. A pH 3 HCl solution was selected for *in situ* column regeneration because of its nearly complete desorption of Cu, Zn and Cd, while leaving the geomedia coating intact.

Following longevity tests, columns were regenerated by passing pH 3 HCl through them for 150 pore volumes. Copper, Zn and Cd were released rapidly. Over 96% of the adsorbed Cu, Zn and Cd were recovered from columns that treated NOM-free and NOM-containing simulated stormwater (Figures S7 and S8). In both conditionds, approximately 0.2% of the adsorbed Pb was recovered.

If the infiltration system were hydraulically isolated through the use of geotextile liners and valved underdrains, the effluent regenerant solution and desorbed metal ions could be collected for disposal or further treatment.

In NOM-free columns, approximately 290 μg of Mn were lost during regeneration (Figure S9) and the coating density was unchanged (1.30 ± 0.23 mg Mn/g geomedia). In columns treating NOM-containing simulated stormwater, 1200 μg of Mn were lost during regeneration the Mn coating density decreased approximately 13% to 1.02 ± 0.05 mg Mn/g geomedia.

Longevity tests following regeneration demonstrated that, in all stormwater conditions and for all metal ions, the regenerated geomedia had a similar adsorptive capacity and longevity to that of the virgin geomedia (Figure 1). This result implies that the useful lifetime of systems employing this geomedia could be at least doubled by regeneration with a mild acid.

Geomedia Lifetime

Given its high capacity for metal ions in stormwater, manganese oxide-coated sand geomedia may be an attractive technology for managed aquifer recharge, provided that the geomedia exhibits a suitable lifetime. The typical lifetime of a system employing this geomedia to remove metal ions can be projected by dividing the adsorption capacity of a bed of manganese oxide coated-sand geomedia (determined from column experiments) by the typical metal ion load in stormwater.

$$\frac{\text{media capacity [moles]}}{\text{metal load}\left[\frac{\text{moles}}{\text{yr}}\right]} = \text{lifetime [years]} \qquad \text{(Eq. 3)}$$

We projected the lifetimes (Figure 4) for typical infiltration systems covering a 50 m^2 area with a 0.5 m-deep layer of manganese oxide-coated sand, assuming average stormwater metals concentrations (Table S1).

Copper and Pb in NOM-free simulated stormwater did not exhibit breakthrough in the column experiments and the Freundlich model (unlike the Langmuir model) cannot be used to calculate a theoretical adsorptive capacity (i.e., q_{max}). Therefore, we estimated the minimum operational lifetime of these systems based on column experiment duration.

Actual lifetimes would likely be longer by a factor of approximately 2 (for Cu) to 10 (for Pb), based on previously measured adsorption capacities.[27,36]

Lifetime calculations (SI: Lifetime Estimation, Table S8) indicate that the system described could operate for several decades before the complete loss of adsorption capacity for any metal ion tested. The geomedia lifetime could be significantly prolonged by periodic regeneration with pH 3 HCl. Regeneration could occur before the complete breakthrough of a metal ion in order to maintain maximum pollutant removal and to minimize the risk of desorption.

System lifetime may be less in highly contaminated stormwater with elevated concentrations of metal ions. Further, co-contamination by metals is probable in stormwater. Lead adsorption is unlikely to be affected by the presence other metal ions.[26] However, co-contamination could result in faster breakthrough of Cu, Zn and Cd than predicted individually.[27,28] Large loads of oxidizable organic carbon in the stormwater matrix may also diminish the number of adsorptive sites on the geomedia and increase competition by Mn^{2+}.[49]

Conclusions

This research demonstrates that manganese oxide-coated sand can remove metal contaminants from stormwater for extended periods. The geomedia is relatively simple to produce and regenerate without excavation, making it practical for use in aquifer recharge or municipal water treatment applications. Regeneration could extend the lifetime of the geomedia, but a mild acid wash could pose some environmental risks. For example, if not captured, the released metal ions could contaminate aquifers and the acidic regenerant solution could release adsorbed species, such as arsenic in the aquifer.[66]

Metal ion breakthrough is unlikely to limit the lifetime of stormwater infiltration systems employing this geomedia. Other failure mechanisms, including clogging by suspended sediments and biofilm growth, would probably limit the system lifetime before adsorption capacity is exhausted.[10,67] Additional research should be conducted to assess manganese oxide-coated sand performance under field conditions.

Manganese oxide-coated sand can oxidize organic contaminants in stormwater. These results suggest that Cd and Pb could be removed from stormwater for longer than the predicted lifetime for the oxidative removal of organic contaminants.[11]

Acknowledgements

This research was supported by the National Science Foundation (NSF) through the Engineering Research Center for Re-Inventing the Nation's Water Infrastructure (ReNUWIt) EEC-1028968 and by the National Science Foundation Graduate Research Fellowship under Grant No. DGE 1106400.

The authors thank Francis Ledesma for his assistance in performing adsorption isotherm experiments.

Supporting Information

Details of methodology, SEM/EDS micrographs, detailed results of batch isotherms and column experiments, and estimation of geomedia lifetime.

References

(1) Page, D.; Miotliński, K.; Gonzalez, D.; Barry, K.; Dillon, P.; Gallen, C. Environmental Monitoring of Selected Pesticides and Organic Chemicals in Urban Stormwater Recycling Systems Using Passive Sampling Techniques. *J. Contam. Hydrol.* 2014, *158*, 65–77. https://doi.org/10.1016/j.jconhyd.2014.01.004.

(2) Edwards, E. C.; Harter, T.; Fogg, G. E.; Washburn, B.; Hamad, H. Assessing the Effectiveness of Drywells as Tools for Stormwater Management and Aquifer Recharge and Their Groundwater Contamination Potential. *J. Hydrol.* 2016, *539*, 539–553. https://doi.org/10.1016/j.jhydrol.2016.05.059.

(3) Regnery, J.; Lee, J.; Kitanidis, P.; Illangasekare, T.; Sharp, J. O.; Drewes, J. E. Integration of Artificial Recharge and Recovery Systems for Impaired Water Sources in Urban Settings: Overcoming Current Limitations and Engineering Challenges. *Environ. Eng. Sci.* 2013, *30* (8), 409–420. https://doi.org/10.1089/ees.2012.0186.

(4) Andres, A. S.; Ballestero, T. P.; Musick, M. L. Stormwater Management: When Is Green Not So Green? *Groundwater* 2018, *56* (3), 357–358. https://doi.org/10.1111/gwat.12653.

(5) Masoner, J. R.; Kolpin, D. W.; Cozzarelli, I. M.; Barber, L. B.; Burden, D. S.; Foreman, W. T.; Forshay, K. J.; Furlong, E. T.; Groves, J. F.; Hladik, M. L.; et al. Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants to Surface and Groundwaters in the United States. *Environ. Sci. Technol.* 2019. https://doi.org/10.1021/acs.est.9b02867.

(6) Pitt, R.; Maestre, A.; Morquecho, R. National Stormwater Quality Database, Version 4.02. Dept. of Civil and Environmental Engineering, University of Alabama,Tuscaloosa March 17, 2015.

(7) Los Angeles County Flood Control District; City of Los Angeles Department of Public Works Bureau of Sanitation. *Concept Report: Strathern Pit Multiuse Project*; Concept Report; 2006.

(8) Page, D.; Dillon, P.; Vanderzalm, J.; Toze, S.; Sidhu, J.; Barry, K.; Levett, K.; Kremer, S.; Regel, R. Risk Assessment of Aquifer Storage Transfer and Recovery with Urban Stormwater for Producing Water of a Potable Quality. *J. Environ. Qual.* 2010, *39* (6), 2029–2039. https://doi.org/10.2134/jeq2010.0078.

(9) Daigger, G. T. Evolving Urban Water and Residuals Management Paradigms: Water Reclamation and Reuse, Decentralization, and Resource Recovery. *Water Environ. Res.* 2009, *81* (8), 809–823. https://doi.org/10.2175/106143009X425898.

(10) Hatt, B. E.; Fletcher, T. D.; Deletic, A. Hydraulic and Pollutant Removal Performance of Fine Media Stormwater Filtration Systems. *Environ. Sci. Technol.* 2008, *42* (7), 2535–2541. https://doi.org/10.1021/es071264p.

(11) Charbonnet, J. A.; Duan, Y.; van Genuchten, C. M.; Sedlak, D. L. Chemical Regeneration of Manganese Oxide-Coated Sand for Oxidation of Organic Stormwater Contaminants. *Environ. Sci. Technol.* 2018, *52* (18), 10728–10736. https://doi.org/10.1021/acs.est.8b03304.

(12) O'Reilly, S. E.; Hochella, M. F. Lead Sorption Efficiencies of Natural and Synthetic Mn and Fe-Oxides. *Geochim. Cosmochim. Acta* 2003, *67* (23), 4471–4487. https://doi.org/10.1016/S0016-7037(03)00413-7.

(13) Adams, J. P.; Kirst, R.; Kearns, L. E.; Krekeler, M. P. S. Mn-Oxides and Sequestration of Heavy Metals in a Suburban Catchment Basin of the Chesapeake Bay Watershed. *Environ. Geol.* 2009, *58* (6), 1269–1280. https://doi.org/10.1007/s00254-008-1628-y.

(14) Wan, S.; Qu, N.; He, F.; Wang, M.; Liu, G.; He, H. Tea Waste-Supported Hydrated Manganese Dioxide (HMO) for Enhanced Removal of Typical Toxic Metal Ions from Water. *RSC Adv* 2015, *5* (108), 88900–88907. https://doi.org/10.1039/C5RA16556C.

(15) Murray, J. W. The Interaction of Metal Ions at the Manganese Dioxide-Solution Interface. *Geochim. Cosmochim. Acta* 1975, *39* (4), 505–519. https://doi.org/10.1016/0016-7037(75)90103-9.

(16) Liu, D.; Sansalone, J. J.; Cartledge, F. K. Comparison of Sorptive Filter Media for Treatment of Metals in Runoff. *J. Environ. Eng.* 2005, *131* (8), 1178–1186. https://doi.org/10.1061/(ASCE)0733-9372(2005)131:8(1178).

(17) McKenzie, R. M. The Surface Charge on Manganese Dioxides. *Soil Res.* 1981, *19* (1), 41–50.

(18) Stone, A. T.; Morgan, J. J. Reduction and Dissolution of Manganese (III) and Manganese (IV) Oxides by Organics: 2. Survey of the Reactivity of Organics. *Environ. Sci. Technol.* 1984, *18* (8), 617–624.

(19) Peña, J.; Kwon, K. D.; Refson, K.; Bargar, J. R.; Sposito, G. Mechanisms of Nickel Sorption by a Bacteriogenic Birnessite. *Geochim. Cosmochim. Acta* 2010, *74* (11), 3076–3089. https://doi.org/10.1016/j.gca.2010.02.035.

(20) Villalobos, M.; Bargar, J.; Sposito, G. Mechanisms of Pb(II) Sorption on a Biogenic Manganese Oxide. *Environ. Sci. Technol.* 2005, *39* (2), 569–576. https://doi.org/10.1021/es049434a.

(21) Boonfueng, T.; Axe, L.; Yee, N.; Hahn, D.; Ndiba, P. K. Zn Sorption Mechanisms onto Sheathed Leptothrix Discophora and the Impact of the Nanoparticulate Biogenic Mn Oxide Coating. *J. Colloid Interface Sci.* 2009, *333* (2), 439–447. https://doi.org/10.1016/j.jcis.2009.02.033.

(22) McKenzie, R. The Adsorption of Lead and Other Heavy Metals on Oxides of Manganese and Iron. *Aust. J. Soil Res.* 1980, *18* (1), 61. https://doi.org/10.1071/SR9800061.

(23) Misono, M.; Ochiai, E.; Saito, Y.; Yoneda, Y. A New Dual Parameter Scale for the Strength of Lewis Acids and Bases with the Evaluation of Their Softness. *J. Inorg. Nucl. Chem.* 1967, *29* (11), 2685–2691. https://doi.org/10.1016/0022-1902(67)80006-X.

(24) Sposito, G. *The Chemistry of Soils*, 2nd ed.; Oxford University Press: New York, 2008.

(25) Li, X.; Pan, G.; Qin, Y.; Hu, T.; Wu, Z.; Xie, Y. EXAFS Studies on Adsorption–Desorption Reversibility at Manganese Oxide–Water Interfaces. *J. Colloid Interface Sci.* 2004, *271* (1), 35–40. https://doi.org/10.1016/j.jcis.2003.11.029.

(26) Catts, J. G.; Langmuir, D. Adsorption of Cu, Pb and Zn by Delta-MnO2: Applicability of the Site Binding-Surface Complexation Model. *Appl. Geochem.* 1986, *1*, 255–264.

(27) Gadde, R. Rao.; Laitinen, H. A. Heavy Metal Adsorption by Hydrous Iron and Manganese Oxides. *Anal. Chem.* 1974, *46* (13), 2022–2026. https://doi.org/10.1021/ac60349a004.

(28) Zasoski, R. J.; Burau, R. G. Sorption and Sorptive Interaction of Cadmium and Zinc on Hydrous Manganese Oxide. *Soil Sci. Soc. Am. J.* 1988, *52* (1), 81. https://doi.org/10.2136/sssaj1988.03615995005200010014x.

(29) Drewes, J. E. Ground Water Replenishment with Recycled Water-Water Quality Improvements during Managed Aquifer Recharge. *Ground Water* 2009, *47* (4), 502–505. https://doi.org/10.1111/j.1745-6584.2009.00587_5.x.

(30) Grebel, J. E.; Mohanty, S. K.; Torkelson, A. A.; Boehm, A. B.; Higgins, C. P.; Maxwell, R. M.; Nelson, K. L.; Sedlak, D. L. Engineered Infiltration Systems for Urban Stormwater Reclamation. *Environ. Eng. Sci.* 2013, *30* (8), 437–454. https://doi.org/10.1089/ees.2012.0312.

(31) Ulrich, B. A.; Loehnert, M.; Higgins, C. P. Improved Contaminant Removal in Vegetated Stormwater Biofilters Amended with Biochar. *Environ. Sci. Water Res. Technol.* 2017, *3* (4), 726–734. https://doi.org/10.1039/C7EW00070G.

(32) Amrhein, C.; Strong, J. E.; Mosher, P. A. Effect of Deicing Salts on Metal and Organic Matter Mobilization in Roadside Soils. *Environ. Sci. Technol.* 1992, *26* (4), 703–709. https://doi.org/10.1021/es00028a006.

(33) US Environmental Protection Agency. *Preliminary Data Summary of Urban Stormwater Best Management Practices*; 1999; p Chapter 4.

(34) Grebel, J. E.; Charbonnet, J. A.; Sedlak, D. L. Oxidation of Organic Contaminants by Manganese Oxide Geomedia for Passive Urban Stormwater Treatment Systems. *Water Res.* 2016, *88*, 481–491. https://doi.org/10.1016/j.watres.2015.10.019.

(35) Gustafsson, J. P. *Visual MINTEQ 3.1 User Guide*; KTH, Department of Land and Water Recources: Stockholm, Sweden, 2014.

(36) Fu, G.; Allen, H.; Cowan, C. Adsorption of Cadmium and Copper by Manganese Oxide. *Soil Sci.* 1991, *152* (2), 72–81.

(37) van Lienden, C.; Shan, L.; Rao, S.; Ranieri, E.; Young, T. M. Metals Removal from Stormwater by Commercial and Non-Commercial Granular Activated Carbons. *Water Environ. Res.* 2010, *82* (4), 351–356. https://doi.org/10.2175/106143009X12487095236874.

(38) Wang, Z. J.; Stumm, W. Heavy Metal Complexation by Surfaces and Humic Acids: A Brief Discourse on Assessment by Acidimetric Titration. *Neth. J. Agric. Sci.* 1987, *35*, 231–240.

(39) Benjamin, M. M.; Lawler, D. F. *Water Quality Engineering: Physical / Chemical Treatment Processes*; John Wiley & Sons, 2013.

(40) Halsey, G.; Taylor, H. S. The Adsorption of Hydrogen on Tungsten Powders. *J. Chem. Phys.* 1947, *15* (9), 624–630. https://doi.org/10.1063/1.1746618.

(41) Loganathan, P.; Burau, R. G. Sorption of Heavy Metal Ions by a Hydrous Manganese Oxide. *Geochim. Cosmochim. Acta* 1973, *37* (5), 1277–1293. https://doi.org/10.1016/0016-7037(73)90061-6.

(42) Caliskan, N.; Kul, A. R.; Alkan, S.; Sogut, E. G.; Alacabey, İ. Adsorption of Zinc(II) on Diatomite and Manganese-Oxide-Modified Diatomite: A Kinetic and Equilibrium Study. *J. Hazard. Mater.* 2011, *193*, 27–36. https://doi.org/10.1016/j.jhazmat.2011.06.058.

(43) Frimmel, F. H.; Huber, L. Influence of Humic Substances on the Aquatic Adsorption of Heavy Metals on Defined Mineral Phases. *Environ. Int.* 1996, *22* (5), 507–517.

(44) Cabaniss, S. E. Forward Modeling of Metal Complexation by NOM: I. *A Priori* Prediction of Conditional Constants and Speciation. *Environ. Sci. Technol.* 2009, *43* (8), 2838–2844. https://doi.org/10.1021/es8015793.

(45) Stevenson, F. J. Stability Constants of Cu2+, Pb2+, and Cd2+ Complexes with Humic Acids. *Soil Sci Soc Am J* 1976, *40* (5), 665–672.

(46) Takamatsu, T.; Yoshida, T. Determination of Stability Constants of Metal-Humic Acid Complexes by Potentiometric Titration and Ion-Selective Electrodes. *Soil Sci.* 1978, *125* (6), 377–386.

(47) Saar, R. A.; Weber, J. H. Lead(II)-Fulvic Acid Complexes. Conditional Stability Constants, Solubility, and Implications for Lead(II) Mobility. *Environ. Sci. Technol.* 1980, *14* (7), 877–880. https://doi.org/10.1021/es60167a001.

(48) Christensen, J. B.; Christensen, T. H. Complexation of Cd, Ni, and Zn by DOC in Polluted Groundwater: A Comparison of Approaches Using Resin Exchange, Aquifer Material Sorption, and Computer Speciation Models (WHAM and MINTEQA2). *Environ. Sci. Technol.* 1999, *33* (21), 3857–3863. https://doi.org/10.1021/es981105t.

(49) Godtfredsen, K. L.; Stone, A. T. Solubilization of Manganese Dioxide-Bound Copper by Naturally Occurring Organic Compounds. *Environ. Sci. Technol.* 1994, *28* (8), 1450–1458. https://doi.org/10.1021/es00057a012.

(50) Schmitt, D.; Saravia, F.; Frimmel, F. H.; Schuessler, W. NOM-Facilitated Transport of Metal Ions in Aquifers: Importance of Complex-Dissociation Kinetics and Colloid Formation. *Water Res.* 2003, *37* (15), 3541–3550. https://doi.org/10.1016/S0043-1354(01)00525-5.

(51) Christensen, J. B.; Jensen, D. L.; Christensen, T. H. Effect of Dissolved Organic Carbon on the Mobility of Cadmium, Nickel and Zinc in Leachate Polluted Groundwater. *Water Res.* 1996, *30* (12), 3037–3049. https://doi.org/10.1016/S0043-1354(96)00091-7.

(52) California Department of Transportation. *Storm Water Monitoring & Data Management: 2002-2003 Annual Data Summary Report*; CTSW-RT-03-069.51.42; Sacramento, CA, 2003.

(53) Kim, H.-C.; Dempsey, B. A. Membrane Fouling Due to Alginate, SMP, EfOM, Humic Acid, and NOM. *J. Membr. Sci.* 2013, *428*, 190–197. https://doi.org/10.1016/j.memsci.2012.11.004.

(54) Niederer, C.; Schwarzenbach, R. P.; Goss, K.-U. Elucidating Differences in the Sorption Properties of 10 Humic and Fulvic Acids for Polar and Nonpolar Organic Chemicals. *Environ. Sci. Technol.* 2007, *41* (19), 6711–6717. https://doi.org/10.1021/es0709932.

(55) James, R. O.; Stiglich, P. J.; Healy, T. W. Analysis of Models of Adsorption of Metal Ions at Oxide/Water Interfaces. *Faraday Discuss. Chem. Soc.* 1975, *59*, 142. https://doi.org/10.1039/dc9755900142.

(56) Loganathan, P.; Burau, R. G.; Fuerstenau, D. W. Influence of PH on the Sorption of Co2+, Zn2+ and Ca2+ by a Hydrous Manganese Oxide1. *Soil Sci. Soc. Am. J.* 1977, *41* (1), 57. https://doi.org/10.2136/sssaj1977.03615995004100010020x.

(57) James, R. O.; Healy, T. W. Adsorption of Hydrolyzable Metal Ions at the Oxide—Water Interface. III. A Thermodynamic Model of Adsorption. *J. Colloid Interface Sci.* 1972, *40* (1), 65–81. https://doi.org/10.1016/0021-9797(72)90174-9.

(58) Han, R.; Zou, W.; Zhang, Z.; Shi, J.; Yang, J. Removal of Copper(II) and Lead(II) from Aqueous Solution by Manganese Oxide Coated Sand. *J. Hazard. Mater.* 2006, *137* (1), 384–395. https://doi.org/10.1016/j.jhazmat.2006.02.021.

(59) Liu, A.; Liu, L.; Li, D.; Guan, Y. Characterizing Heavy Metal Build-up on Urban Road Surfaces: Implication for Stormwater Reuse. *Sci. Total Environ.* 2015, *515–516*, 20–29. https://doi.org/10.1016/j.scitotenv.2015.02.026.

(60) Sunda, W. G.; Huntsman, S. A.; Harvey, G. R. Photoreduction of Manganese Oxides in Seawater Ant Its Geochemical and Biological Implications. *Nature* 1983, *301*, 234–236.

(61) Driver, S. J.; Perdue, E. M. Acidic Functional Groups of Suwannee River Natural Organic Matter, Humic Acids, and Fulvic Acids. In *ACS Symposium Series*; Rosario-Ortiz, F., Ed.; American Chemical Society: Washington, DC, 2014; Vol. 1160, pp 75–86. https://doi.org/10.1021/bk-2014-1160.ch004.

(62) Sain, A. E.; Dietrich, A. M. Rethinking Aesthetic Guidelines for Manganese and Iron in Drinking Water. *J. Water Supply Res. Technol. - Aqua* 2015, *64* (7), 775–782. https://doi.org/10.2166/aqua.2014.091.

(63) US Environmental Protection Agency. *National Recommended Water Quality Criteria*; Office of Science and Technology: Office of Water: Washington, DC, 2004.

(64) Ulrich, B. A.; Im, E. A.; Werner, D.; Higgins, C. P. Biochar and Activated Carbon for Enhanced Trace Organic Contaminant Retention in Stormwater Infiltration Systems. *Environ. Sci. Technol.* 2015, *49* (10), 6222–6230. https://doi.org/10.1021/acs.est.5b00376.

(65) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C1 and C2 Organic Substances in Sl Units*, 1982nd ed.; Journal of Physical and Chemical Reference Data; National Bureau of Standards: Washington, D.C., 1982; Vol. 11, Supplement No. 2.

(66) Kocar, B. D.; Polizzotto, M. L.; Benner, S. G.; Ying, S. C.; Ung, M.; Ouch, K.; Samreth, S.; Suy, B.; Phan, K.; Sampson, M.; et al. Integrated Biogeochemical and Hydrologic Processes Driving Arsenic Release from Shallow Sediments to Groundwaters of the Mekong Delta. *Appl. Geochem.* 2008, *23* (11), 3059–3071. https://doi.org/10.1016/j.apgeochem.2008.06.026.

(67) Feng, W.; Hatt, B. E.; McCarthy, D. T.; Fletcher, T. D.; Deletic, A. Biofilters for Stormwater Harvesting: Understanding the Treatment Performance of Key Metals That Pose a Risk for Water Use. *Environ. Sci. Technol.* 2012, *46* (9), 5100–5108. https://doi.org/10.1021/es203396f.

Tables and Figures

Table 1. Removal of typical stormwater concentrations of metal ion contaminants in batch experiments in the presence of 18.4 mg/L manganese oxide-coated sand.

		pH 7 Simulated Stormwater, No NOM			pH 7 Simulated Stormwater, 8.0 mg-C/L Suwannee River NOM		
Metal	Average Stormwater Conc.(nM)*	Initial Conc. (nM)	Final Conc. (nM)	Removal	Initial Conc. (nM)	Final Conc. (nM)	Removal
Cu	252	310 ± 3	0.28 ± 0.02	100%	312 ± 3	164 ± 2	48%
Zn	1790	1570 ± 20	760 ± 10	52%	2940 ± 30	920 ± 10	69%
Cd	13	40 ± 1	2.1 ± 0.4	95%	41 ± 1	1 ± 0	98%
Pb	38	76 ± 1	0.68 ± 0.14	99%	75 ± 1	7 ± 0	90%

*Pitt et al. (2015)

Table 2. Freundlich constants estimated for metal ions with manganese oxide-coated sand in batch tests.

		$K_F \left[\frac{(\mathrm{mol\ Me})^{(1-\frac{1}{n})} * L^{\frac{1}{n}}}{\mathrm{mg\ MnO_x}}\right]$	n
pH 5 NOM-Free Simulated Stormwater	Cu	1.20	1.60
	Zn	0.66	1.48
	Cd	0.78	1.51
	Pb	1.20 x 10^5	0.95
pH 7 NOM-Free Simulated Stormwater	Cu	0.36	2.16
	Zn	8.6	1.20
	Cd	1.4	7.51
	Pb	N/A	N/A
pH 7 Simulated Stormwater, 8 mg-C/L Suwannee River NOM	Cu	7.5 x 10^5	0.66
	Zn	0.86	1.75
	Cd	1.7	1.72
	Pb	1.2 x 10^4	0.92
pH 7 Simulated Stormwater, 6.3 mg-C/L Sigma Humic Acid	Cu	420	0.97
	Zn	0.44	1.92
	Cd	56.0	1.20
	Pb	10 x 10^5	0.73

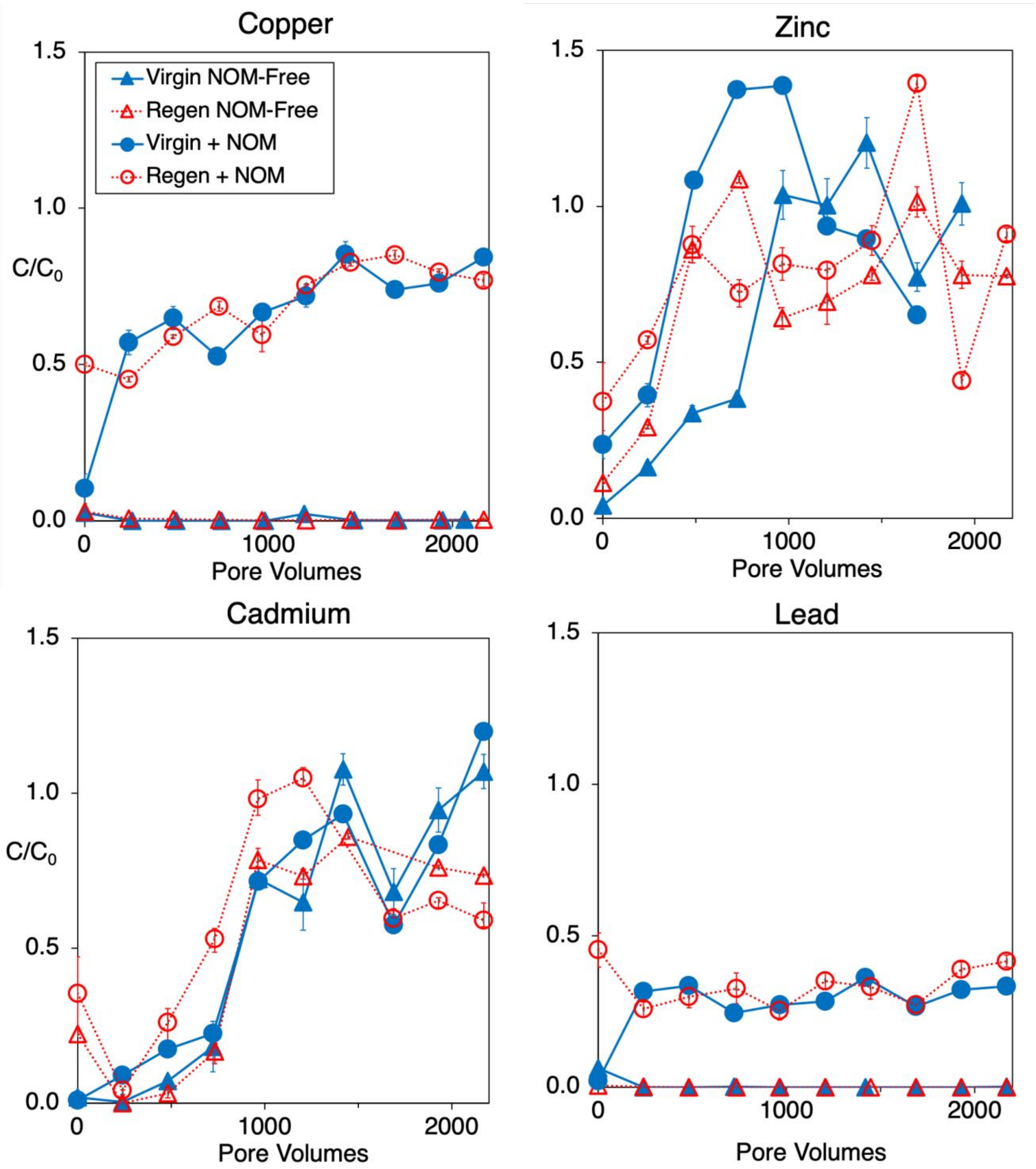


Figure 1. Relative concentration of metal ions in pH 7 simulated stormwater in effluent from columns. The X-axis designates pore volumes of experimentation beginning at 0 for both virgin (blue solid symbols and lines) and regenerated (red open symbols and dashed lines) geomedia. Simulated stormwater was either NOM-free (triangles) or contained 6.3 mg-C/L Sigma humic acid (circles). Error bars are smaller than some symbols.

Table 3. Predicted fraction of dissolved metals present as divalent cations or hydrolysis species and as metal-NOM complexes in pH 7 simulated stormwater fed to columns.

	NOM-Free Stormwater	NOM-Containing Stormwater	
	($[Me^{2+}] + [Me(OH)^{+}] + [Me(OH)_2^0]$)/$Me_T$	($[Me^{2+}] + [Me(OH)^{+}] + [Me(OH)_2^0]$)/$Me_T$	$[Me\text{-}NOM]_T / Me_T$
Cu	0.42	0.02	0.96
Zn	0.92	0.75	0.19
Cd	0.83	0.63	0.24
Pb	0.44	0.01	0.97

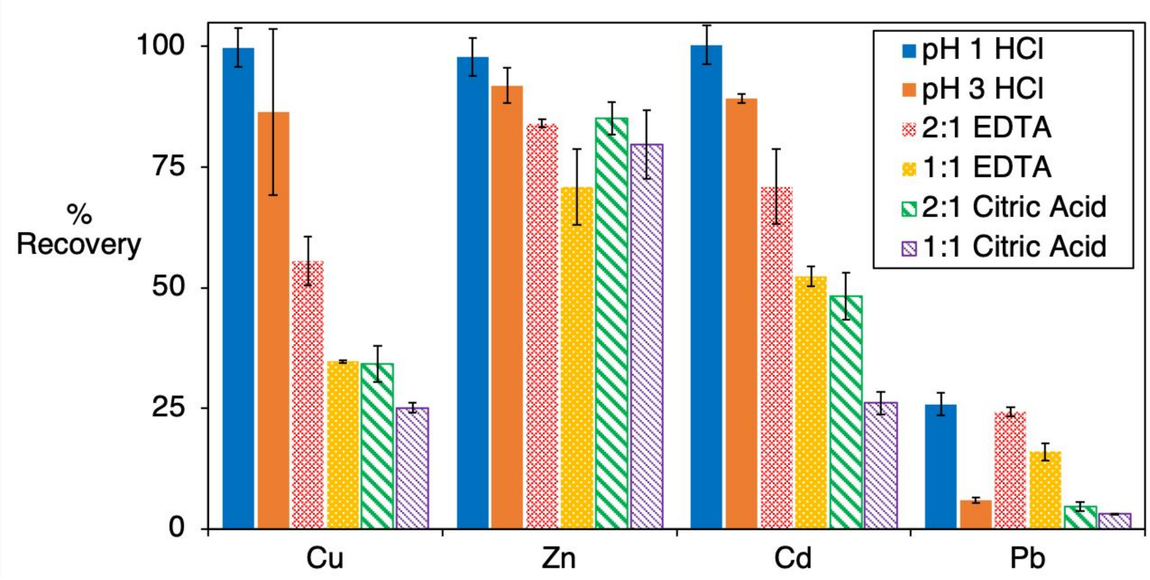


Figure 2. Percentage of the total adsorbed metal ions that were released after 3.5 h batch regeneration. 1 g of metal-saturated geomedia from column testing was shaken in 50 mL of regenerant solution containing either pH 1 or pH 3 HCl (solid), EDTA at a 2:1 or 1:1 stoichiometric ratio to the mass of adsorbed metal ion (dotted) or citric acid at a 2:1 or 1:1 stoichiometric ratio to the mass of adsorbed metal ion (striped). Error bars are from triplicate experiments.

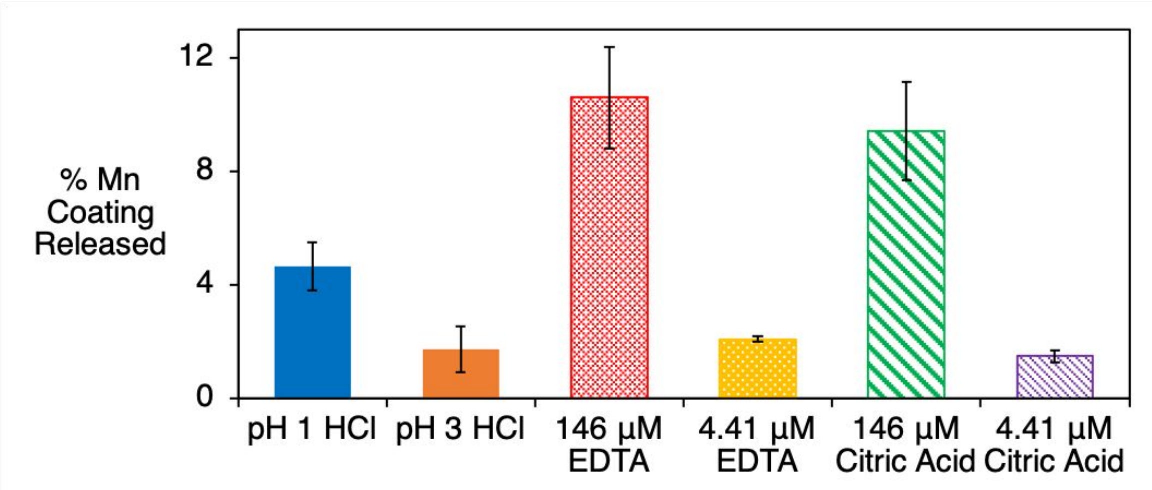


Figure 3. Percentage of geomedia coating lost during batch regeneration. 1 g of metal-saturated geomedia from column testing was stirred in 50 mL of regenerant solution. Data are shown for regeneration with pH 1 and pH 3 HCl (solid), 4.41 μM and 146 μM EDTA (dotted) and 4.41 μM or 146 μM citric acid (striped).

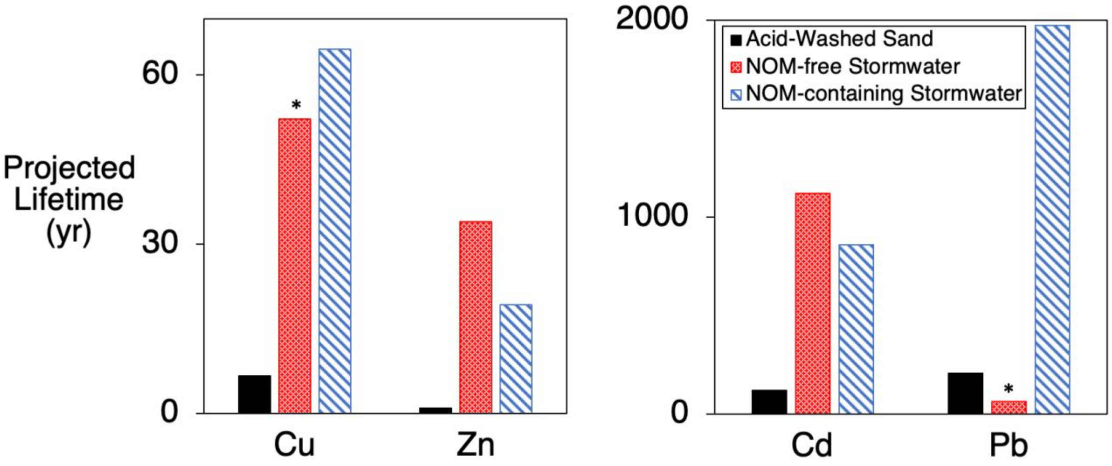
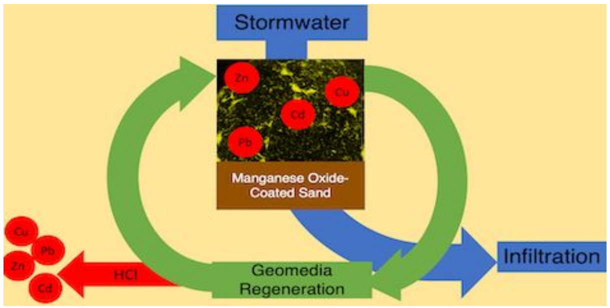


Figure 4. Projected time-to-breakthrough of a full-sized infiltration system containing acid washed sand (black), manganese oxide-coated sand treating NOM-free stormwater (red dotted) and stormwater containing 6.3 mg-C/L NOM (blue striped). Estimates for time before complete breakthrough of typical concentrations (Table S1) of Cu, Zn (left), Cd and Pb (right) without co-contaminants. *Due to lack of breakthrough, lifetime projections for Cu and Pb in NOM-free systems are the most conservative minimum operational lifetime. Based on previously measured adsorption capacities, actual lifetimes are expected to be longer.



Manganese oxide-coated sand can remove toxic metals from stormwater for years before regeneration with a mild acid. This geomedia could facilitate the use of stormwater as a water supply.