Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2022

Supporting Information for

Environmental Science: Water Research and Technology

Performance of biochars for the elimination of trace organic contaminants and metals from urban stormwater

Stephanie Spahr^{*,a,b,c}, Marc Teixidó^{b,d,e}, Sarah S. Gall^{a,b,f}, James C. Pritchard^{a,b}, Nikolas Hagemann^{g,h}, Brigitte Helmreich^f, and Richard G. Luthy^{*,a,b}

^aDepartment of Civil and Environmental Engineering, Stanford University, Stanford, CA, USA ^bNSF Engineering Research Center for Re-inventing the Nation's Urban Water Infrastructure (ReNUWIt), USA

^cDepartment of Ecohydrology and Biogeochemistry, Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Berlin, Germany

^dDepartment of Civil and Environmental Engineering, University of California, Berkeley, CA, USA

^eInstitute of Environmental Assessment and Water Research, IDAEA-CSIC, Barcelona, Spain ^fChair of Urban Water Systems Engineering, School of Engineering and Design, Technical University of Munich, Garching, Germany ^gIthaka Institute, Freiburg, Germany

^hAgroscope, Zürich, Switzerland

*Corresponding authors email: stephanie.spahr@igb-berlin.de and luthy@stanford.edu

31 Pages, 21 Figures, 31 Tables, 6 Equations

Contents

| S 1 | Chemicals & analytical parameters | 3 |
|---------------|--|-----------|
| $\mathbf{S2}$ | Synthetic stormwater | 5 |
| $\mathbf{S3}$ | Biochars | 5 |
| $\mathbf{S4}$ | Statistical analyses | 5 |
| $\mathbf{S5}$ | 48-hour batch sorption experiments for biochar screening | 6 |
| S6 | Biochar batch experiments with metals and TrOCs | 9 |
| S 7 | Column experiments | 14 |
| S7. | 1 Porosity | 14 |
| S7.2 | 2 Bromide tracer tests | 15 |
| S7.3 | 3 Dissolved organic carbon and total nitrogen | 16 |
| S7.4 | 4 Dissolved oxygen | 17 |
| S7.5 | 5 Nutrients | 18 |
| S7.6 | 6 Additional water quality parameters | 21 |
| S 8 | Metal removal in flow-through column experiments | 23 |
| S 9 | TrOC removal in flow-through column experiments | 25 |
| S1 (|) Forward-prediction transport model | 27 |
| S10 | 0.1 Model equations, input parameters, and references | 27 |
| S10 | 0.2 Sorption parameters from column breakthrough curves | 28 |
| S10 | 0.3 Case study to predict filter longevity | 30 |

S1 Chemicals & analytical parameters

All chemicals in this study were used as received.

| Name | Abbreviation | Purity | Supplier |
|--|---|---|--|
| Calcium chloride Magnesium chloride Ammonium chloride Sodium sulfate Sodium bicarbonate Sodium nitrate Sodium dihydrogen phosphate monohydrate | $\begin{array}{c} CaCl_2\\ MgCl_2\\ NH_4Cl\\ Na_2SO_4\\ NaHCO_3\\ NaHO_3\\ NaH_2PO_4\cdot H_2O \end{array}$ | $\geq 99.5\%$ >99% $\geq 98\%$ 99% 99% 99% | Fluka, Switzerland Fluka, Switzerland Merck, Switzerland Fluka, Switzerland Sigma-Aldrich, Germany Sigma-Aldrich, Germany Sigma-Aldrich, Germany |
| Potassium bromide | KBr | $\geq 99.0\%$ | Sigma-Aldrich |
| Cadmiumchloride Copper(II) chloride dihydrate Nickel(II)chloride hexahydrate Lead(II)Chloride Zinc chloride | $\begin{array}{c} CdCl_2\\ CuCl_2 \cdot 2 \ H_2O\\ NiCl_2 \cdot 6 \ H_2O\\ PbCl_2\\ ZnCl_2 \end{array}$ | 99.99% BioReagent BioReagent 99.999% 99.99% | Sigma-Aldrich, USA Sigma-Aldrich, USA Sigma-Aldrich, USA Sigma-Aldrich, USA Sigma-Aldrich, USA |
| Atenolol 1H-Benzotriazole (1H-BT) Dicamba Diuron Fipronil Mecoprop Terbutryn | | $\begin{array}{c} \geq 99.5\% \\ \geq 99.5\% \\ \geq 99.5\% \\ > 99\% \\ 99\% \\ \geq 98\% \\ 99\% \end{array}$ | Fluka, Switzerland Fluka, Switzerland Fluka, Switzerland Fluka, Switzerland Merck, Switzerland Fluka, Switzerland Sigma-Aldrich, Germany |
| Atenolol-d7 1H-Benzotriazole-4,5,6,7-d4 Dicamba-d3 Diuron-d6 Fipronil sulfide 2,4 D-d3 Atrazine-d5 | | $\geq 97\%$ 99.8% D 99.1% D 99% D 98.3% D 99% D | Sigma-Aldrich, USA CDN, Canada Sigma-Aldrich, USA CDN, Canada Sigma-Aldrich, USA CDN, Canada Sigma-Aldrich, USA |

Table S1 Metals, organic compounds, and other chemicals used in this study.

Analyte stock solutions were prepared in methanol (Optima for HPLC, 99.9%, Fisher Scientific). Aqueous solutions were prepared with deionized water ($18.1 \text{ M}\Omega \cdot \text{cm}$, Barnstead NANOpure Diamond Water Purification System). The pH-value of the synthetic stormwater was adjusted by addition of hydrochloric acid (trace metal grade, Fisher Scientific).

For metal analysis, all samples were acidified with nitric acid (Fischer Scientific, trace metal grade 67-70%). A standard mix containing 10 mg/L of cadmium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, phosphorus, potassium, sodium, and zinc in 5% v/v HNO₃ was obtained from Inorganic Ventures, USA.

| | CAS number | Usage class | Molecular mass | basic pKa | acidic pKa | Speciation at pH 7.4 | $\log D_{ow}^{a}$ at pH 7.4 | ${{ m K}_{oc}}^{ m b}$ (L/kg) |
|------------------|---------------|------------------------|-------------------|--------------|---------------|-------------------------|--------------------------------|-------------------------------|
| 1H-Benzotriazole | 95-14-7 | Corrosion inhibitor | 119.12 | 1.6 | 8.4 | neutral | 1.4 | 49.0 |
| Atenolol | 29122-68-7 | Pharma- ceutical | 266.34 | 9.6 | - | cationic | -1.9 | 302 |
| Dicamba | 1918-00-9 | Herbicide | 221.03 | - | 1.9 | anionic | -0.4 | 31.6 |
| Diuron | 330-54-1 | Herbicide/ Biocide | 233.09 | - | 13.8 | neutral | 2.7 | 251 |
| Fipronil | 120068-37-3 | Insecticide | 437.14 | - | - | neutral | 4.0 | 411 |
| Mecoprop | 93-65-2 | Herbicide/ Biocide | 214.65 | - | 3.1 | anionic | -0.7 | 20.0 |
| Terbutryn | 886-50-0 | Herbicide/ Biocide | 241.36 | 4.3 | - | neutral | 3.7 | 708 |

Table S2 Usage class and physicochemical properties of the selected organic compounds.

^a Predicted octanol-water distribution coefficient; source: ChemSpider, ACD/Labs. For neutral compounds: Octanol-water partition coefficient; source: US EPA CompTox Chemicals Dashboard

^b Soil adsorption coefficient; source: US EPA CompTox Chemicals Dashboard

Table S3 Substance-specific MS/MS settings for quantification of trace organic contaminants in batch and column studies.

| | Precursor mass | m/z Product mass (Quantifier) | Product mass (Qualifier) | $\mathrm{ESI}^{\mathrm{a}}$ mode | $\begin{array}{c} \mathrm{DP^b} \\ \mathrm{(V)} \end{array}$ | FP^{c} (V) | Collision energy (V) | $\begin{array}{c} \mathrm{CXP}^\mathrm{d} \\ \mathrm{(V)} \end{array}$ |
|---------------------|-------------------|-------------------------------------|-----------------------------|-------------------------------------|--|--------------|-------------------------|--|
| 1H-Benzotriazole | 120.0 | 65.1 | | (+) | 46 | 210 | 31 | 4 |
| | 120.0 | | 92.1 | (+) | 46 | 210 | 25 | 6 |
| 1H-Benzotriazole-d4 | 124.2 | 69.1 | | (+) | 71 | 360 | 33 | 6 |
| | 124.2 | | 68.1 | (+) | 71 | 360 | 31 | 6 |
| Atenolol | 267.2 | 145.0 | | (+) | 46 | 210 | 37 | 10 |
| | 267.2 | | 190.0 | (+) | 46 | 210 | 27 | 14 |
| Atenolol-d7 | 274.2 | 145.1 | | (+) | 41 | 240 | 39 | 10 |
| | 274.2 | | 190.1 | (+) | 41 | 240 | 27 | 14 |
| Dicamba | 219.0 | 174.8 | | (-) | -76 | -350 | -10 | -11 |
| | 220.9 | | 176.7 | (-) | -56 | -270 | -10 | -11 |
| Dicamba-d3 | 221.9 | 177.9 | | (-) | -46 | -260 | -10 | -13 |
| | 223.8 | | 180.0 | (-) | -41 | -220 | -10 | -11 |
| Diuron | 233.0 | 72.0 | | (+) | 41 | 200 | 43 | 6 |
| | 235.0 | | 72.0 | (+) | 51 | 240 | 43 | 6 |
| Diuron-d6 | 239.1 | 78.2 | | (+) | 51 | 260 | 41 | 6 |
| | 241.1 | | 78.2 | (+) | 46 | 290 | 41 | 6 |
| Fipronil | 434.9 | 329.8 | | (-) | -56 | -250 | -24 | -11 |
| | 434.9 | | 249.9 | (-) | -56 | -250 | -40 | -17 |
| Fipronil sulfide | 418.9 | 261.8 | | (-) | -91 | -290 | -38 | -17 |
| | 418.9 | | 382.8 | (-) | -91 | -290 | -20 | -13 |
| Mecoprop | 213.0 | 140.8 | | (-) | -96 | -310 | -20 | -9 |
| | 213.0 | | 71.0 | (-) | -96 | -310 | -20 | -5 |
| 2,4-D-d3 | 222.0 | 163.8 | | (-) | -71 | -340 | -22 | -9 |
| | 224.0 | | 165.8 | (-) | -76 | -350 | -20 | -11 |
| Terbutryn | 242.2 | 185.9 | | (+) | 66 | 260 | 27 | 14 |
| | 242.2 | | 68.0 | (+) | 66 | 260 | 59 | 6 |
| Atrazine-d5 | 221.1 | 179.0 | | (+) | 41 | 230 | 27 | 14 |
| | 221.1 | | 101.0 | (+) | 41 | 230 | 37 | 8 |

^a Electrospray ionization ^b Declustering potential ^c Fragmentor voltage ^d Collision cell exit potential

S2 Synthetic stormwater

| Constituent | Concentration | Unit |
|---------------------------------------|---------------|----------------------------|
| NO_3^- | 4.4 | $\mathrm{mg/L}$ |
| NH_4^+ | 1.3 | $\mathrm{mg/L}$ |
| $H_2PO_4^-$ | 1.5 | $\mathrm{mg/L}$ |
| SO_4^{2-} | 31 | $\mathrm{mg/L}$ |
| HCO_3^- | 60 | $\mathrm{mg/L}$ |
| Mg^{2+} | 1.8 | $\mathrm{mg/L}$ |
| Ca^{2+} | 30 | $\mathrm{mg/L}$ |
| Na ⁺ | 40 | $\mathrm{mg/L}$ |
| Cl^- | 61 | $\mathrm{mg/L}$ |
| Dissolved organic carbon ^a | 5 | $\mathrm{mg} \mathrm{C/L}$ |
| pH | 7.5 | |

Table S4 Synthetic stormwater composition for the batchand column experiments.

^a For batch experiments: Suwannee river natural organic matter (International Humic Substances Society). For column studies: humic acid (Sigma Aldrich).

S3 Biochars

| Table S5 | Specific | surface | areas o | f the st | tudied | biochars | obtained | from | BET | measurements |
|----------|----------|---------|---------|----------|--------|----------|----------|------|-----|--------------|
|----------|----------|---------|---------|----------|--------|----------|----------|------|-----|--------------|

| Biochar | Specific surface area | Total pore volume | Mean pore diameter |
|-------------------------|-----------------------|------------------------------|--------------------|
| | (m^2/g) | $(\mathrm{cm}^3/\mathrm{g})$ | (nm) |
| $400^{\circ}\mathrm{C}$ | 94 | 0.0580 | 2.47 |
| $580^{\circ}\mathrm{C}$ | 29 | 0.0212 | 2.94 |
| $750^{\circ}\mathrm{C}$ | 400 | 0.3111 | 3.11 |
| MCG | 610 | 0.3395 | 2.23 |

Table S6 Pore size distribution of MCG biochar obtained from Hg porosimetry.

| Biochar | Macro pores | Meso pores | Micro pores |
|---------|------------------------------|------------------------------|------------------------------|
| | $(\mathrm{cm}^3/\mathrm{g})$ | $(\mathrm{cm}^3/\mathrm{g})$ | $(\mathrm{cm}^3/\mathrm{g})$ |
| MCG | 1.1729 | 0.0426 | 0.5545 |

S4 Statistical analyses

Two-way analysis of variance (ANOVA) or the Students t-test were performed to evaluate differences between multiple or two paired groups, respectively. ANOVA tests were followed by post-hoc Tukey's Honest Significant Difference (HSD) tests. The level of significance was set at 0.05. All statistical analyses and data processing were conducted with GraphPad Prism[®] 2020 (version 9) and the Data Analysis Tool included within Microsoft Office EXCEL[®] 2019.



S5 48-hour batch sorption experiments for biochar screening

Figure S1 Sorption of cadmium, nickel, zinc, copper and lead onto three biochars produced at (a) 400°C, (b) 580°C, and (c) 750°C as well as onto (d) MCG gasification biochar. Batch experiments contained 5 mg, 20 mg, or 40 mg of the biochars in 200 mL synthetic stormwater at pH 7.5 corresponding to 0.025 g biochar/L, 0.1 g biochar/L and 0.2 g biochar/L, respectively. Batches for 0.3 g biochar/L, 0.4 g biochar/L and 0.5 g biochar/L contained 15 mg, 20 mg and 25 mg in 50 mL synthetic stormwater, respectively. Reported is the concentration c measured after 48 h of contact time divided by the measured concentration $c_0 = 50 \,\mu g/L$ in the control batches without biochar.



Figure S2 Sorption of dicamba, mecoprop, fipronil, terbutryn, atenolol, 1H-benzotriazole (1H-BT), and diuron onto three different biochars produced at (a) 400°C, (b) 580°C, and (c) 750°C as well as (d) onto MCG gasification biochar. Batch experiments contained 5 mg, 20 mg, or 40 mg of the respective biochar in 200 mL synthetic stormwater at pH 7.5 corresponding to 0.025 g biochar/L, 0.1 g biochar/L and 0.2 g biochar/L. Reported is the concentration c measured after 48 h of contact time divided by the measured concentration $c_0 = 100 \,\mu g/L$ in the control batches without biochar.

| _ | 1H- | \mathbf{BT} | Dica | mba | Diu | ron | Fipr | onil | Mecc | prop | Terbı | ıtryn |
|---------------|--------|---------------|--------------------|---------|---------------------|---------|--------|---------|--------|---------|---------------------|---------|
| | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value |
| $SSA (m^2/g)$ | 0.999 | 0.001 | <mark>0.991</mark> | 0.009 | <mark>0.996</mark> | 0.004 | 0.982 | 0.018 | 0.995 | 0.005 | <mark>066.0</mark> | 0.010 |
| Ash (%) | 0.856 | 0.144 | 0.802 | 0.198 | 0.804 | 0.198 | 0.910 | 0.090 | 0.841 | 0.159 | 0.862 | 0.138 |
| H (%) | -0.942 | 0.058 | -0.897 | 0.103 | <mark>-0.966</mark> | 0.034 | -0.944 | 0.056 | -0.905 | 0.095 | <mark>-0.969</mark> | 0.031 |
| C (%) | 0.010 | 0.990 | 0.061 | 0.939 | 0.109 | 0.891 | 0.013 | 0.987 | 0.069 | 0.931 | 0.094 | 0.906 |
| N (%) | -0.138 | 0.862 | -0.227 | 0.773 | -0.048 | 0.952 | -0.113 | 0.887 | -0.226 | 0.774 | -0.044 | 0.956 |
| 0 (%) | -0.479 | 0.521 | -0.368 | 0.632 | -0.542 | 0.458 | -0.524 | 0.476 | -0.387 | 0.613 | -0.571 | 0.429 |
| S (%) | 0.746 | 0.254 | 0.730 | 0.270 | 0.671 | 0.329 | 0.786 | 0.214 | 0.763 | 0.237 | 0.720 | 0.280 |
| H/C ratio | -0.914 | 0.086 | -0.859 | 0.141 | -0.942 | 0.058 | -0.922 | 0.078 | -0.870 | 0.130 | -0.950 | 0.050 |
| O/C ratio | -0.445 | 0.555 | -0.334 | 0.666 | -0.510 | 0.490 | -0.490 | 0.510 | -0.353 | 0.647 | -0.539 | 0.461 |
| (N+O)/C ratio | -0.449 | 0.551 | -0.337 | 0.663 | -0.514 | 0.486 | -0.494 | 0.506 | -0.356 | 0.644 | -0.542 | 0.458 |
| | | | | | | | | | | | | |

Table S7 Linear semi-log correlation coefficients (r) between log K_d values of the TrOCs and physicochemical properties of biochar. Significance accepted at p-value<0.05 (yellow), p-value<0.1 (green), and p-value<0.2 (blue).

Table S8 Linear semi-log correlation coefficients (r) between log K_d values of the metals and physicochemical properties of biochar. Significance accepted at p-value<0.05 (yellow), p-value<0.1 (green), and p-value<0.2 (blue).

I

| _ | C | n | Z | u | Ь | b b | 4 | 1i | 0 | p; |
|---------------|---------------------|---------|--------------------|---------|--------|---------|--------------------|--------------|--------|---------|
| | r | p-value | r | p-value | r | p-value | r | p-value | r | p-value |
| $SSA (m^2/g)$ | 0.953 | 0.047 | <mark>0.999</mark> | 0.001 | 0.726 | 0.274 | <mark>0.996</mark> | 0.004 | 0.998 | 0.002 |
| Ash $(\%)$ | 0.733 | 0.267 | 0.845 | 0.155 | 0.267 | 0.733 | 0.879 | 0.121 | 0.863 | 0.137 |
| H (%) | <mark>-0.998</mark> | 0.002 | -0.948 | 0.052 | -0.830 | 0.170 | -0.942 | 0.058 | -0.949 | 0.051 |
| C (%) | 0.320 | 0.680 | 0.031 | 0.969 | 0.605 | 0.395 | 0.002 | 0.998 | 0.026 | 0.974 |
| N (%) | -0.174 | 0.826 | -0.119 | 0.881 | -0.433 | 0.567 | -0.139 | 0.861 | -0.119 | 0.881 |
| 0 (%) | -0.712 | 0.288 | -0.493 | 0.507 | -0.696 | 0.304 | -0.488 | 0.512 | -0.500 | 0.500 |
| S (%) | 0.536 | 0.464 | 0.731 | 0.269 | 0.053 | 0.947 | 0.767 | 0.233 | 0.764 | 0.254 |
| H/C ratio | <mark>-0.991</mark> | 0.009 | -0.921 | 0.079 | -0.831 | 0.169 | -0.916 | 0.084 | -0.923 | 0.077 |
| O/C ratio | -0.687 | 0.313 | -0.460 | 0.540 | -0.687 | 0.313 | -0.454 | 0.546 | -0.467 | 0.533 |
| (N+O)/C ratio | -0.690 | 0.310 | -0.463 | 0.537 | -0.688 | 0.312 | -0.457 | 0.543 | -0.470 | 0.530 |



Figure S3 Sorption of five metals ($c_0 = 50 \,\mu g/L$, each) onto 0.2 g MCG biochar/L (a, c, e, g, i) and 0.2 g 750°C biochar/L (b, d, f, h, j) over 7 days in the presence and absence of seven TrOCs ($c_0 = 50 \,\mu g/L$, each) in synthetic stormwater (pH 7.5). Control experiments contained five metals and seven TrOCs ($c_0 = 50 \,\mu g/L$, each). Error bars represent standard deviations of triplicate experiments.

(j) ^{1.4}

1.2-

1.0

0.4

0.2 0.0

ò

1

2

ပို ၁ ၁ ၁ 0.6 ∇

¢

7

Lead

 \cap

3 4 Time (days)

5

6

 ∇

7

Lead

3 4 Time (days)

5

6

2

(i) ^{1.4-}

ပို သိုပ် ၁

0.4

0.2-

0.0

ò

1

1.2 -1.0 -



Figure S4 Sorption of seven TrOCs ($c_0 = 50 \,\mu g/L$, each) onto (a) 0.2 g MCG biochar/L and (b) 0.2 g 750°C biochar/L over 7 days in the presence of five metals ($c_0 = 50 \,\mu g/L$, each) in synthetic stormwater at pH 7.5.

Table S9 Comparison of batch experiments with 0.2 g biochar/L and five metals $(c_0 = 50 \ \mu g/L, each)$ in the presence and absence of seven TrOCs $(c_0 = 50 \ \mu g/L, each)$ after 7 days in synthetic stormwater at pH 7.5. Significance accepted at p-value <0.05 (yellow) and p-value <0.2 (blue).

| | p-va | alue | |
|----------|-------------|-------------------------|--|
| Compound | MCG biochar | 750° C biochar | |
| Cadmium | 0.001 | 0.014 | |
| Nickel | 0.021 | 0.042 | |
| Zinc | 0.0002 | 0.001 | |
| Copper | 0.705 | 0.263 | |
| Lead | 0.149 | 0.790 | |



Figure S5 Sorption of seven TrOCs ($c_0 = 50 \,\mu g/L$, each) onto 0.025 g MCG biochar/L (a, c, e, g) and 0.025 g 750°C biochar/L (b, d, f, h) over 7 days in the presence and absence of five metals ($c_0 = 50 \,\mu g/L$, each) in synthetic stormwater (pH 7.5). Control experiments contained seven TrOCs and five metals ($c_0 = 50 \,\mu g/L$, each). Error bars represent standard deviations of triplicate experiments.



Figure S6 Sorption of seven TrOCs ($c_0 = 50 \ \mu g/L$, each) onto 0.025 g MCG biochar/L (a, c, e) and 0.025 g 750°C biochar/L (b, d, f) over 7 days in the presence and absence of five metals ($c_0 = 50 \ \mu g/L$, each) in synthetic stormwater (pH 7.5). Control experiments contained seven TrOCs and five metals ($c_0 = 50 \ \mu g/L$, each). Error bars represent standard deviations of triplicate experiments.



Figure S7 Sorption of five metals ($c_0 = 50 \,\mu g/L$, each) onto (a) 0.025 g MCG biochar/L and (b) 0.025 g 750°C biochar/L over 7 days in the presence of seven TrOCs ($c_0 = 50 \,\mu g/L$, each) in synthetic stormwater at pH 7.5.

Table S10 Comparison of batch experiments with 0.025 g biochar/L and seven TrOCs ($c_0 = 50 \ \mu g/L$, each) in the presence and absence of five metals ($c_0 = 50 \ \mu g/L$, each) after 7 days in synthetic stormwater at pH 7.5. Significance accepted at p-value <0.05 (yellow) and p-value <0.2 (blue).

| | p-va | alue |
|------------------|-------------|---------------------------------|
| Compound | MCG biochar | $750^{\circ}\mathrm{C}$ biochar |
| Dicamba | 0.972 | 0.2813 |
| Mecoprop | 0.743 | 0.367 |
| Fipronil | 0.266 | 0.175 |
| Terbutryn | 0.245 | 0.040 |
| Atenolol | 0.233 | 0.039 |
| 1H-benzotriazole | 0.183 | 0.120 |
| Diuron | 0.226 | 0.117 |

Table S11 7-day log K_d values for sorption of the organic compounds onto the biochar produced at 750°C and onto MCG biochar in the absence and presence of five metals. Batch experiments contained 5 mg of the respective biochar in 200 mL synthetic stormwater at pH 7.5 corresponding to 0.025 g biochar/L. The seven organic contaminants were present as a mixture in solution with initial concentrations of 50 μ g/L, each. Log K_d values are reported for 10 - 90% sorption. A (-) is shown where less than 10% or more than 90% of the organic compound mass was sorbed. The corresponding c/c₀ data are shown in Figures S5 and S6 and in Figure 2 of the main manuscript.

| | Dicamba | Mecoprop | Fipronil | $\log \mathbf{K}_d$ Terbutryn | Atenolol | 1H-Benzo- triazole | Diuron |
|---|---------|--------------------------------|--------------------------------|---|---|--|---|
| 750° C biochar 750° C biochar + metals | - | 4.0 ± 0.1 | 4.6 ± 0.2 | $\begin{array}{c} 4.8\pm0.1\\ 4.2\pm0.4\end{array}$ | $\begin{array}{c} 4.8\pm0.1\\ 4.2\pm0.3\end{array}$ | $\begin{array}{c} 4.9\pm0.02\\ 4.2\pm0.4\end{array}$ | $\begin{array}{c} 5.3\pm0.1\\ 4.4\pm0.5\end{array}$ |
| MCG biochar MCG biochar + metals | - | 4.4 ± 0.1 4.3 ± 0.6 | 5.0 ± 0.1 4.4 ± 0.7 | 5.3 ± 0.1 4.8 ± 0.5 | -5.1 ± 0.4 | 5.4 ± 0.03 5.0 ± 0.3 | 5.3 ± 0.5 |

S7 Column experiments



Figure S8 Laboratory column setup. Upflow columns labeled with S1-S3 contained silica sand, C1-C3 contained silica sand mixed with 20 wt% carbonate sand, SB1-SB3 contained silica sand mixed with 1 wt% MCG biochar, CB1-CB3 contained silica sand mixed with 20 wt% carbonate sand and 1 wt% MCG biochar.

S7.1 Porosity

After filling the columns with the different filter materials, we determined the dry weight of the packed columns. Subsequently, the columns were filled with water at a flow rate of $0.5 \,\mathrm{mL/min}$. After 48 hours, the wet weight of the columns was determined and the porosity of the filter material was calculated as difference between wet and dry weight of the columns.

S7.2 Bromide tracer tests

Bromide tracer tests were conducted to determine the hydraulic retention time (HRT) in the column at a flow rate of $1.25 \,\mathrm{mL/min}$. The columns were spiked with a $0.4 \,\mathrm{g/L}$ bromide solution for eighty seconds corresponding to an injected volume of $1.7 \,\mathrm{mL}$. Over a period of 180 minutes, samples were collected at all column effluents in pre-determined time intervals. Samples were analyzed with a bromide probe (Hanna Instruments) and a multi-parameter meter (Orion 5 Star, Thermo Scientific) using an external calibration curve from $0.080 \,\mathrm{mg/L}$ to $40 \,\mathrm{mg/L}$ bromide.



Figure S9 Bromide tracer tests for columns filled with (a) silica sand and silica sand mixed with 1 wt% MCG biochar and (b) silica sand mixed with 20 wt% carbonate sand and silica sand mixed with 20 wt% carbonate sand and 1 wt% MCG biochar. Error bars represent standard deviations of the triplicate column systems.

| Column | Porosity (-) | Hydraulic retention time (min) |
|--|------------------|-----------------------------------|
| Silica sand | 0.36 ± 0.047 | 97.1 ± 0.4 |
| + 20 wt% carbonate s and | 0.35 ± 0.006 | 92.3 ± 2.1 |
| $+$ $1\mathrm{wt}\%$ MCG biochar | 0.39 ± 0.019 | 109.7 ± 4.8 |
| + 20 wt% carbonate sand + 1 wt% MCG biochar | 0.41 ± 0.011 | 126.1 ± 5.9 |

Table S12 Average porosity and hydraulic retention times of the different triplicate column configurations including standard deviations.

S7.3 Dissolved organic carbon and total nitrogen

Dissolved organic carbon (DOC) and total nitrogen (TN) were analyzed using a Shimadzu total organic carbon analyzer (TOC-L) with a Shimadzu ASI-L autosampler. DOC was analyzed as non-purgeable organic carbon (NPOC) using a liquid organic carbon standard (100 mg/L C, RICCA Chemical Company) for the calibration in the range of 2-50 mg/L C. A nitrate nitrogen standard (10 mg/L N, RICCA Chemical Company) was diluted to a calibration range from 1-10 mg/L N. Prior to DOC and TN analyses, samples were filtered with 0.45 μ m PES syringe filters (TISCH Scientific).

Table S13 Dissolved organic carbon (DOC) concentrations in the mixing chamber and the column effluents over time measured as non-purgeable organic carbon including the standard deviations of the triplicate columns.

| | Dissolved organic carbon (mg C/L) | | | | | | | | | |
|-------------------------------------|-----------------------------------|---------------|---------------|---------------|---------------|--|--|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 1000 | PV 1524 | PV 2185 | | | | | |
| Mixing chamber | 3.4 | 4.2 | 2.1 | 2.3 | 2.0 | | | | | |
| Silica sand | 5.5 ± 3.3 | 3.8 ± 0.6 | 2.2 ± 0.1 | 2.2 ± 0.1 | 2.2 ± 0.2 | | | | | |
| + 20 wt% carbonate sand | 3.4 ± 0.2 | 4.2 ± 0.4 | 2.5 ± 0.3 | 2.1 ± 0.3 | 2.1 ± 0.1 | | | | | |
| + 1 wt% MCG biochar | 2.1 ± 0.2 | 3.6 ± 0.3 | 2.2 ± 0.3 | 1.9 ± 0.1 | 1.7 ± 0.1 | | | | | |
| $+20 \mathrm{wt\%}$ carbonate sand | 1.9 ± 0.1 | 2.9 ± 0.2 | 1.9 ± 0.2 | 1.7 ± 0.5 | 2.0 ± 0.1 | | | | | |
| $+ \ 1 \ \mathrm{wt}\%$ MCG biochar | | I | Ι | I | I | | | | | |



Figure S10 Dissolved organic carbon (DOC) concentrations (c) measured over time at the column effluents divided by the DOC influent concentrations (c_0) in synthetic stormwater in the mixing chamber. Error bars represent the standard deviation of the triplicate column systems.

| | Total nitrogen (mg/L) | | | | | | | |
|-------------------------------------|-----------------------|---------------|---------------|---------------|-------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 1000 | PV 1524 | PV 2185 | | | |
| Mixing chamber | 1.8 | 2.0 | 2.5 | 2.4 | 2.5 | | | |
| Silica sand | 1.9 ± 0.1 | 1.9 ± 0.03 | 2.5 ± 0.03 | 2.3 ± 0.1 | 2.6 ± 0.1 | | | |
| + 20 wt% carbonate sand | 1.8 ± 0.1 | 2.0 ± 0.01 | 2.5 ± 0.1 | 2.4 ± 0.03 | 2.6 ± 0.1 | | | |
| + 1 wt% MCG biochar | 1.8 ± 0.1 | 1.9 ± 0.02 | 2.3 ± 0.03 | 2.3 ± 0.1 | 2.6 ± 0.1 | | | |
| $+20 \mathrm{wt\%}$ carbonate sand | 1.8 ± 0.03 | 1.8 ± 0.1 | 2.4 ± 0.1 | 2.1 ± 0.5 | 2.6 ± 0.1 | | | |
| $+ \ 1 \ \mathrm{wt}\%$ MCG biochar | | I | 1 | 1 | 1 | | | |

Table S14 Total nitrogen (TN) concentrations in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).



Figure S11 Total nitrogen (TN) concentrations (c) measured over time at the column effluents divided by the TN influent concentrations (c_0) in synthetic stormwater in the mixing chamber. Error bars represent the standard deviation of the triplicate column systems.

S7.4 Dissolved oxygen

Dissolved oxygen was quantified using a digital optical dissolved oxygen meter (ProODO, YSI). A flow-through cell was attached at the column effluent and dissolved oxygen measurements were recorded after 15 minutes when the value was stable.

Table S15 Dissolved oxygen concentrations in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| | Dissolved oxygen (mg/L) | | | | | | | | | |
|------------------------------------|-------------------------|---------------|---------------|--|--|--|--|--|--|--|
| Pore Volumes | PV 147 | PV 1195 | PV 1735 | | | | | | | |
| Mixing chamber | 8.6 | 8.7 | 8.5 | | | | | | | |
| Silica sand | 6.6 ± 0.5 | 6.8 ± 0.5 | 6.8 ± 0.7 | | | | | | | |
| $+20 \mathrm{wt\%}$ carbonate sand | 6.9 ± 0.1 | 6.5 ± 0.2 | 6.7 ± 0.8 | | | | | | | |
| + 1 wt% MCG biochar | 7.1 ± 0.2 | 5.7 ± 0.5 | 5.7 ± 0.2 | | | | | | | |
| + 20 wt% carbonate sand | 7.3 ± 0.6 | 6.1 ± 0.2 | 5.7 ± 0.2 | | | | | | | |
| $+$ $1\mathrm{wt}\%$ MCG biochar | | 1 | 1 | | | | | | | |

S7.5 Nutrients

Nitrate, ammonium, nitrite, and phosphate were analyzed using a SmartChem 200 Discrete Analyzer from Westco Scientific Instruments. Prior to analysis, samples were filtered with $0.45 \,\mu\text{m}$ PES syringe filters (TISCH Scientific). The calibration range was from $0.2 \cdot 22 \,\text{mg/L}$ for nitrate, $0.06 \cdot 6.4 \,\text{mg/L}$ for ammonium, $0.07 \cdot 6.6 \,\text{mg/L}$ for nitrite (not detected in any of the samples), and $0.01 \cdot 3 \,\text{mg/L}$ for phosphate. Sulfate was quantified using ion chromatography (Dionex Integrion HPIC with an IonPac AS11 column, Thermo Scientific). External calibration standards in the range from $1 \cdot 30 \,\text{mg/L}$ were prepared from a sulfate standard (Inorganic Ventures).

| Table S16 | Nitrate | concentrations | in the | mixing | chamber | and | the | column | effluents | including | the |
|-------------|----------|-------------------|---------|--------|---------|-----|-----|--------|-----------|-----------|-----|
| standard de | viations | of the triplicate | e colun | nns. | | | | | | | |

| | Nitrate concentration (mg/L) | | | | | | | | |
|----------------------------------|------------------------------|---------------|-------------|-------------|---------------|-------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1001 | PV 1525 | PV 2185 | | | |
| Mixing chamber | 3.4 | 4.9 | 9.7 | 7.8 | 7.0 | 6.5 | | | |
| Silica sand | 3.8 ± 0.1 | 4.8 ± 0.1 | 9.7 ± 0.3 | 8.6 ± 0.9 | 7.3 ± 1.0 | 8.3 ± 1.4 | | | |
| +20 wt% carbonate sand | 3.8 ± 0.2 | 4.9 ± 0.3 | 9.3 ± 0.3 | 6.7 ± 0.8 | 8.2 ± 1.5 | 9.1 ± 0.2 | | | |
| + 1 wt% MCG biochar | 3.7 ± 0.1 | 4.8 ± 0.2 | 9.4 ± 0.4 | 7.7 ± 0.8 | 9.2 ± 0.4 | 8.3 ± 1.6 | | | |
| +20 wt% carbonate sand | 3.7 ± 0.1 | 4.8 ± 0.1 | 9.5 ± 0.3 | 7.2 ± 2.0 | 6.7 ± 2.5 | 6.9 ± 0.7 | | | |
| $+$ $1\mathrm{wt}\%$ MCG biochar | | I | I | | I | | | | |



Figure S12 Nitrate concentrations (c) measured over time at the column effluents divided by the nitrate influent concentrations (c_0) in synthetic stormwater in the mixing chamber. Error bars represent the standard deviation of the triplicate column systems.

| | Ammonium concentration (mg/L) | | | | | | | | |
|-------------------------|-------------------------------|--------------|---------------|--------------|--------------|--------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1001 | PV 1525 | PV 2185 | | | |
| Mixing chamber | 1.5 | 1.1 | 0.1 | 0.3 | 0.1 | 0.2 | | | |
| Silica sand | 1.3 ± 0.06 | 1.0 ± 0.03 | 0.1 ± 0.003 | 0.1 ± 0.02 | 0.1 ± 0.01 | 0.1 ± 0.01 | | | |
| + 20 wt% carbonate sand | 1.3 ± 0.01 | 1.0 ± 0.01 | 0.1 ± 0.003 | 0.1 ± 0.01 | 0.1 ± 0.02 | 0.2 ± 0.01 | | | |
| + 1 wt% MCG biochar | 1.4 ± 0.02 | 1.0 ± 0.02 | 0.1 ± 0.002 | 0.2 ± 0.02 | 0.1 ± 0.01 | 0.2 ± 0.01 | | | |
| + 20 wt% carbonate sand | 1.3 ± 0.05 | 1.0 ± 0.06 | 0.1 ± 0.006 | 0.1 ± 0.02 | 0.1 ± 0.01 | 0.2 ± 0.01 | | | |
| + 1 wt% MCG biochar | | I | I | I | | I | | | |

Table S17 Ammonium concentrations in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.



Figure S13 Ammonium concentrations (c) measured over time at the column effluents divided by the ammonium influent concentrations (c_0) in synthetic stormwater in the mixing chamber. Error bars represent the standard deviation of the triplicate column systems.

| | Phosphate concentration (mg/L) | | | | | | | | |
|-------------------------|--------------------------------|--------------|--------------|--------------|--------------|--------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1001 | PV 1525 | PV 2185 | | | |
| Mixing chamber | 0.5 | 0.5 | 0.5 | 0.5 | 0.6 | 0.6 | | | |
| Silica sand | 0.7 ± 0.19 | 0.4 ± 0.02 | 0.5 ± 0.01 | 0.5 ± 0.03 | 0.5 ± 0.04 | 0.6 ± 0.05 | | | |
| + 20 wt% carbonate sand | 0.6 ± 0.02 | 0.4 ± 0.01 | 0.4 ± 0.02 | 0.5 ± 0.03 | 0.5 ± 0.03 | 0.6 ± 0.01 | | | |
| + 1 wt% MCG biochar | 0.6 ± 0.02 | 0.5 ± 0.02 | 0.5 ± 0.01 | 0.5 ± 0.05 | 0.5 ± 0.05 | 0.6 ± 0.02 | | | |
| + 20 wt% carbonate sand | 0.5 ± 0.02 | 0.5 ± 0.01 | 0.5 ± 0.01 | 0.5 ± 0.04 | 0.5 ± 0.07 | 0.6 ± 0.01 | | | |
| + 1 wt% MCG biochar | | I | I | I | I | I | | | |

Table S18 Phosphate concentrations in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.



Figure S14 Phosphate concentrations (c) measured over time at the column effluents divided by the phosphate influent concentrations (c_0) in synthetic stormwater in the mixing chamber. Error bars represent the standard deviation of the triplicate column systems.

| Table S19 | Sulfate o | concentration | s in | the | mixing | chamber | and | the | column | effluents |
|--------------|------------|---------------|------|-------|-----------|----------|-----|-----|--------|-----------|
| including th | ie standar | rd deviations | of t | he tr | riplicate | columns. | | | | |

| Sulfate concentration (mg/L) | | | | | | | | |
|------------------------------------|----------------|----------------|-----------------|--|--|--|--|--|
| Pore Volumes | PV 1525 | PV 1766 | PV 2185 | | | | | |
| Mixing chamber | 31.3 | 31.1 | 31.1 | | | | | |
| Silica sand | 31.0 ± 0.4 | 31.1 ± 0.1 | 30.9 ± 0.01 | | | | | |
| + 20 wt% carbonate sand | 31.3 ± 0.4 | 30.6 ± 0.6 | 31.0 ± 0.02 | | | | | |
| $+ 1 \mathrm{wt\%}$ MCG biochar | 31.1 ± 0.1 | 31.2 ± 0.3 | 30.9 ± 0.1 | | | | | |
| + 20 wt% carbonate sand | 30.9 ± 0.2 | 31.2 ± 0.1 | 35.2 ± 7.3 | | | | | |
| $+ \ 1 \mathrm{wt}\%$ MCG biochar | | 1 | 1 | | | | | |

S7.6 Additional water quality parameters

Samples collected from the mixing chamber and the column effluents were analyzed for pH, oxidation reduction potential, electrical conductivity, total dissolved solids, and temperature using a multi-parameter probe from HANNA Instruments (HI98195). Turbidity was measured with a turbidimeter from HANNA Instruments (HI98713).

Table S20 pH values in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| | pH | | | | | | |
|--|-----------------|-----------------|-----------------|-----------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | | |
| Mixing chamber | 7.60 | 7.51 | 7.57 | 7.33 | | | |
| Silica sand | 7.05 ± 0.26 | 6.89 ± 0.40 | 7.14 ± 0.03 | 7.14 ± 0.02 | | | |
| + 20 wt% carbonate sand | 7.72 ± 0.04 | 7.64 ± 0.04 | 7.43 ± 0.22 | 7.23 ± 0.01 | | | |
| + 1 wt% MCG biochar | 7.79 ± 0.06 | 7.62 ± 0.23 | 7.42 ± 0.26 | 6.98 ± 0.07 | | | |
| + 20 wt\% carbonate sand + 1 wt\% MCG biochar | 7.93 ± 0.03 | 7.85 ± 0.04 | 7.72 ± 0.07 | 7.15 ± 0.04 | | | |
| | | | | | | | |

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).

Table S21 Oxidation reduction potential (ORP) values in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| | ORP (mV) | | | | | |
|----------------------------------|--------------|--------------|--------------|--------------|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | |
| Mixing chamber | 178 | 221 | 235 | 268 | | |
| Silica sand | 212 ± 12 | 273 ± 18 | 252 ± 1 | 256 ± 1 | | |
| + 20 wt% carbonate sand | 181 ± 3 | 231 ± 3 | 256 ± 15 | 253 ± 1 | | |
| + 1 wt% MCG biochar | 178 ± 7 | 230 ± 8 | 232 ± 33 | 268 ± 4 | | |
| + 20 wt% carbonate sand | 167 ± 2 | 218 ± 3 | 224 ± 12 | 250 ± 12 | | |
| $+$ $1\mathrm{wt}\%$ MCG biochar | | I | I | 1 | | |

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).

Table S22 Electrical conductivity in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| Electrical conductivity (μ S/cm) | | | | | | | |
|---------------------------------------|-------------|-------------|--------------|-------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | | |
| Mixing chamber | 449 | 369 | 370 | 371 | | | |
| Silica sand | 451 ± 2 | 303 ± 72 | 364 ± 10 | 370 ± 2 | | | |
| +20 wt% carbonate sand | 458 ± 3 | 372 ± 7 | 363 ± 12 | 370 ± 1 | | | |
| + 1 wt% MCG biochar | 457 ± 3 | 377 ± 7 | 369 ± 5 | 371 ± 4 | | | |
| + 20 wt% carbonate sand | 462 ± 4 | 383 ± 2 | 372 ± 4 | 372 ± 1 | | | |
| $+ 1 \mathrm{wt\%}$ MCG biochar | | I | | I | | | |

Table S23 Total dissolved solids (TDS) in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| Total dissolved solids (TDS, mg/L) | | | | | | | |
|-------------------------------------|-------------|--------------|-------------|-------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | | |
| Mixing chamber | 224 | 184 | 185 | 186 | | | |
| Silica sand | 225 ± 1 | 151 ± 36 | 183 ± 5 | 185 ± 1 | | | |
| + 20 wt% carbonate sand | 229 ± 2 | 186 ± 4 | 182 ± 6 | 185 ± 1 | | | |
| + 1 wt% MCG biochar | 229 ± 2 | 188 ± 4 | 185 ± 2 | 185 ± 1 | | | |
| $+ 20 \mathrm{wt\%}$ carbonate sand | 231 ± 2 | 192 ± 1 | 186 ± 2 | 185 ± 2 | | | |
| $+$ $1\mathrm{wt}\%$ MCG biochar | | I | | I | | | |

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).

Table S24 Temperature in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| | Temperature ($^{\circ}$ C) | | | | | | |
|-------------------------|-----------------------------|----------------|--------------|----------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | | |
| Mixing chamber | 21.1 | 21.7 | 22.0 | 22.6 | | | |
| Silica sand | 21.5 ± 0.1 | 21.3 ± 0.4 | 22.0 ± 0.1 | 22.4 ± 0.2 | | | |
| + 20 wt% carbonate sand | 21.5 ± 0.1 | 21.7 ± 0.1 | 22.0 ± 0.1 | 22.7 ± 0.1 | | | |
| + 1 wt% MCG biochar | 21.4 ± 0.1 | 21.4 ± 0.1 | 21.8 ± 0.2 | 23.0 ± 0.1 | | | |
| + 20 wt% carbonate sand | 21.3 ± 0.1 | 21.6 ± 0.1 | 21.9 ± 0.1 | 23.0 ± 0.1 | | | |
| + 1 wt% MCG biochar | | | 1 | 1 | | | |

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).

Table S25 Turbidity in the mixing chamber and the column effluents including the standard deviations of the triplicate columns.

| | 1 | Turbidity (FNU) | | | | | |
|------------------------------------|---------------|-----------------|-------------------|---------------|--|--|--|
| Pore Volumes | $PV 0^{a}$ | PV 147 | PV 205 | PV 1524 | | | |
| Mixing chamber | 4.4 | 3.9 | 3.5 | 4.1 | | | |
| Silica sand | 5.1 ± 0.5 | 3.9 ± 0.5 | 4.1 ± 0.03 | 3.1 ± 0.3 | | | |
| $+20 \mathrm{wt\%}$ carbonate sand | 6.0 ± 0.5 | 3.5 ± 0.1 | n.m. ^b | 3.5 ± 0.2 | | | |
| + 1 wt% MCG biochar | 3.7 ± 0.1 | 4.4 ± 0.1 | 3.8 ± 0.4 | 3.3 ± 0.2 | | | |
| $+20 \mathrm{wt\%}$ carbonate sand | 3.2 ± 0.2 | 4.8 ± 0.8 | 4.0 ± 0.3 | 3.9 ± 0.5 | | | |
| $+$ $1\mathrm{wt}\%$ MCG biochar | | I | I | I | | | |

^a 24 hours before starting the challenge test (i.e, before introducing metals and TrOCs).

^b not measured

S8 Metal removal in flow-through column experiments



Figure S15 Breakthrough of nickel (initial concentration $c_0 = 50 \ \mu g/L$) from synthetic stormwater (pH 7.5) in columns containing (i) silica sand, (ii) silica sand mixed with 20 wt% carbonate sand, (iii) silica sand mixed with 1 wt% MCG biochar, and (iv) silica sand mixed with 20 wt% carbonate sand and 1 wt% MCG biochar. The concentrations c and c_0 were measured at the column effluents and in the mixing chamber, respectively. Error bars represent standard deviations of triplicate columns.



Figure S16 Concentration of the five metals in the mixing chamber over the time course of the column experiment.

Table S26 Tukey's Honest Significant Difference (HSD) post-hoc test to compare the different sand and biochar treatments concerning metal removal in column experiments ($\alpha = 0.05$). Significantly different means are indicated with a star (*).

| | 1 | | p-value | | |
|------------------------------------|----------------|----------------|----------------|----------------|----------------|
| Comparison | Cd | Ni | Zn | Cu | Pb |
| S ^a vs. SC ^b | 0.0023* | 0.9998 | 0.0036^{*} | >0.9999 | 0.062 |
| S vs. SB ^c | 0.0017^{*} | 0.0036^{*} | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| S vs. SCB ^d | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SC vs. SB | 0.9996 | 0.0045^{*} | 0.0061^{*} | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SC vs. SCB | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SB vs. SCB | $< 0.0001^{*}$ | 0.4146 | $< 0.0001^{*}$ | 0.6031 | $< 0.0001^{*}$ |

^aS: Silica sand

^b SC: Silica sand + 20 wt% carbonate sand

 $^{\rm c}\,{\rm SB:}$ Silica sand + $1\,{\rm wt}\%$ MCG biochar

 $^{\rm d}\,{\rm SCB}:$ Silica s and + 20 wt% carbonate s and + 1 wt% MCG biochar

S9 TrOC removal in flow-through column experiments



Figure S17 Breakthrough of mecoprop (initial nominal concentration $c_0 = 50 \ \mu g/L$) from synthetic stormwater (pH 7.5) in columns containing (i) silica sand, (ii) silica sand mixed with 20 wt% carbonate sand, (iii) silica sand mixed with 1 wt% MCG biochar, and (iv) silica sand mixed with 20 wt% carbonate sand and 1 wt% MCG biochar. The concentrations c and c_0 were measured at the column effluents and in the mixing chamber, respectively. Error bars represent standard deviations of triplicate columns.



Figure S18 Breakthrough of 1H-benzotriazole (initial nominal concentration $c_0 = 50 \ \mu g/L$) from synthetic stormwater (pH 7.5) in columns containing (i) silica sand, (ii) silica sand mixed with 20 wt% carbonate sand, (iii) silica sand mixed with 1 wt% MCG biochar, and (iv) silica sand mixed with 20 wt% carbonate sand and 1 wt% MCG biochar. The concentrations c and c_0 were measured at the column effluents and in the mixing chamber, respectively. Error bars represent standard deviations of triplicate columns.



Figure S19 Concentration of the seven trace organic contaminants in the mixing chamber over the time course of the column experiment.

Table S27 Tukey's Honest Significant Difference (HSD) post-hoc test to compare the different sand and biochar treatments concerning TrOCs removal ($\alpha = 0.05$). Significantly different means are indicated with a star (*).

| | | | | p-value | | | |
|------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Comparison | Dicamba | Mecoprop | Fipronil | Terbutryn | Atenolol | 1H-BT | Diuron |
| S ^a vs. SC ^b | >0.9999 | >0.9999 | >0.9999 | >0.9999 | >0.9999 | >0.9999 | >0.9999 |
| S vs. SB^{c} | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| S vs. SCB ^d | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SC vs. SB | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SC vs. SCB | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ | $< 0.0001^{*}$ |
| SB vs. SCB | 0.9642 | >0.9999 | >0.999 | >0.9999 | >0.9999 | >0.9999 | >0.9999 |

^aS: Silica sand

 $^{\rm b}\,{\rm SC}:$ Silica s and + 20 wt% carbonate s and

 $^{\rm c}\,{\rm SB:}$ Silica sand + $1\,{\rm wt}\%$ MCG biochar

 $^{\rm d}\,{\rm SCB}:$ Silica s and + 20 wt% carbonate s and + 1 wt% MCG biochar

S10 Forward-prediction transport model

S10.1 Model equations, input parameters, and references

A one-dimensional numerical model for the transport of trace organic contaminants in the biochar columns was adopted from Werner et al. 2012^2 and Ulrich et al. 2015.¹ The movement of organic contaminant molecules in or out of the biochar particles was described by intraparticle diffusion. For the diffusion-limited sorption kinetics, the mass transport equation was²

$$\frac{dc_w}{dt} = E_{disp} \frac{\partial^2 c_w}{\partial x^2} - u_x \frac{\partial c_w}{\partial x} - \frac{1 - \theta_w - \theta_{sand}}{\theta_w} \frac{d}{dt} \left[3 \int_0^1 y^2 S dy \right] \tag{1}$$

where c_w (moles/m³) is the aqueous concentration of the organic contaminant, t (s) is the time, E_{disp} (m²/s) is the hydrodynamic dispersion coefficient, x (m) is the distance from the column inlet in the flow direction, u_x (m/s) is the porewater velocity, θ_w (–) is the volumetric water content of the column external to the grains, θ_{sand} (–) is the volumetric fraction of the column filled with sand, y (–) is the ratio of the radial distance r (m) from the center of the biochar particle divided by the biochar particle radius R (m), S (moles/m³) is the volumetric concentration of the contaminants in the biochar particle.

The intraparticle diffusion is described by 2

$$\frac{\partial S}{\partial t} = \frac{D_{app}}{R^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial S}{\partial r} \right) \tag{2}$$

where D_{app} (m²/s) is the apparent intraparticle diffusion coefficient.² The non-linear Freundlich isotherm is described by

$$c_s = K_{fr} \cdot c_w^{^N} \tag{3}$$

$$N = \frac{1}{n_{fr}} \tag{4}$$

where c_s (kg/kg) is the solid phase concentration of the organic contaminant, K_{fr} is the Freundlich coefficient in (moles/kg)(m³/moles)^N, and N is the Freundlich exponent (–).

Assuming the non-linear Freundlich isotherm, the apparent diffusion coefficient D_{app} depends on the aqueous contaminant concentration as described by²

$$D_{app} = \frac{D_{aq}p_{bc}}{(d_s K_{fr} N c_w^{N-1} + p_{bc})\tau}$$

$$\tag{5}$$

where D_{aq} (m²/s) is the molecular diffusion coefficient in water, p_{bc} (-) is the intraparticle porosity of biochar, d_s (kg/m³) is the solid (skeletal) density of the grains, and τ (-) is the intraparticle tortuosity. The molecular diffusion coefficients D_{aq} were estimated according to¹

$$D_{\rm aq} = \frac{2.7 \cdot 10^{-8}}{\rm MW^{0.71}} \tag{6}$$

where MW is the molecular weight of the organic contaminants ($MW_{dicamba} = 221.04 \text{ g/mol}$; $MW_{fipronil} = 437.15 \text{ g/mol}$; $MW_{terbutryn} = 241.36 \text{ g/mol}$).

| Parameter | | Parameter value | Source |
|---|-------------------------------|---|-----------------------|
| Column length | | $L_c = 0.48 \mathrm{m}$ | measured |
| Inner column radius | | $R_c = 0.015875 \mathrm{m}$ | measured |
| Dry mass of biochar in the column | $(0.87\mathrm{wt\%})$ | $M_{bc} = 0.0058 \mathrm{kg}$ | measured |
| Dry mass of sand in the column | | $M_{sand} = 0.660 \mathrm{kg}$ | measured |
| Flow through the column | | $Q = 2.08167 \cdot 10^{-8} m^3/s$ | measured |
| Hydrodynamic dispersion coefficient | nt | $E_{disp} = 4.4 \cdot 10^{-7} \text{ m}^2/\text{s}$ | Br tracer fitting |
| Solid density of sand particles | | $d_{sand} = 2650 \text{ kg/m}^3$ | Fisher Scientific |
| Radius of the sand particles | | $R_{sand} = 3.5 \cdot 10^{-4} \mathrm{m}$ | Fisher Scientific |
| Sorption coefficient for the sand pa | articles | $K_{sand} = 0 m^3/kg$ | assumed |
| Radius of the MCG biochar partic | les | $R_{bc} = 3.5 \cdot 10^{-4} m$ | sieved biochar |
| Solid skeletal density of MCG biod | char | $d_{bc} = 1784 \text{ kg/m}^3$ | measured ^a |
| Intraparticle porosity of MCG biochar particles | | $p_{bc} = 0.70 [-]$ | $measured^{b}$ |
| Different biochar amounts | | | |
| Dry mass of biochar in the column | 1 wt% MCG | $M_{bc} = 0.0059 \mathrm{kg}$ | $calculated^{c}$ |
| | $2.5\mathrm{wt}\%$ MCG | $M_{bc} = 0.0133 \mathrm{kg}$ | $calculated^{c}$ |
| | $5\mathrm{wt}\%~\mathrm{MCG}$ | $M_{bc} = 0.0228 \mathrm{kg}$ | $calculated^{c}$ |
| | $10{\rm wt}\%~{\rm MCG}$ | $M_{bc} = 0.0352 \mathrm{kg}$ | $calculated^{c}$ |
| Dry mass of sand in the column | $1\mathrm{wt}\%~\mathrm{MCG}$ | $M_{sand} = 0.5889 \mathrm{kg}$ | $calculated^{c}$ |
| | $2.5\mathrm{wt}\%$ MCG | $M_{sand} = 0.5201 \mathrm{kg}$ | $calculated^{c}$ |
| | $5\mathrm{wt}\%~\mathrm{MCG}$ | $M_{sand} = 0.4323 \mathrm{kg}$ | $calculated^{c}$ |
| | $10\mathrm{wt}\%$ MCG | $\mathrm{M}_{sand}=0.3167\mathrm{kg}$ | $calculated^{c}$ |

Table S28 Input parameters for model calculations, parameter values and references.

^a Helium pycnometry (Particle Technology Labs, PTL, US)

^b Mercury intrusion porosimetry (Particle Technology Labs, PTL, US)

 $^{\rm c}$ Using bulk densities of $181.5\,\rm kg/m^3$ for MCG biochar and $1690\,\rm kg/m^3$ for sand

S10.2 Sorption parameters from column breakthrough curves

The intraparticle tortuosity τ (–) of the MCG biochar as well as the Freundlich coefficient (K_{fr}) and the Freundlich exponent (N = 1/n_{fr}) were obtained from fitting the measured effluent data for dicamba in columns containing sand mixed with 0.87 wt% MCG biochar. The intraparticle tortuosity obtained from fitting the dicamba data was further used for the fitting of fipronil and terbutryn breakthrough curves.

Table S29 Sorption parameters and the corresponding standard deviations obtained from fitting the column breakthrough data of the three replicate columns to the transport model. K_{fr} is the Freundlich coefficient and N is the Freundlich exponent. The tortuosity value τ was obtained from the dicamba data and applied to all compounds. The root mean squared error (RMSE) is reported to evaluate the goodness of fit.

| Compound | ${f K_{fr}} \ ({ m moles}/{ m kg}) ({ m m}^3/{ m moles})^{ m N}$ | N (-) | au (-) | $\begin{array}{c} \mathbf{RMSE} \\ (\mathrm{moles}/\mathrm{m}^3) \end{array}$ |
|-----------|--|------------------|--------------|---|
| Dicamba | 0.56 ± 0.10 | 0.49 ± 0.021 | 4.1 ± 0.44 | $1.1 \cdot 10^{-5}$ |
| Fipronil | 1.42 ± 0.24 | 0.51 ± 0.023 | 4.1 ± 0.44 | $2.4\cdot 10^{-6}$ |
| Terbutryn | 1.19 ± 0.15 | 0.46 ± 0.018 | 4.1 ± 0.44 | $2.8\cdot 10^{-6}$ |



Figure S20 Trace organic contaminant breakthrough curves in columns containing sand mixed with 0.87 wt% MCG biochar. (a) The forward-prediction transport model was fitted to the measured dicamba effluent concentrations using the Freundlich parameters (K_{fr} and N) and the tortuosity (τ) as fitting parameters. (c, e) The forward-prediction transport model was fitted to the measured fipronil and terbutryn effluent concentrations using the Freundlich parameters (K_{fr} and N) as fitting parameters. (b, d, f) Simulated breakthrough curves for constant influent concentration using the obtained tortuosity and Freundlich parameters from the fitting.

S10.3 Case study to predict filter longevity

| Parameter | Value | Unit |
|--|-----------------|---------------------------|
| Total volume of stormwater captured per year | $1.1\cdot 10^6$ | m^3/a |
| Infiltration period | 122 | days |
| Stormwater volume infiltrated per day | 9016 | m^3/d |
| Filter area | 4046.86 | m^2 |
| Filter depth | 1 | m |
| Porosity of filter material 1 wt\% MCG | 0.39 | _ |
| $2.5\mathrm{wt\%}$ MCG | 0.42 | — |
| $5{ m wt}\%{ m MCG}$ | 0.46 | — |
| $10{ m wt\%}~{ m MCG}$ | 0.51 | — |
| Pore volume of the filter 1 wt\% MCG | 1563 | m^3 |
| $2.5\mathrm{wt\%}$ MCG | 1692 | m^3 |
| $5\mathrm{wt}\%\mathrm{MCG}$ | 1855 | m^3 |
| $10\mathrm{wt\%}$ MCG | 2074 | m^3 |

Table S30 Parameters for case study calculations.



Figure S21 Simulated breakthrough curves for dicamba in columns containing 1 wt%, 2.5 wt%, 5 wt%, and 10 wt% MCG biochar using initial nominal dicamba concentrations of (a) $c_0 = 50 \,\mu g/L$ and (b) $c_0 = 5 \,\mu g/L$.

Table S31 Pore volumes until breakthrough of dicamba (defined as $c/c_0 = 0.2$) and estimated lifetime of biochar filters containing different weight percents of biochar (1 wt%, 2.5 wt%, 5 wt%, and 10 wt%) in years under ideal conditions with dicamba influent concentrations of $c_0 = 50 \,\mu\text{g/L}$ and $c_0 = 5 \,\mu\text{g/L}$.

| | $50\mu{ m g}/$ | L | $5\mu{ m g}/{ m I}$ | J |
|--------------------|--------------------|----------|---------------------|----------|
| Biochar | Pore volumes | Lifetime | Pore volumes | Lifetime |
| amendment | _ | years | _ | years |
| $1 \mathrm{wt}\%$ | $1.1 \cdot 10^{3}$ | 1.6 | $3.6 \cdot 10^3$ | 5.1 |
| $2.5\mathrm{wt}\%$ | $2.6 \cdot 10^3$ | 4.0 | $8.4 \cdot 10^3$ | 12.9 |
| $5\mathrm{wt}\%$ | $4.0 \cdot 10^{3}$ | 6.7 | $1.3\cdot 10^4$ | 21.7 |
| $10{ m wt}\%$ | $5.3 \cdot 10^3$ | 9.9 | $1.7\cdot 10^4$ | 32.1 |

References

- Ulrich, B. A., Im, E. A., Werner, D., and Higgins, C. P. (2015). Biochar and activated carbon for enhanced trace organic contaminant retention in stormwater infiltration systems. *Environ. Sci. Technol.*, 49(10):6222–6230.
- [2] Werner, D., Karapanagioti, H. K., and Sabatini, D. A. (2012). Assessing the effect of grainscale sorption rate limitations on the fate of hydrophobic organic groundwater pollutants. J. Contam. Hydrol., 129-130:70–79.