Supporting Information

Application of a full-scale wood gasification biochar as soil improver to reduce organic pollutant leaching risks

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1. Materials and experimental methods

Soil and biochar (BC). Skeletal densities were determined in a pycnometer (50 ml, n = 3). Bulk densities were measured by weighting the mass introduced in a calibrated volume. For structure analysis, soil and biochar samples (10 g, n = 3) were pre-treated according to standard methods [1]. Particle distributions of soil and biochar samples were determined by the laser scattering and diffraction method (Malvern Master 2000). Diameters of soil and biochar particles were calculated as geometric mean.

Soil water content was determined according the standardized method ISO 11465 (2003) by drying soil (10 g, n = 5) in an oven (Swallow, LTE Scientific Ltd., UK) at 105 ^{o}C until a constant mass was reached. Then samples were re-weighted and the water content was calculated as following:

Water content = (Mass air dry – Mass oven dry)/Mass air dry . 100

The soil organic matter content was determined (5 g, n = 5) by loss of ignition in an electrical muffle furnace (Anderman, Cestradent Ltd., UK) at 450 ^{o}C overnight as follows:

% organic matter = (Mass oven dry – Mass furnace dry) / Mass oven dry . 100

Chemicals. Sulfamethazine (SMZ), [benzene ring-UL-^{14}C]-SMZ, phenanthrene (PHE), [9-^{14}C]-PHE were purchased from Sigma-Aldrich (UK). Isoproturon (IPU) was purchased from ARC (UK). [Benzene ring-U-^{14}C]-IPU was purchased from Amersham Biosciences (UK). Scintillation cocktail liquid (UltimaGold XR) and sample oxidiser cocktails (Carbosorb and Permafluor) were obtained from Perkin Elmer (UK). Other chemicals were analytical grade (99%). Table S1 presents the physico-chemical properties of these compounds.

38 **Table S1.** Physico-chemical properties of the tested chemicals

	Sulfamethazine	**Isoproturon**	**Phenanthrene**
CAS No.	57-68-1	34123-59-6	85-01-8
Formula	$C_{12}H_{14}N_4O_2S$	$C_{12}H_{18}N_2O$	$C_{14}H_{10}$
IUPAC name	4-amino-*N*-(4,6-dimethylpyrimidin-2-yl) benzenesulfonamide	3 - (4-isopropylphenyl) -1,1-dimethylurea	Phenanthrene
Molecular Weight (MW) (g mol^{-1})	278.33	206.29	178.2
Water Solubility (mg l^{-1})	1500 (29 ºC) [2]	65 (22 ºC) [3]	1.18 (25 ^{0}C) [4]
Partition coefficients:			
Log K_{OW} (20 ^{0}C)	0.28 [5]	2.50 [3]	4.46 [4] 4.52 [5]
Density (g cm^{-3})	---	1.2 [3]	1.1147 [4]
Vapour pressure (25 ºC, Pa)	1.15×10^{-6} [2]	8.1×10^{-6} [3]	5.23×10^{-2} [4]
Henry's Law constant at (25 ^{0}C, Pa.m^3 mol^{-1})	3.1×10^{-8} [2]	1.46×10^{-5} [3]	3.9×10^{-5} [6]

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Column leaching experiment

Figure S1 presents a set-up of the column leaching experiments. After water-saturating the columns overnight, flow rate was measured for BC0, BC1, and BC5 column (n = 3).

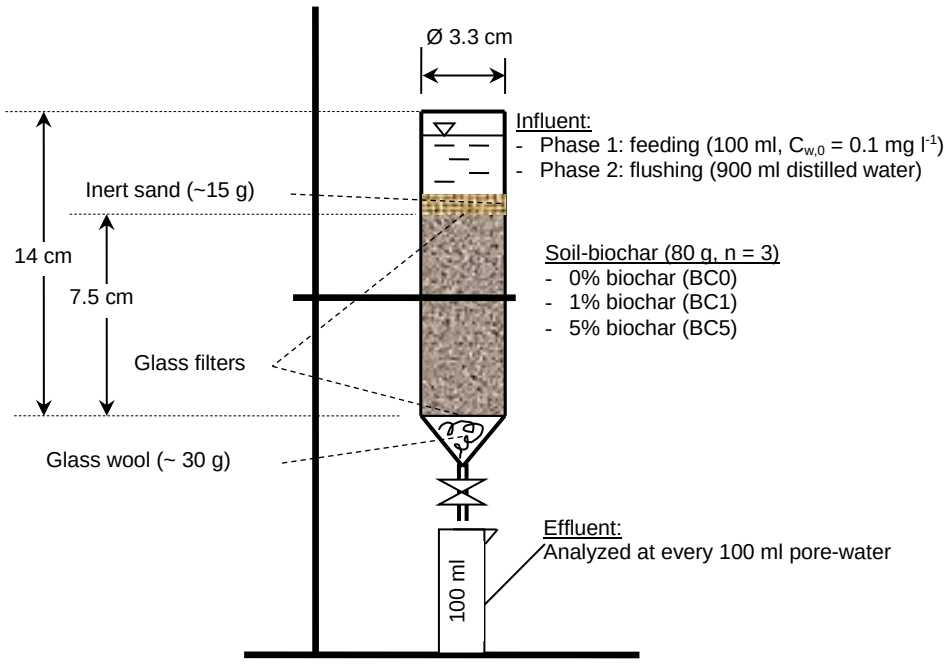

Figure S1. A set-up of the column leaching experiments

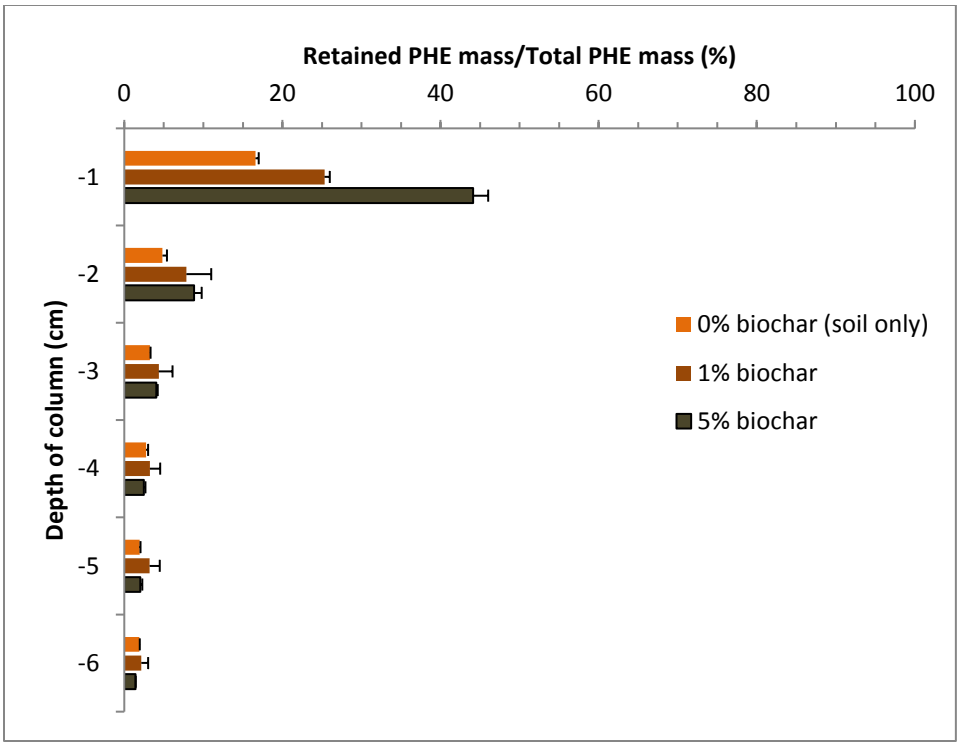

Figure S2. Profile of phenanthrene retained in the soil-biochar mixture along the length of the leaching column (n = 3)

Table S2: Independent and dependant variables and input parameters for the batch sorption kinetic model

Variables and input parameters	Description	Input parameter values	Source
t (s)	Time	0 – 30.86400	Measured
r (m)	Radial distance from the BC particle centre	$0 – 0.1 \times 10^{-3}$	Measured
C_w (moles m^{-3}) $C_{w,0}$ (moles m^{-3})	Pollutant concentration in external water Initial concentration of C_w	Dependant variable 0.1/MW with MW = 278.33 (SMZ); 206.29 (IPU); 178.2 (PHE)	Simulated Measured
$C_{s,rev}$ (moles kg^{-1})	Reversibly bound pollutant concentration associated with the soil solids	Dependant variable	Simulated
$C_{s,irrev}$ (moles kg^{-1})	Irreversibly bound pollutant concentration associated with the soil solids	Dependant variable	Simulated
$C_{BC,ippw}$ (moles m^{-3})	Pollutant concentration in the BC intraparticle pore-water	Dependant variable	Simulated
K_s (m^3 kg^{-1})	Reversible soil-water partitioning coefficient for a specific pollutant	3.46×10^{-3} (SMZ) 6.41×10^{-3} (IPU) 20.55×10^{-3} (PHE)	Measured
K_{BC} (m^3 kg^{-1})	Reversible BC-water partitioning coefficient for a specific pollutant	1500×10^{-3} (SMZ) 4000×10^{-3} (IPU) 600×10^{-3} (PHE)	Measured and calibrated
V_w (m^3)	Water volume in the batch outside of particles	30×10^{-6}	Measured
M_{pol} (moles)	Amount of pollutant added to the batch	3×10^{-6}/MW	Measured
M_s (kg)	Dry soil mass in the batch	$3(1 - x) \times 10^{-3}$ with x = 0, 0.01, 0.05 and 1 for BC0, BC1, BC5, and BC100	Measured
M_{BC} (kg)	Dry BC mass in the batch	$3x \times 10^{-3}$ with x = 0; 0.01; 0.05 and 1 for BC0, BC1, BC5, and BC100	Measured
R_{BC} (m)	BC particle radius	0.1×10^{-3}	Measured
$\theta_{BC,w}$ (-)	Water-filled BC intraparticle porosity	0.65	Literature [7]
d_{BC} (kg m^{-3})	Solid density of the BC skeleton	1.5×10^3	Measured

Table S2: Independent and dependant variables and input parameters for the batch sorption kinetic model (continued)

Variables and input parameters	Description	Input parameter values	Source
τ (-)	BC pore network tortuosity factor	BC1: 14000 (SMZ); 9000 (IPU); 1600 (PHE) BC5: 1200 (SMZ); 1000 (IPU); 1500 (PHE) BC100: 300 (SMZ); 400 (IPU); 1000 (PHE)	Fitted
D_{aq} ($m^2 s^{-1}$)	The molecular diffusion coefficient of the pollutant in water	$2.7 \times 10^{-8}/MW^{0.71}$	Literature [8]
$k_{s,rev}$ (s^{-1})	First-order kinetic sorption rate for reversibly bound pollutants	0.8×10^{-6} (SMZ) 10×10^{-6} (IPU) 20×10^{-6} (PHE)	Fitted
$k_{s,irrev}$ (s^{-1})	First-order kinetic sorption rate for irreversibly bound pollutants	0.1 (SMZ) 0.01 (IPU) 0.05 (PHE)	Fitted
$C_{s,irrev,max}$ (moles kg^{-1})	Maximum concentration of a specific pollutant which can be irreversibly sorbed by soil particles	$0.022K_sC_{w,0}$ (SMZ) $0.015K_sC_{w,0}$ (IPU) $0.038K_sC_{w,0}$ (PHE)	Fitted

MW – Molecular Weight

Table S3: Independent and dependant variables and input parameters of the column transport models

Variables and input parameters	Description	Values	Source
t (s)	Time: Feeding time Eluting time	$0 – 0.1\times10^{-3}/Q_{BC}$ $0.1\times10^{-3}/Q_{BC} – 1\times10^{-3}/Q_{BC}$	Measured
Q_{BC} (m^3s^{-1})	Infiltration flow rates of BC0, BC1, and BC5 columns	0.4401×10^{-6} (BC0) 0.1895×10^{-6} (BC1) 0.0773×10^{-6} (BC5)	Measured
x (m)	Distance from the column inlet	0 – 0.075	Measured
r (m)	Radial distance from the BC particle centre	$0 – 0.1\times10^{-3}$	Measured
C_w (moles m^{-3}) $C_{in} = C_{w,0}$ (moles m^{-3})	Pollutant concentration in interparticle water between soil and BC particles Feeding pollutant concentration	Dependant variable 0.1/MW with MW = 278.33 (SMZ); 206.29 (IPU); 178.2 (PHE)	Simulated Measured
$C_{s,rev}$ (moles kg^{-1})	Reversibly bound pollutant concentration associated with the soil solids	Dependant variable	Simulated
$C_{s,irrev}$ (moles kg^{-1})	Irreversibly bound pollutant concentration associated with the soil solids	Dependant variable	Simulated
$C_{BC,ippw}$ (moles m^{-3})	Pollutant concentration in the BC intraparticle pore-water	Dependant variable	Simulated
K_s (m^3kg^{-1})	Reversible soil solid-water partitioning coefficient for the pollutant	3.46×10^{-3} (SMZ) 6.41×10^{-3} (IPU) 20.55×10^{-3} (PHE)	Measured
K_{BC} (m^3kg^{-1})	Reversible BC solid-water partitioning coefficient for the pollutant	1500×10^{-3} (SMZ) 4000×10^{-3} (IPU) 600×10^{-3} (PHE)	Measured
L (m)	Length of the column	0.075	Measured
R_C (m)	Radius of the column	0.0165	Measured
v_x (m s^{-1})	Pore-water velocity between the soil and BC particles in the x (downward) direction	$= Q_{BC}/(\pi R_C^2\theta)$ with θ is the interparticle porosity of BC	Measured
D_{disp} (m^2 s^{-1})	Hydrodynamic dispersion coefficient for pollutants in the water in between the soil and BC particles	3.1×10^{-8}	Literature [9]

61 **Table S3**: Independent and dependant variables and input parameters of the column transport models

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Variables and input parameters	Description	Values	Source
M_s (kg)	Dry soil mass in the columns	$80(1 - x) \times 10^{-3}$ with x = 0, 0.01, and 0.05 for BC0, BC1, and BC5	Measured
d_s (kg m^{-3})	Solid density of the soil particles	2.49×10^{3}	Measured
M_{BC} (kg)	Dry BC mass in the columns	$80.x\times10^{-3}$ with x = 0, 0.01, and 0.05 for BC0, BC1, and BC5	Measured
R_{BC} (m)	BC particle radius	0.1×10^{-3}	Measured
$\theta_{BC,w}$ (-)	Water-filled BC intraparticle porosity	0.65	Literature [7]
d_{BC} (kg m^{-3})	Solid density of the BC skeleton	1.5×10^{3}	Measured
τ (-)	BC pore network tortuosity factor	BC1: 14000 (SMZ); 9000 (IPU); 1600 (PHE) BC5: 1200 (SMZ); 1000 (IPU); 1500 (PHE) BC100: 300 (SMZ); 400 (IPU); 1000 (PHE)	Fitted from batch experiments
D_{aq} (m^{2}s^{-1})	The molecular diffusion coefficient of the pollutant in water	2.7×10^{-8} /MW$^{0.71}$	Literature [8]
$k_{s,rev}$ (s^{-1})	First-order kinetic sorption rate for reversibly bound pollutants	0.8×10^{-6} (SMZ) 10×10^{-6} (IPU) 20×10^{-6} (PHE)	Fitted from batch experiments
$k_{s,irrev}$ (s^{-1})	First-order kinetic sorption rate for irreversibly bound pollutants	0.1 (SMZ) 0.01 (IPU) 0.05 (SMZ)	Fitted
$C_{s,irrev,max}$ (moles kg^{-1})	The maximum concentration of pollutant which can be irreversibly sorbed by the soil particles	$0.022K_sC_{w,0}$ (SMZ) $0.015K_sC_{w,0}$ (IPU) $0.038K_sC_{w,0}$ (PHE)	Fitted

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References

1. Pansu M and Gautheyrou J, Handbook of soil analysis: mineralogical, organic and inorganic methods. Springer, Berlin (2006).
2. NCBI, National Center for Biotechnology Information. PubChem Compound Database; CID=5327, https://pubchem.ncbi.nlm.nih.gov/compound/5327, Accessed on 16 Dec 2015 (2015).
3. Tomlin C, The pesticide manual : a world compendium. Alton : British Crop Protection Council (2006).
4. Yaws CL, Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health Related Properties for Organic and Inorganic Chemicals. McGraw-Hill, New York (1999).
5. Sangster J, Octanol-Water Partition Coefficients: Fundamentals and Physical Chemistry, in Wiley Series in Solution Chemistry. John Wiley & Sons, Chichester - New York (1997).
6. Riser_Roberts E, Remediation of Petroleum Contaminated Soils: Biological, Physical, and Chemical Processes. Lewis Publishers (1998).
7. Brewer CE, Chuang VJ, Masiello CA, Gonnermann H, Gao X, Dugan B, Driver LE, Panzacchi P, Zygourakis K and Davies CA, New approaches to measuring biochar density and porosity. *Biomass and Bioenergy* **66**: 176-185 (2014).
8. Schwarzenbach RP, Gschwend PM and Imboden DM, Environmental Organic Chemistry. Wiley-Interscience, Hoboken, N.J. (2003).
9. Zheng C and Bennett GD, Applied contaminant transport modeling : theory and practice. Wiley-Interscience, New York (2002).