Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
This journal is © The Royal Society of Chemistry 2019

Supplemental Information for:
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)

Table S1. Typical dissolved concentrations and water quality standards for selected trace metals in stormwater.[5]

Metal	**Concentration (μg/L)**		**Water Quality Standards (μg/L)**	
	Mean	**Maximum**	**Surface Water***	**Drinking Water†**
Cu	16	1800	3	1300
Zn	117	13000	81	5000
Cd	1.5	62	0.72	5
Pb	8	525	2.5	15

*U.S. EPA recommended water quality criteria, normalized to 100 mg/L - $CaCO_3$ hardness

†U.S. EPA drinking water maximum contaminant level

Table S2. Simulated stormwater composition.

Constituent	**Concentration**	**Unit**
Ca^{2+}	0.75	mM
Mg^{2+}	0.075	mM
Na^+	1.8	mM
NH_4^+	0.072	mM
SO_4^{2-}	0.33	mM
HCO_3^-	1.0	mM
Cl^-	1.7	mM
NO_3^-	0.072	mM
$H_2PO_4^-$ *	0.016	mM
Ionic Strength	4.6	mM
Suwannee River NOM†	8.0	mg-C/L
Sigma Humic Acid‡	6.3	mg-C/L
pH	7.0	

*not included in experiments with Pb, ionic strength maintained with 0.016 mM NaCl. †Included when indicated in batch experiments

‡Included when indicated in batch and column experiments

ICP-MS Analysis

Each sample had a pre-run uptake of 45 seconds at 0.35 rotations per second (RPS) of the nebulizer pump followed by a pre-run stabilization of 30 seconds and acquisition at a pump rate determined by tuning (approximately 0.27 RPS). After acquisition, the probe was rinsed for 7 seconds in the sample and 30 seconds in each of two separate 1% HCl and 0.5% HNO_3 rinse ports at 0.35 RPS. Tuning and PA calibration were carried out using Agilent standard tuning and PA solutions without further purification. Tune parameters are listed in Table S3. Samples were quantified using a 9-point calibration curve ($R^2>0.98$ for each analyte). Samples were analyzed in triplicate with 50 sweeps per replicate and a relative standard deviation quality control threshold for analysis of <5%. Two blank verification samples were analyzed after every 20 experimental sample to assess carryover; concentrations were always below 1nM. 5% of samples were analyzed in duplicate for quality control and always had < 10% variation.

Table S3. Tuning parameters for ICP-MS Analysis.

Parameter	Value
Plasma	
RF Power	1550 W
RF Matching	1.80 V
Sample Depth	8 mm
Carrier Gas	0.56 L/min
Option Gas	0%
Nebulizer Pump	0.27 RPS
S/C Temp	5 °C
Gas Switch	Dilution Gas
Dilution Gas	0.45 L/min
Lenses	
Extract 1	0 V
Extract 2	-200.0 V
Omega Bias	-120 V
Omega Lens	10.0 V
Cell Entrance	-40 V
Cell Exit	-60 V
Deflect	0.0 V
Plate Bias	-60 V
Cell	
He Flow	4.3 mL/min
Oct P bias	-18.0 V
Oct P RF	180 V
Energy Discrimination	5.0 V

Table S4. Concentrations of ligands used in geomedia regeneration experiments.

Failed Geomedia	Concentration EDTA or Citric Acid (μM)	
	1:1 Ratio	2:1 Ratio
Cu Treatment	21.5	43.0
Zn Treatment	73.0	146
Cd Treatment	18.9	37.8
Pb Treatment	4.4	8.8

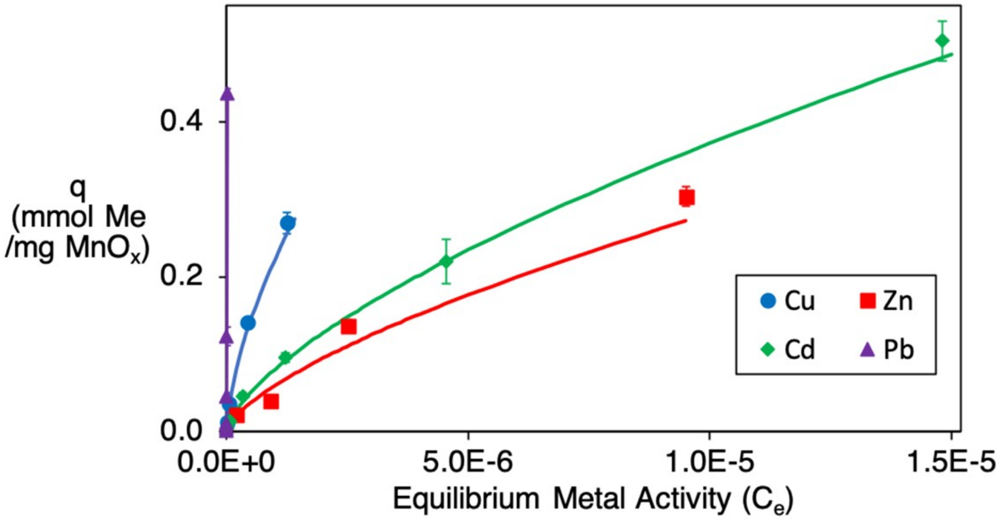


Figure S1. Batch adsorption isotherms and Freundlich model fits for Cu, Zn, Cd and Pb with 500 mg manganese oxide-coated sand in NOM-free simulated stormwater at pH 5. Samples equilibrated for 24 h. Error bars from triplicate experiments smaller than symbols in some cases.

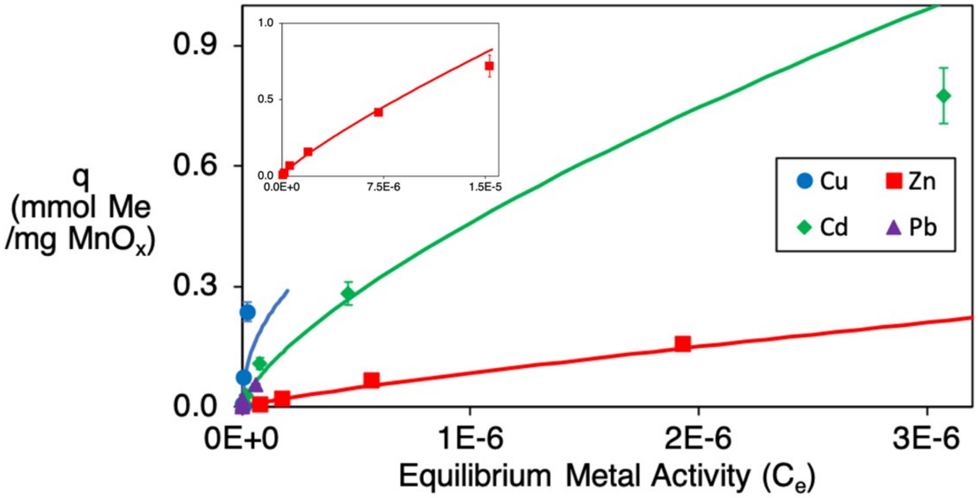


Figure S2. Batch adsorption isotherms and Freundlich model fits for Cu, Zn, Cd and Pb with 500 mg manganese oxide-coated sand in NOM-free simulated stormwater at pH 7. Samples equilibrated for 24 h. No isotherm model was developed to fit Pb due to low aqueous equilibrium concentrations. Zn data are truncated to illustrate the relative trends of metals; the complete Zn isotherm is inset. Error bars from triplicate experiments smaller than symbols in some cases.

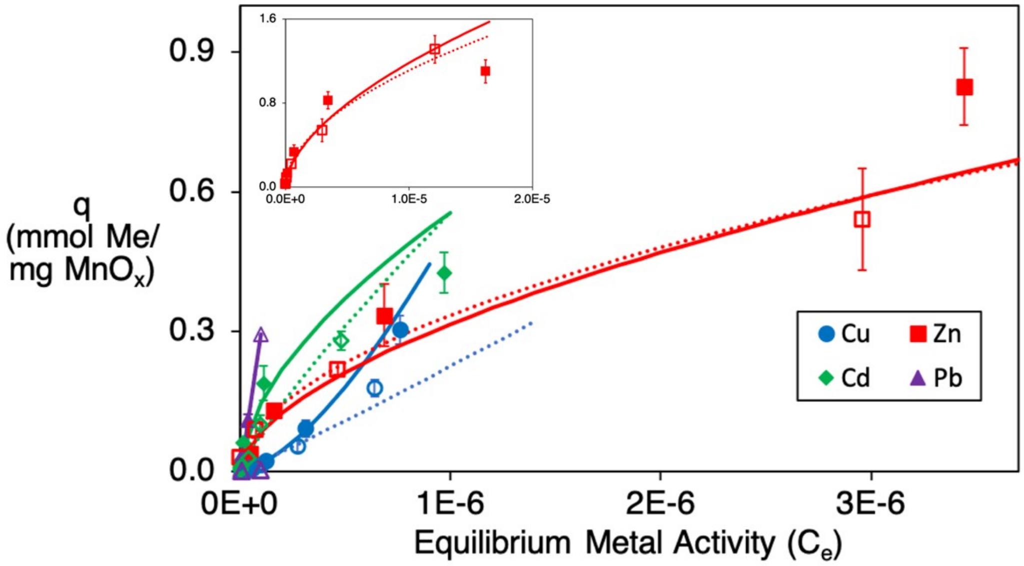


Figure S3. Batch adsorption isotherms and Freundlich model fits for Cu, Zn, Cd and Pb with 500 mg manganese oxide-coated sand in simulated stormwater with 8.0 mg-C/L Suwannee River (closed symbols, solid line) NOM and 6.3 mg-C/L Sigma humic acid (open symbols, dotted line). Samples equilibrated for 24 h. Zn data are truncated to illustrate the relative trends of metals; the complete Zn isotherm is inset. Error bars from triplicate experiments smaller than symbols in some cases.

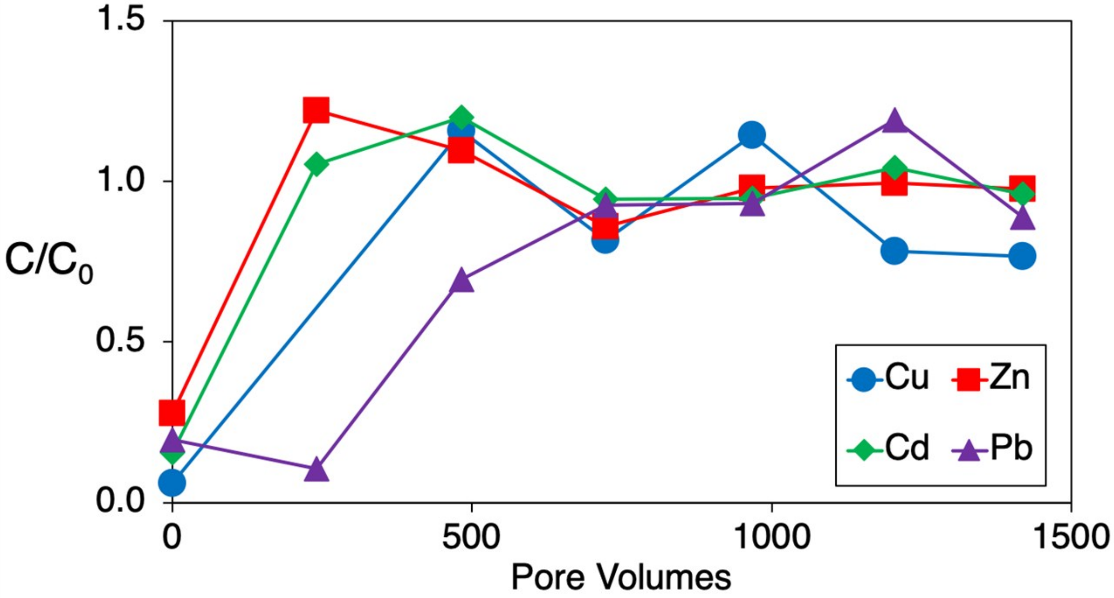
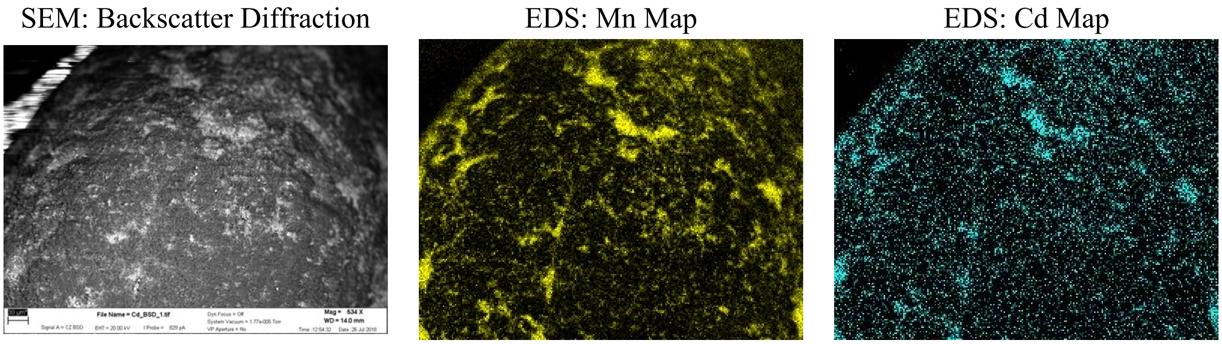


Figure S4. Relative concentration of metals in effluent from control columns of acid-washed sand. Experiments conducted in pH 7 NOM-free simulated stormwater.


SEM: Backscatter Diffraction

EDS: Mn Map

EDS: Cd Map

Figure S5. Backscatter diffraction scanning electron micrograph (left) and energy dispersive X-ray spectroscopy element maps (center, right) of representative geomedia used to treat of Cd-containing stormwater in columns. All images are magnified by a factor of approximately 530X. In the SEM image, Mn-oxide appears bright. In the element maps, Mn appears yellow and Cd appears cyan.

Table S5. Adsorbed metal concentration (mmol Me/g MnO_x) on front and back halves of geomedia following column tests in pH 7 NOM-free stormwater.

Column	Front half geomedia	Back half geomedia	Reported adsorption capacity
Cu	1.9 ± 0.2	0.06 ± 0.01	1.54 (at pH 5.5)*
Zn	2.5 ± 0.3	3.2 ± 0.5	2.73 (at pH 6)†
Cd	0.82 ± 0.03	0.74 ± 0.05	1.93 (at pH 6)†
Pb	0.06 ± 0.01	0.03 ± 0.01	6.37 (at pH 6)†

*Fu et al., 1991; †Gadde and Laitinen, 1974

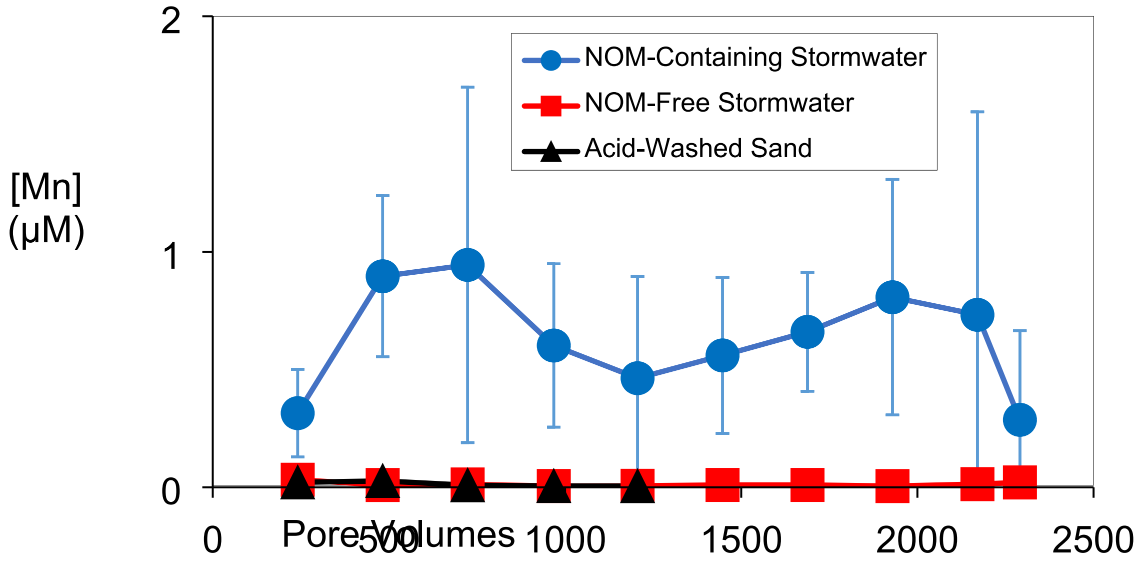


Figure S6. Average concentration of Mn in effluent from columns treating metals in NOM-containing (orange circles) and NOM-free (green squares) simulated stormwater. Mn in effluent from acid-washed sand control column was negligible (black triangles). Some error bars are smaller than the data symbols.

Table S6. Initial and final pH of batch EDTA regenerant solutions.

Treatment	Initial pH	Final pH
1:1 Cu	5.46	6.34
2:1 Cu	5.37	6.41
1:1 Zn	5.30	6.01
2:1 Zn	5.14	6.23
1:1 Cd	5.49	6.18
2:1 Cd	5.31	6.18
1:1 Pb	5.60	6.43
2:1 Pb	5.46	6.30

Table S7. Initial and final pH of batch citric acid regenerant solutions.

Treatment	Initial pH	Final pH
1:1 Cu	4.55	6.21
2:1 Cu	4.29	5.99
1:1 Zn	4.10	6.24
2:1 Zn	3.88	6.22
1:1 Cd	4.58	6.19
2:1 Cd	4.29	6.12
1:1 Pb	5.08	6.50
2:1 Pb	4.80	6.33

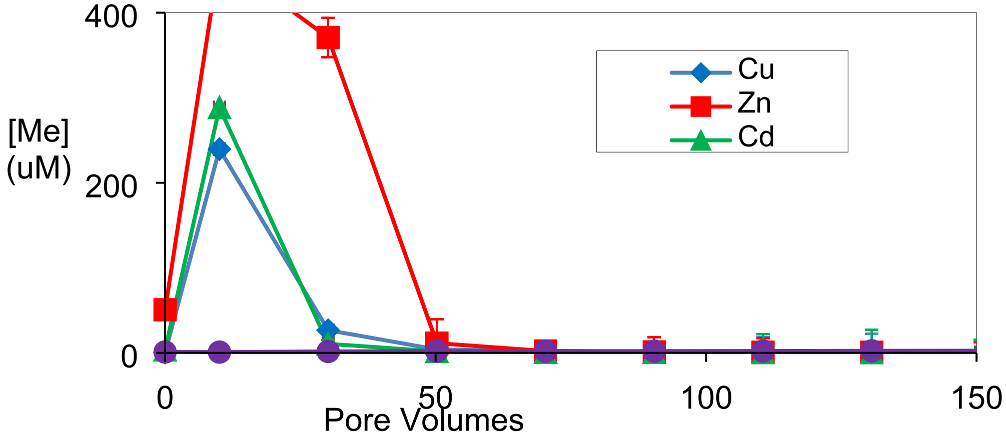


Figure S7. Concentrations of effluent Cu, Zn, Cd and Pb during regeneration with pH 3 HCl of columns that treated NOM-free stormwater. X-axis designates pore volumes of regenerant treatment, immediately following column adsorption tests. Error bars represent standard error of multiple sample tests.

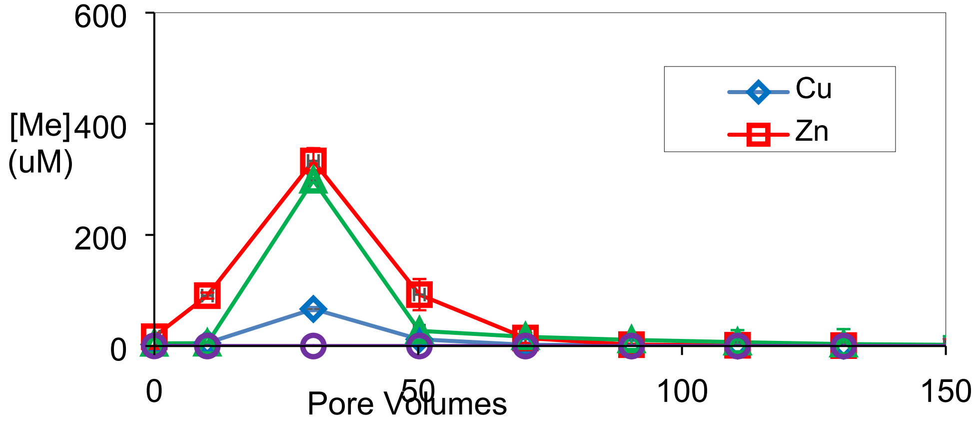


Figure S8. Concentrations of effluent Cu, Zn, Cd and Pb during regeneration with pH 3 HCl of columns that treated NOM-containing stormwater. X-axis designates pore volumes of regenerant treatment, immediately following column adsorption tests. Error bars represent standard error of multiple sample tests.

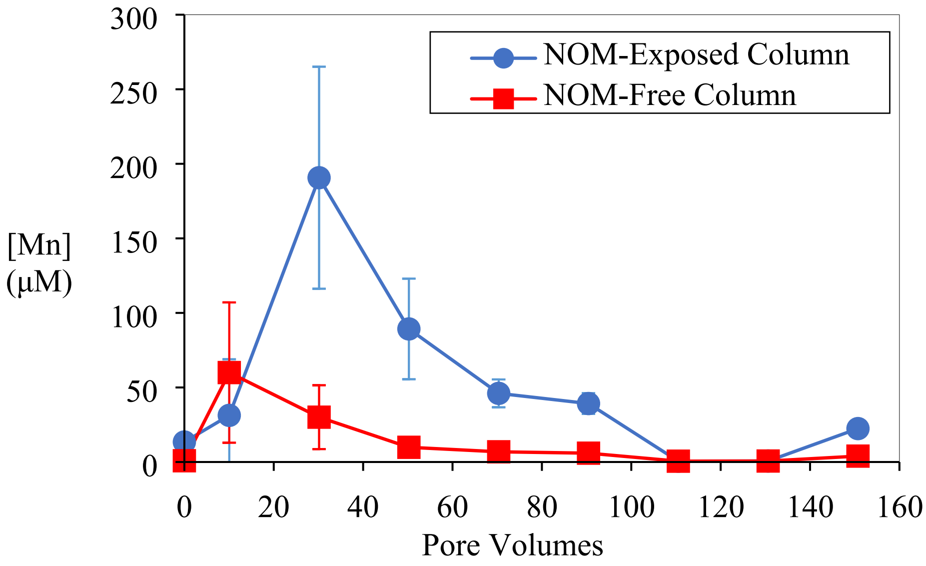


Figure S9. Concentrations of Mn in the column effluent during regeneration with pH 3 HCl. Results are shown for columns that treated metals in NOM-containing stormwater (circles) and NOM-free (squares) simulated stormwater. The x-axis designates pore volumes of regenerant treatment, immediately following column adsorption tests. Error bars represent standard error from all regeneration experiments

Lifetime Estimation

The lifetime of a typical stormwater treatment system employing manganese oxide-coated sand as a reactive geomedia for organic contaminants could be determined by:

$$lifetime\ [years] = \frac{metal\ loading\ capacity\ [moles]}{metal\ load\ \left[\frac{moles}{yr}\right]} \quad \text{(Eq. S1)}$$

Where metal loading capacity can be determined by:

$$metal\ loading\ cap.\ [moles] = bed\ mass[g] * adsorptive\ capacity\ \left[\frac{moles}{g}\right] \quad \text{(Eq. S2)}$$

- Assuming an infiltration bed 50 m^2 in area containing a 0.5 m-depth zone of manganese oxide-coated sand with a bulk density of 870 kg/m^3 yields a bed mass of 22x10^6 g manganese oxide-coated sand.
- Per Eq. S2, multiplying bed mass by the adsorptive capacities (before $C/C_0=1$) measured in this study of:
    - 1.48 µmoles Cu/g manganese oxide-coated sand (with NOM present), yields 32.5 moles Cu loading capacity.
    - 5.52 µmoles Zn/g manganese oxide-coated sand (without NOM present), yields 121.5 moles Zn loading capacity.
    - 3.12 µmoles Zn/g manganese oxide-coated sand (with NOM present), yields 68.7 moles Zn loading capacity.

  - 1.32 µmoles Cd/g manganese oxide-coated sand (without NOM present), yields 29.1 moles Cd loading capacity.
  - 1.01 µmoles Cd/g manganese oxide-coated sand (with NOM present), yields 22.3 moles Cd loading capacity.
  - 6.81 µmoles Pb/g manganese oxide-coated sand (with NOM present), yields 149.9 moles Pb loading capacity.

Metal load can be determined by:

$$metal\ load\left[\frac{moles}{yr}\right] = stormwater\ load\left[\frac{L}{yr}\right] * metal\ conc.\ [M] \quad \text{(Eq. S3)}$$

- Assuming stormwater catchment of 4000 m^2 receiving 0.5 m of rainfall/yr and a runoff coefficient of 1 yields $2x10^6$ L stormwater/yr.[65]
- Multiplying stormwater load by an average of 0.522 µM total Cu per Eq. S3 yields a load of 1.04 moles Cu/yr.
- Multiplying stormwater load by an average of 3.04 µM total Zn per Eq. S3 yields a load of 6.08 moles Zn/yr.
- Multiplying stormwater load by an average of 0.031 µM total Cd per Eq. S3 yields a load of 0.06 moles Cd/yr.
- Multiplying stormwater load by an average of 0.162 µM total Pb per Eq. S3 yields a load of 0.32 moles Pb/yr.

Dividing oxidative loading capacity by oxidizable organic load per Eq. S1 yields an estimated lifetime of

- $\frac{32.5\ moles}{1.04\ moles/yr}$ = 31.2 years before breakthrough of Cu (with NOM present).
- $\frac{121.5\ moles}{6.08 moles/yr}$ = 20.0 years before breakthrough of Zn (without NOM present).
- $\frac{68.7\ moles}{6.08\ moles/yr}$ = 11.3 years before breakthrough of Zn (with NOM present).
- $\frac{29.1\ moles}{0.06\ moles/yr}$ = 471 years before breakthrough of Cd (without NOM present).
- $\frac{22.3\ moles}{0.06\ moles/yr}$ = 361 years before breakthrough of Cd (with NOM present).
- $\frac{149.9\ moles}{0.32\ moles/yr}$ = 463 years before breakthrough of Pb (with NOM present).

Table S8. Parameters for projecting the lifetime of a full-sized infiltration system containing manganese oxide-coated sand before complete breakthrough of metals in a sand in stormwater with no NOM and with 8 mg-C/L NOM.

		Adsorp. cap. (µmol Me/g)	Media cap. (mol Me)	Ave. metal conc. (µM)	Metal load (mol/yr)	Projected lifetime (yr)
Cu	NOM Absent	2.85*	62.7*	0.252	0.50	52.2*
	NOM Present†	1.48	32.5	0.252	0.50	65.0
Zn	NOM Absent	5.52	121	1.79	3.58	33.9
	NOM Present†	3.12	68.7	1.79	3.58	19.2
Cd	NOM Absent	1.32	29.1	0.013	0.03	1120
	NOM Present	1.01	22.3	0.013	0.03	858
Pb	NOM Absent	11.8*	259*	0.038	0.08	61.8*
	NOM Present†	6.81	150	0.038	0.08	1970

†Only partial removal of the metal before complete breakthrough is anticipated; *due to lack of breakthrough, lifetime projections for these systems are the most conservative minimum operational lifetime. Based on previously measured adsorption capacities, actual lifetimes are expected to be much longer.