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Supplementary Information:

Mechanisms of Distinct Activated Carbon and Biochar Amendment Effects on Petroleum Vapor Biofiltration in Soil

Khaled M. Bushnaf[1,*], George Mangse[2,*], Paola Meynet[2], Russell J. Davenport[2], Olaf A. Cirpka[3] and David Werner[2,§]

[1]*Department of Earth and Environmental Sciences, El-Mergib University, Khoms, Libya*

[2]*School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, England, United Kingdom*

[3]*Center for Applied Geoscience, University of Tübingen, 72074 Tübingen, Germany*

[*]These authors contributed equally to the work

[§]Corresponding author: Phone 0044 191 208 5099, Fax 0044 191 208 6502, e-mail: david.werner@ncl.ac.uk

Additional method descriptions:

Batches experiments. Amber vials (65 mL, Jencons, a VWR Division, Leicestershire, UK) closed with Teflon Mininert valves (Supelco, Bellefonte, USA) were prepared in triplicates, and contained wet construction sand without sorbent amendment (soil), and with 2% d.w. biochar amendment (soil & BC) or 2% d.w. activated carbon amendment (soil & AC). Similarly, sterilized controls were prepared by autoclaving the same soil types at 121 °C for 30 min. Water contents of the vials were determined by the weight loss of control vials upon drying in the oven at 105 ºC. Three kinds of batch experiments were performed. Firstly, VPH headspace concentrations were monitored after injecting 0.002 mL of VPH mixture as liquid into the batches containing 40, 25 and 13 g of wet construction sand for soil, soil & BC, and soil & AC, respectively, to determine VPH vapor biodegradation rates (live soils) and sorption coefficients (sterile soils). Secondly, to study the effects of nutrients on the biodegradation of VPHs, VPH residuals were extracted 30 days after the addition of 0.03 mL of VPH mixture to 15 g wet construction sand, equivalent to 0.018 g VPH-carbon, from the various soil types (soil, soil & BC, soil & AC) with and without the addition of 0.0018 g of nitrogen in the form of NH_4Cl and/or 0.00018 g of phosphorus in the form of KH_2PO_4 (i.e., nitrogen and phosphorus were added together or separately). Autoclaved controls with and without VPH mixture addition were also set up in parallel. On day 4 and day 6, 10 mL of the headspace air in the nutrient amended batches containing soil with or without biochar were replaced with pure air using gas-tight syringes to keep the batch aerobic, and the amount of VPHs removed with the syringe was measured and considered as non-degraded VPHs in the mass balance. Thirdly, batch experiments were performed to investigate soil microbiology. CO_2 was monitored in the headspace of batches with and without 0.03 mL of VPH mixture addition, with and without nutrient addition, or with

the addition of 0.03 mL of equal weight mixtures of either the straight chain alkanes, the branched and cyclic alkanes, or the monoaromatic hydrocarbons. After between 8 and 15 days, soil DNA was extracted for 16s rRNA gene sequencing. Batch study data interpretation followed protocols described by Bushnaf et al. [1]. The apparent first-order biodegradation rates in the gas phase [2, 3] was estimated by linear regression of the natural logarithm of the VPH concentration in soil air versus time in the part of the experimental data that showed a clear decrease, e.g. after an eventual lag phase, and the rate had to be greater than the one observed in the sterile control. Exemplary data is shown in Figure S1 for hexane (no lag phase) and isooctane (lag phase). First-order biodegradation rates in the water were derived from these measurements as explained in Bushnaf et al. [1].

Ammonium quantification. Readily available nutrients were extracted using 1:1 w:w ratios of soil:$CaCl_2$ 0.01 M ($CaCl_2$ from VWR, Leicestershire, UK) in centrifuge tubes which were shaken for 20 h. The slurries were centrifuged at 4,000 rpm for 10 min and the supernatant was immediately filtered through syringe filters (pore size 0.2µm, VWR, Leicestershire, UK). Ammonium determination was carried out using an ammonium reagent kit (Merck no. 1.4752.002, Merck, Darmstadt, Germany) and a Spectroquant Nova 60 photometer (Merck, Germany). The sample of supernatant solution (5 ml) was put into test tube, and 0.6 ml of sodium hydroxide buffer solution and 0.5 g of EDTA was added. After 5 min of shaking 3 drops of sodium nitroprusside indicator were added.

Nitrate, sulphate and phosphate quantification. Nitrate, sulphate and phosphate analysis was performed on a Dionex ICS 1000 Ion Chromatography system provided with a conductivity detector (Dionex, Sunnyvale, CA, USA). An aliquot of the sample (5 mL) was injected by a Dionex AS40 automated sampler. The separation was performed on an Ionic pac AS14A

analytical column (250 mm × 4 mm i.d., Dionex, Sunnyvale, CA, USA). The Ion Chromatograph was held isothermally at 20°C with 8.0 mM Na_2CO_3/1.0 mM $NaHCO_3$ solution as the mobile phase (flow rate of 1 ml min^{-1}, initial pressure 1800 psi).

Total carbon and total organic carbon. Total carbon (TC) and total organic carbon (TOC) contents of soil, biochar, activated carbon and soil with 2% biochar or activated carbon were measured using a Leco CS230 carbon-sulphur analyser (LECO Corporation, Michigan, USA). Samples for TOC were treated with 50% hydrochloric acid to remove carbonate before measuring the carbon content.

CO_2, O_2 and SF_6 quantification. GC-MS analysis of CO_2, O_2 and SF_6 was performed on a Fisons 8060 Gas Chromatograph linked to a Fisons MD800 MS (electron voltage 70 eV, filament current 4A, source current 800uA, source temperature 200°C, multiplier voltage 500V, interface temperature 150°C). The sample (60 µL) was injected in split mode with a 100 µL Hamilton gastight syringe. The separation was performed on a HP-PLOT-Q capillary column (30 m x 0.32 mm i.d) packed with 20 µm Q phase (Agilent Technologies, Palo Alto, USA). The GC was held isothermally at 35°C with helium as the carrier gas (flow rate of 30 mL min^{-1}, initial pressure 65 kPa, split at 100 mL min^{-1}). The instrument was calibrated using standard CO_2, O_2, and N_2O (Scientific and Technical Gases, Staffordshire, UK) and SF_6 (Sigma –Aldrich, Dorset, UK) gases for a five point calibration.

VPH quantification: GC-FID analysis was performed on an Agilent HP-7890 Gas Chromatograph (Agilent Technologies, Palo Alto, USA). The gas sample (60 µL) of headspace gas was injected with a 100 µL Hamilton gastight syringe. The separation was performed on a HP-5 capillary column (30 m × 0.25 mm i.d.) with 0.25 µm film thickness (Agilent Technologies, Palo Alto, USA). The injection port used a split ratio of 10 and was heated to

200°C. The gas chromatography column temperature was held at 30°C for 5 minutes, increased to 120°C at a rate of 10°C min^{-1}, and then held constant for 6 min with hydrogen as carrier gas. The instrument was calibrated using dilutions of headspace gas concentrations sampled from Mininert-valve (Supelco, Bellefonte, USA) closed batches containing the VPH mixture liquid for a five point calibration.

VPH residual quantification. To examine VPHs residuals, 15 g soil samples were extracted twice for 24 hours in 10 mL dichloromethane/pentane mixture (40:60 by volume). The combined extracts were passed through a glass chromatographic column (45 cm×10 mm i.d.) pre-packed with 3 g activated silica gel topped by 1.5 g sodium sulphate (Sigma–Aldrich, Dorset, UK). Columns were rinsed with an additional 20 mL of the dichloromethane/pentane solvent and all solvent was collected in 40 mL amber vials from which 1 mL was transferred into a 1.0 mL GC-vial for analysis. Pentane could not be quantified by this method because of incomplete separation from the solvent peak. Compounds in cleaned-up solvent extracts were identified and quantified by GC-FID analysis on a Hewlett Packard 5890 series II in split less mode, injector temperature at 280°C. The separation was performed on an Agilent fused silica capillary column (30 m × 0.25 mm i.d.) coated with 0.25 μm diethyl poly-siloxane (HP-5) phase (Agilent Technologies, Palo Alto, USA). The GC temperature was programmed from 50-310°C at 5°C/min and held at the final temperature for 20 min with hydrogen as the carrier gas.

Amplicons library preparation for next-generation sequencing assays. For both pyrosequencing and Ion Torrent assays, individual sequencing libraries were prepared from each DNA sample by amplifying the V4 and most of the V5 regions of the 16S rRNA gene, using primer set 515f (5'-GTGNCAGCMGCCGCGGTAA-3') and 926r (5'-CCGYCAATTYMTTTRAGTTT-3'). The primers contained the specific adapters for

pyrosequencing (GS FLX Titanium adapter A, 5' - CGTATCGCCTCCCTCGCGCCATCAG – 3', and adapter B, 5' – CTATGCGCCTTGCCAGCCCGCTCAG – 3') or for the Ion Torrent (Ion adapter A, 5'- CCATCTCATCCCTGCGTGTCTCCGACTCAG-3', and Ion adapter trP1, 5'-CCTCTCTATGGGCAGTCGGTGAT-3'). Samples were differentiated by a unique 8 bp (pyrosequencing) or 12bp (Ion Torrent) barcode, added to the 5' –end of both the forward and reverse primers through a GA linker (pyrosequencing) or to the 5'-end of the forward primers through a GAT spacer (Ion Torrent). Each PCR reaction was composed of 0.5 µl DNA template, 0.4 µmol l^{-1} primers, 0.2 mmol l^{-1} dNTPs (PCR grade Nucleotide Mix, Roche), FastStart High Fidelity Enzyme Blend (2.5U/reaction), 1.8 mM $MgCl_2$ in the FastStart High Fidelity Reaction Buffer (Roche Diagnostics GmbH, Mannheim, Germany). The following PCR thermal cycling programme was used: an initial denaturation cycle at 95 °C for 4 minutes; 25 cycles of denaturation at 95 °C for 1 minute, annealing of primers at 55 °C for 45 seconds, and elongation at 72 °C for 1 minute; one final elongation step at 72 °C for 7 minutes. For samples in which the product was not sufficiently concentrated, multiplex PCR were prepared, pooled together and cleaned using the QIAquick PCR purification kit (QUIAGEN, Crawley, UK). For the Ion Torrent, single libraries were further purified and size selected using double-sided solid-phase reversible immobilisation (SPRI) beads (Agencourt AMPure XP system, Beckman Coulter), following the manufacturer's instructions. The single libraries were then individually quantified using a Qubit dsDNA HS Assay on a Qubit 2.0 Fluorometer (Invitrogen, UK), following the manufacturer's instruction, pooled together in equimolar amounts and sequenced on a Roche 454 GS FLX+ System by NewGene Ltd (International Centre for Life, Newcastle upon Tyne, UK) or (for the batch study in which the biodegradation of the straight chain alkanes, the branched and cyclic alkanes, and the monoaromatic hydrocarbons in soil was investigated separately) on a

Personal Genome Machine (PGM) at the School of Civil Engineering and Geosciences, Newcastle University, using a 316 ion chip. The raw sequences were processed using the QIIME (v 1.7.0) bioinformatics pipeline. Briefly, the reads were filtered for quality (filtering criteria: perfect match to sequence barcode/primer, 200bp minimum sequencing length). For pyrosequencing data, QIIME Denoiser [4] was used to detect and correct sequencing errors, and the data were reintegrated into the QIIME pipeline by inflation. Sequences were then clustered into Operational Taxonomic Unit (OTU) at 97% sequence similarity level by the uclust algorithm. A representative sequence from each OTU was selected and taxonomically identified using the Greengenes database [5, 6]. Representative sequences and correspondent taxonomic assignment were used to build a table of OTU abundances at different levels of taxonomy. Microbial community diversity within and across the samples was determined by using the QIIME (v.1.7.0) pipeline [7] and Primer v6 software [8]. The Bray Curtis similarity metric was generated and represented by a 2-dimensional non-metric multidimensional scaling (nMDS) plot.

Tracer test. To examine the tortuosity factor of the packed columns, 10 mL of SF_6 gas were injected into the column center at port 4. The soil air was sampled through the injection point and at a sampling port at 15 and 30 cm distance on either side (ports 3 and 5), after 20 min, 40 min, 60 min, 80 min, 100 min, 130 min and 160 min. Headspace purging was stopped for the duration of the tracer experiment. To avoid artifacts due to the spatial limitation of the experimental system, the duration of the experiments was no longer than 160 min. Samples of 60 µL of soil gas were taken with a gas-tight syringe and injected directly into the gas chromatograph for SF_6 analysis by mass spectrometry. The measured concentration of SF_6 was compared with the modelled concentration which was obtained by interpreting the diffusive transport with an equation for an instantaneous plane source of sulphur hexafluoride (SF_6) in a porous medium as

149 described by Werner and Hohener [9]. Simulated SF_6 concentration when using τ=0.4, 0.6, and 0.8
150 were compared with measured concentrations, and τ=0.8 provided the best fit. Therefore, τ=0.8
151 was used as the tortuosity value to simulate the volatilization and migration of VPHs or CO_2.
152 Such a high value of the tortuosity factor may be due to the fact that the columns were relatively
153 loosely packed in comparison with natural soils.

Modelling

Underpinning assumptions:

The VPH concentrations in soil air above the NAPL source are described by Raoult's law. The VPH concentration on the atmospheric boundary side of the columns is zero, and this results in a net diffusive VPH flux from the NAPL source towards the atmospheric boundary. The VPHs migrate through the column by Fickian diffusion in soil air. Advective gas transport is neglected. The distribution of VPHs between soil air and water is described by Henry's law. VPH sorption to the soil and biochar or activated carbon solid matrix is linear and reversible. The kinetics of the VPH uptake or release by biochar or activated carbon is described by sorption-retarded intraparticle diffusion of VPHs in the biochar or activated carbon pores, which are water-filled. The VPH degrading biomass is present in the water in between, but not within particles, and can simultaneously grow on all the VPH compounds. This biomass can only degrade VPHs which are present in the water in between soil particles. Sorbed VPHs and VPHs in soil air are not directly bioaccessible. The growth rate of VPH degrading biomass is dependent on the VPH concentration in the water in between particles, and limited by a maximum biomass concentration.

Coordinates, time:

z (cm)	Distance from the pollution source zone
t (s)	Time

Soil and carbonaceous sorbent parameters:

θ_a, θ_w, θ_s, θ_c (-)	Air, water, soil solid and carbonaceous sorbent-filled soil volume fractions
ρ_s (gcm^{-3})	Density of the soil solids
τ_a (-)	Tortuosity factor for the air-filled soil pore space

180	ρ_c (gcm^{-3})	Skeletal, solid density of the carbonaceous sorbent
181	$p_{w,c}$ (-)	Water-filled porosity of the carbonaceous sorbent
182	R_c (cm)	Particle radius of the carbonaceous sorbent
183		
184	Chemical parameters for compound k:	
185	$C_{a,k}$ (gcm^{-3})	Concentration of compound k in soil air
186	$S_{c,k}$ (gcm^{-3})	Volumetric concentration of compound k in the carbonaceous sorbent
187	H_k (-)	Dimensionless air-to-water partitioning coefficient (Henry constant)
188	$K_{d,k}$ (cm^3g^{-1})	Soil solid-to-water partitioning coefficient
189	$K_{c,k}$ (cm^3g^{-1})	Carbonaceous sorbent solid-to-water partitioning coefficient
190	$D_{a,k}$ (cm^2s^{-1})	Molecular diffusion coefficient of compound k in soil air
191	$D_{w,k}$ (cm^2s^{-1})	Molecular diffusion coefficient of compound k in water
192	$D_{c,k}$ (cm^2s^{-1})	Apparent diffusion coefficient of compound k in the carbonaceous sorbent
193	x_k (-)	Mole fraction of compound k in the VPH source
194	$C_{pl,k}$ (gcm^{-3})	Pure liquid vapor concentration of compound k
195		
196	Biological parameters:	
197	C_b (gcm^{-3})	Biomass concentration in soil water
198	$C_{b,max}$ (gcm^{-3})	Maximum biomass concentration in soil water
199	dec (s^{-1})	Biomass decay rate
200	g_k (s^{-1})	Biomass growth rate on compound k
201	Y_k (gg^{-1})	Biomass yield coefficient for compound k
202	sg_k ($cm^3g^{-1}s^{-1}$)	Second order growth rate on compound k
203		
204	Column parameters:	
205		
206	r_{column} (cm)	Column radius
207	l_{column} (cm)	Column length
208	r_{neck} (cm)	Source neck radius
209	l_{neck} (cm)	Source neck length
210		

Model equations:

Compound k mass balance equation:

$$\left(\theta_a + \frac{\theta_w}{H_k} + \frac{\rho_s \theta_s K_{d,k}}{H_k}\right) \cdot {}^{\partial}/_{\partial t} C_{a,k}(z,t) = \theta_a \tau_a D_{a,k} \cdot {}^{\partial^2}/_{\partial z^2} C_{a,k}(z,t)$$

$$- \theta_c \cdot {}^{\partial}/_{\partial t}\left[\frac{3}{{R_c}^3}\int_0^{Rc} r^2 S_{c,k}(z,r)dr\right] - \theta_w \cdot \frac{g_k}{Y_k} \cdot C_b(z,t)$$

if time > lag phase

$$g_k = sg_k \cdot \frac{C_{a,k}(z,t)}{H_k} \cdot \frac{C_{b,max} - C_b(z,t)}{C_{b,max}}$$

else

$$g_k = 0$$

Carbonaceous sorbent intraparticle diffusion equation [10]:

$${}^{\partial}/_{\partial t} S_{c,k}(z,r,t) = \frac{D_{c,k}}{r^2} \cdot {}^{\partial}/_{\partial r}\left(r^2 {}^{\partial}/_{\partial r} S_{c,k}(z,r,t)\right)$$

Estimated intraparticle diffusion coefficient [10]:

$$D_{c,k} = \frac{{p_{w,c}}^2}{p_{w,c} + (1 - p_{w,c}) \cdot \rho_c \cdot K_{c,k}} \cdot D_{w,k}$$

Biomass equation:

$${}^{\partial}/_{\partial t} C_b(z,t) = \left(\sum_k g_k - dec\right) \cdot C_b(z,t)$$

Zero-concentration boundary condition at the column outlet:

$$C_{a,k}(z = l_{column}, t) = 0$$

Boundary condition at the NAPL source:

$$C_{a,k}(NAPL\ source, t) = x_k(t) \cdot C_{pl,k}$$

Mass conservation at the NAPL source – soil interface:

$$r_{column}^2 \cdot \theta_a \cdot \tau_a \cdot {}^{\partial}/_{\partial z} C_{a,k}(z = 0, t) \approx r_{neck}^2 \frac{C_{a,k}(z = 0, t) - C_{a,k}(NAPL\ source, t)}{l_{neck}}$$

Boundary condition at the soil water – carbonaceous sorbent interface:

$$S_{c,k}(z, R_c, t) = \left(p_{w,c} + (1 - p_{w,c}) \cdot \rho_c \cdot K_{c,k}\right) \cdot \frac{C_{a,k}(z, t)}{H_k}$$

Boundary condition in the carbonaceous sorbent particle core:

$${}^{\partial}/_{\partial r} S_{c,k}(z, 0, t) = 0$$

255 **Table S1:** Compound-specific parameter values determined in batch experiments.

	Apparent first-order biodegradation rate in water, k_w (s^{-1})	Distribution coefficient K_d (cm^3g^{-1})		
	Soil	Soil	Soil & 2% BC	Soil & 2% AC
n-Pentane	$6.5\pm0.9\times10^{-3}$	53 ±16	86±19	23200±3000
n-Hexane	$5.3\pm0.2\times10^{-3}$	68±6	112±24	133000±27000
n-Octane	$8.1\pm1.9\times10^{-3}$	167±77	334±190	53300±19900
n-Decane	$8.9\pm2.9\times10^{-3}$	805±355	1091±437	39800±6900
n-Dodecane	$2.5\pm0.6\times10^{-2}$	1714±490	2151±295	206900±5800
Methylcyclopentane	$1.2\pm0.07\times10^{-3}$	13±2	18±1	10600±700
Methylcyclohexane	$5.5\pm0.6\times10^{-4}$	15 ±2	26±9	28800±8800
Cyclohexane	$6.0\pm0.3\times10^{-4}$	6±0.8	8±1	3600±260
Isooctane	$1.1\pm0.06\times10^{-2}$	83 ±14	124 ±32	249000±76000
Toluene	$6.9\pm0.9\times10^{-5}$	1.3±0.2	12±5	170±59
m-Xylene	$4.8\pm1.2\times10^{-5}$	1.8±0.6	6±2	59±20
1,2,4 TBM	$1.6\pm0.7\times10^{-4}$	4.4±2.0	10±3	59±10

256

Table S2: Summary of OTUs distinguished at 97% similarity that showed a minimum 16-fold increase in their relative abundance rank fifteen days after the addition of 0.3 mL of different VPH compound classes to soil batches.

Taxon (highest level classification)	Relative abundance rank increase for different treatments compared to the soil only control + 2-fold, ++ 4-fold, +++ 8-fold, ++++ 16-fold, +++++ 32-fold, ++++++ 64-fold, +++++++ 128-fold, , ++++++++ 320-fold or greater, equivalent decrease for minus signs			
	Soil Rank	Soil+monoaromatic hydrocarbons	Soil+straight chain alkanes	Soil+branched and cyclic alkanes
g__Rhodococcus	665	+	++++	
g__Rhodococcus	249	+	++++++	+
f__Nocardioidaceae	107	+	++++	
s__Desulfosporosinus_meridiei	153	+	++++	
g__Tepidibacter	532		+++++	
g__Phenylobacterium	782		+++++	
g__Polaromonas	185	+	++++++	+
g__Perlucidibaca	749		++++	+
f__Pseudomonadaceae	593	+	+++++++	++++++
f__Pseudomonadaceae	230		+++++	++++
g__Pseudomonas	428	+	++++++++	++++++++
g__Pseudomonas	232	++	+++++++	++++++++
s__Pseudomonas__umsongensis	264	+	++++	++++++
g__Pseudoxanthomonas	600		++++	

Table S3: Summary of OTUs distinguished at 97% similarity which showed a minimum 8-fold increase in their relative abundance rank eight days after the addition of 0.3 mL of the VPH mixture to batches with soil, soil + biochar, or soil + activated carbon.

Taxon (highest level classification)	Relative abundance rank increase for different treatments compared to the soil only control + 2-fold, ++ 4-fold, +++ 8-fold, ++++ 16-fold, +++++ 32-fold, ++++++ 64-fold or greater, equivalent decrease for minus signs						
	Soil d0 Rank	Soil+VPHs	Soil+VPHs +nutrients	Soil+BC +VPHs	Soil+BC +VPHs+ nutrients	Soil+AC +VPHs	Soil+AC +VPHs+ nutrients
f__Nocardioidaceae	65			-		++++++	++++++
g__Paenisporosarcina	615	+++++	+++++	++++	++++	+++	
g__Sphingopyxis	615	+	+++	+	+		
o__Burkholderiales	615	++	++	+++	+++	+++	+
g__Achromobacter	93	++++++	++++++	+++++++	++		--
g__Acidovorax	615	++	+++++	++++	++++	++++	+
g__Hydrogenophaga	222			++++	+++	++	+
g__Cupriavidus	562	+	+	+		+	+++
f__Pseudomonadaceae	615	+	++++	+++	+	+	
g__Pseudomonas	24	+++++	+++++	+	++	+	-
s__Pseudomonas__umsongensis	139	+++++	++++	++	++	+	-
g__Arenimonas	615	++	++	+++	+++	+	

Table S4: Summary of OTUs distinguished at 97% similarity which showed a minimum 8-fold increase in their relative abundance rank 430 days after the connection of a VPH NAPL source to columns filled with soil, soil & biochar, or soil & activated carbon.

Taxon (highest level classification)	Relative abundance rank increase for different treatments compared to the soil only control + 2-fold, ++ 4-fold, +++ 8-fold, ++++ 16-fold, +++++ 32-fold, ++++++ 64-fold or greater, equivalent decrease for minus signs									
	Soil d0 Rank	Soil+VPHs d430 source	Soil+VPHs d430 middle	Soil+VPHs d430 Atmos	Soil+BC +VPHs d430 source	Soil+BC +VPHs d430 middle	Soil+BC +VPHs d430 atmos	Soil+AC+ VPHs d430 source	Soil+AC +VPHs d430 middle	Soil+AC+ VPHs d430 atmos
g__Nitrosopumilus	72	++++		---			-	-	--	--
g__Microbacterium	458			+++	+		+			
f__Nocardioidaceae	94			+			+	+++		+
g__Aeromicrobium	495			+	+	+	+		+	+++
g__Pseudonocardia	204	+	+	++	++	++	+++	+++++	+++++	++++++
o__Bacteroidales	629	+++++	+++	+++	+++	++++++	+++++	+	+	
f__Chitinophagaceae	86			++++		+				+
f__Flammeovirgaceae	9			+++	+	++	+	+		+
c__Chloroflexi	458	++	++	++	++	++	++	+++	+++	+++
f__Phyllobacteriaceae	131			+++			+		+	++
g__Oleomonas	629			+++++						+
g__Sphingobium	80	---	--	++++	---	---	+	---	---	+
f__Comamonadaceae	79	++	++	+++	+	++	++	++	+++	+++
g__Hydrogenophaga	116	+	++	++++	++++	++++	+++++	++	+++	+++++
o__Myxococcales	17			+++	-	-			++	++++
f__Haliangiaceae	36				+	+	++	++	++	+++
g__Nannocystis	420	+	+		-	-	-	++++	+++	++
f__Alteromonadaceae	629	+	+		+	++	+++		++	+
g__HB2-32-21	272	++	++++	++	+++	++++	++++	+	++++	+++++
f__Chromatiaceae	629	++++	+++	++	++	++++	++++	+		
o__PYR10d3	181			+++		+	+++++			
f__Pseudomonadaceae	166	+	+++	+	+++	+++++	++++	-	-	
f__Sinobacteraceae	105			++++	+	+		+	++	+
g__Pseudoxanthomonas	235			+++	+	+	++	+	++	++

Table S5: Measured column parameters, and *parameters obtained from the literature* [11].

	Volume fraction air (-)	Volume fraction water (-)	Tortuosity (-)	Weight fraction sorbent amendment (gg^{-1})
Soil	0.44	0.11	0.8	0
Soil & BC	0.48	0.12	0.8	0.02
Soil & AC	0.48	0.11	0.8	0.02

Soil-filled column length 93 (cm); soil-filled column radius 3.9 (cm); source neck length 10 (cm); source neck radius 0.55 (cm); soil solids density 2.5 (gcm^{-3}); *BC solid matrix density* 1.2 (gcm^{-3}) [11]; *AC solid matrix density* 1.96 (gcm^{-3}) [11]; BC and AC intraparticle porosity 0.5 (cm^3cm^{-3}); BC and AC particle radius 0.005 cm.

Table S6: Physicochemical *model parameter values from the literature* [a]

Compound	*Molecular weight* (g/mol)	*Pure liquid vapour conc.* (g/cm^3)	*Henry's constant* (-)	*Diffusion coefficient in water* (gcm^{-2})	*Diffusion coefficient in air* (gcm^{-2})	*Carbon mass fraction* (-)	Initial moles in source (-)
Pentane	72	0.002	50	0.000013	0.082	0.83	0.0086
Hexane	86	0.00065	70	0.000012	0.074	0.84	0.0131
Octane	114	0.000089	120	0.000009	0.064	0.84	0.0097
Decane	142	0.000014	293	0.000008	0.057	0.84	0.0142
Dodecane	170	0.000002	293	0.000007	0.051	0.85	0.0052
Methylcyclopentane	84	0.00060	15	0.000012	0.079	0.86	0.0131
Methylcyclohexane	98	0.00020	4.2	0.000011	0.073	0.86	0.0186
Cyclohexane	84	0.00042	7.3	0.000012	0.080	0.86	0.0147
Isooctane	114	0.00027	132	0.000009	0.064	0.83	0.0181
Toluene	92	0.00014	0.26	0.000011	0.078	0.91	0.0075
m-Xylene	106	0.000047	0.26	0.000010	0.072	0.91	0.0080
1,2,4-TMB	120	0.000015	0.27	0.000009	0.066	0.90	0.0087

[a]Based on [1], pure liquid vapor pressures at 25ºC reported in [3].

Table S7: Biogeochemical model parameter values measured in batch experiments

Compound	Soil-water partitioning coefficient K_d (cm^3g^{-1})	Biochar-water partitioning coefficient K_{bc} (cm^3g^{-1})	AC-water partitioning coefficient K_{ac} (cm^3g^{-1})	Yield coefficient (g biomass-C g^{-1} VPH)
Pentane	53	1596	1157000	0.2183
Hexane	68	2131	6647000	0.2209
Octane	167	8180	2656000	0.2209
Decane	805	13479	1949000	0.2209
Dodecane	1714	20152	10258000	0.2236
Methylcyclopentane	13	237	529000	0.2262
Methylcyclohexane	15	535	1439000	0.2262
Cyclohexane	6	94	180000	0.2262
Isooctane	83	1965	12446000	0.2209
Toluene	1.3	533	8433	0.2393
m-Xylene	1.8	208	2858	0.2393
1,2,4-TMB	4.4	276	2726	0.2367

Table S8: Biogeochemical model parameter values measured in batch experiments or *obtained from the literature* [12], and fitted from the column study data.

Compound	Second-order growth rate, soil batch experiments ($cm^3\ g^{-1}s^{-1}$)	Second-order growth rate, soil column, fitted ($cm^3\ g^{-1}s^{-1}$)	Second-order growth rate, soil & BC column, fitted ($cm^3\ g^{-1}s^{-1}$)	Second-order growth rate, soil & AC column, fitted ($cm^3\ g^{-1}s^{-1}$)
Pentane	97	97	97	292
Hexane	80	80	80	240
Octane	122	122	122	367
Decane	134	134	134	403
Dodecane	382	382	382	1146
Methylcyclopentane	18.5	5.6	3.7	55.6
Methylcyclohexane	8.5	2.6	1.7	25.5
Cyclohexane	9.3	2.8	1.9	27.8
Isooctane	166	50	33	498
Toluene	1.1	1.7	2.3	3.4
m-Xylene	0.79	1.2	1.6	2.4
1,2,4-TMB	2.6	3.9	5.2	7.8

Initial VPH degrading biomass = 0.0000146 (g biomass C/cm^3 water), based on the initial cell count and [12]. Soil biomass carrying capacity derived from available nitrogen contents = 0.0011 (g biomass C/cm^3 water); Soil biomass carrying capacity fitted from the soil column study = 0.00058 (g biomass C/cm^3 water); *biomass decay rate* from [12] = 0.00000025 (s^{-1}); biomass decay rate fitted from the soil column study = 0.00000050 (s^{-1}); lag phase all compounds from batch experiments = 259200 (s); lag phase branched and cyclic alkanes fitted from the soil column study = 518400 (s).

Figure S1: Exemplary data from the batch experiments with soil showing fitted time trends for a) hexane and b) isooctane.

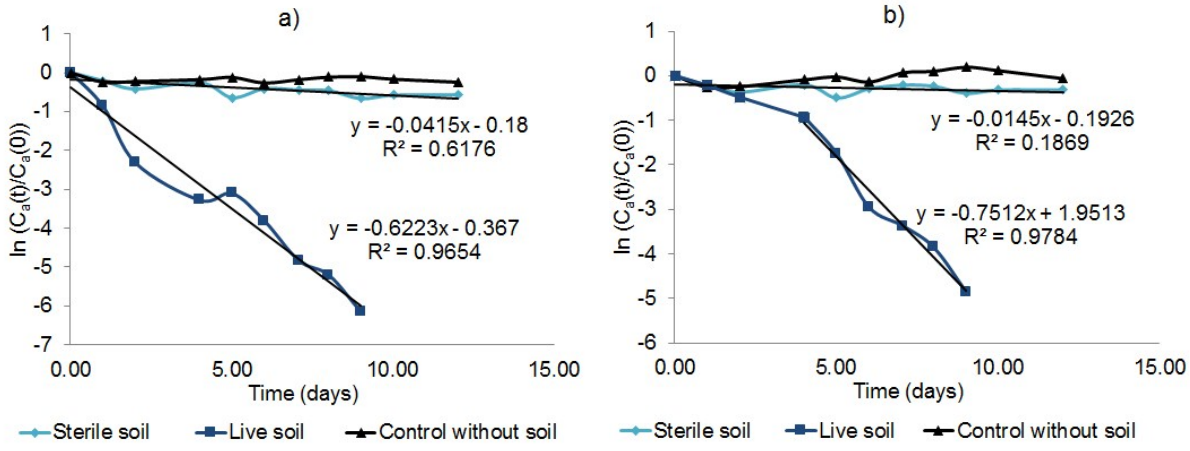


Figure S2: Carbon-content normalized VPH concentrations measured in the middle of the soil column for the sum of the a) straight-chain alkanes, b) branched/cyclic alkanes, c) monoaromatic hydrocarbons, and d) total VPH-carbon emanation from the soil column. Inserts show the early data for the first two months. Measured data is shown as diamond symbols. Solid lines show the model predictions for the unamended soil column (solid blue line) based on parameter values which were independently measured or obtained from the literature (see Tables S5-8).

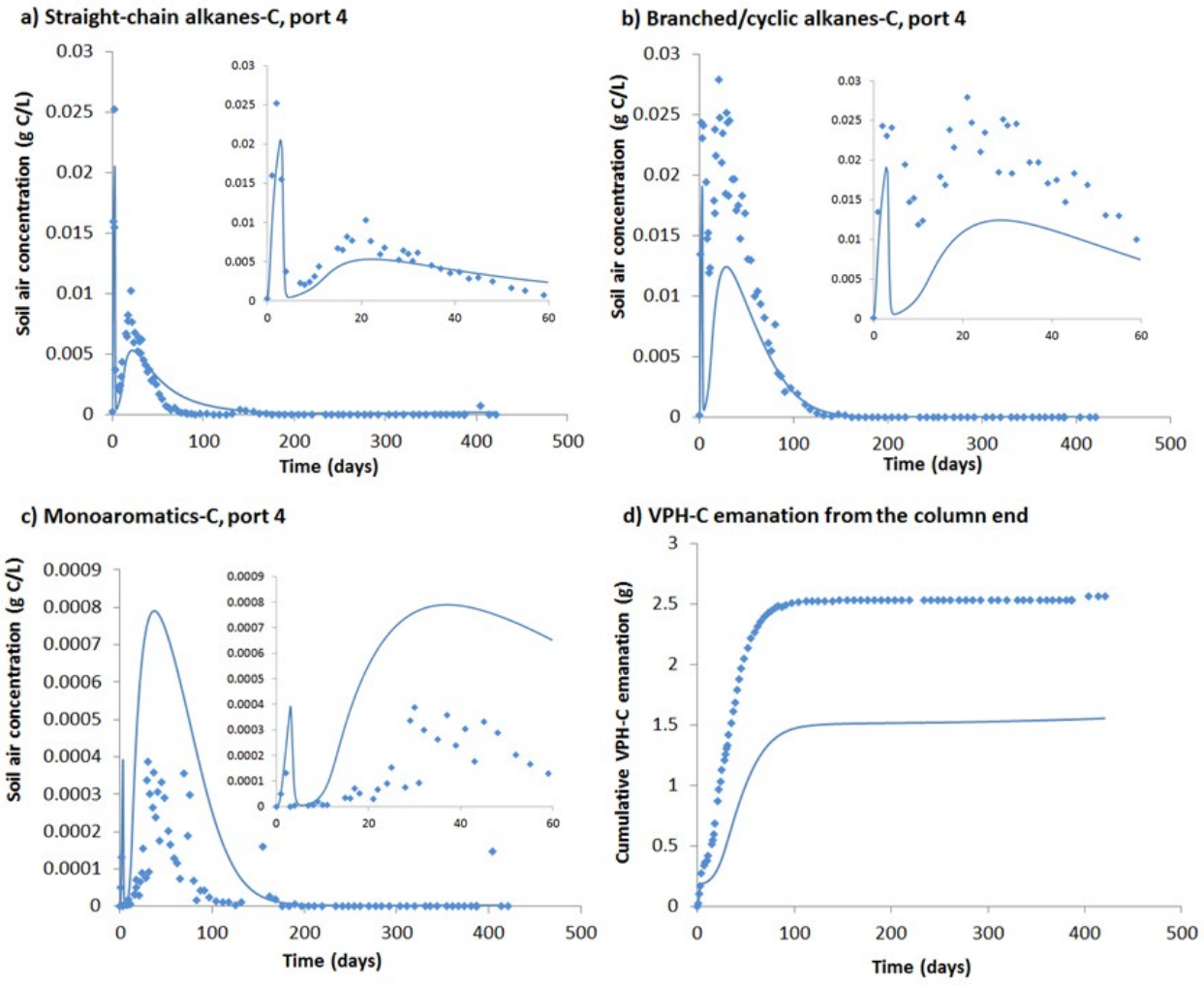
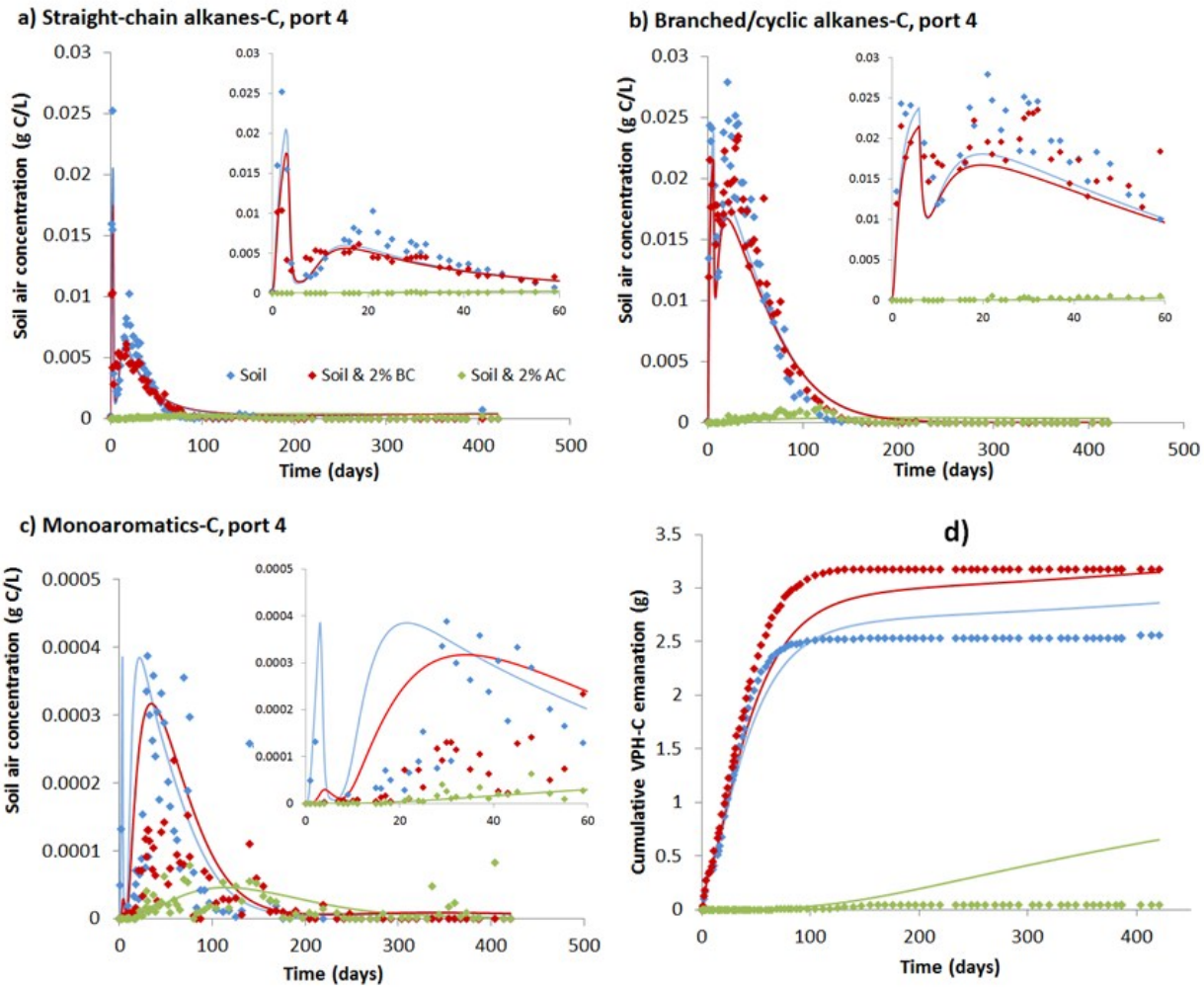


Figure S3: Carbon-content normalized VPH concentrations measured in the middle of the soil column for the sum of the a) straight-chain alkanes, b) branched/cyclic alkanes, c) monoaromatic hydrocarbons, and d) total VPH-carbon emanation from the soil column. Inserts show the early data for the first two months. Measured data is shown as diamond symbols. Solid lines show the model predictions for the unamended soil column (blue), and the soil & biochar column (red) and soil & AC column (green) based on microbiological parameter values optimized for the soil column.



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