The potential of biochar to remove hydrophobic compounds from model sandy soils

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Abstract

Charcoals have long been used to adsorb organics from water and other substrates; we hypothesise that biochar may act in a similar way when mixed with soil, removing hydrophobic organic compounds from the soil surfaces. To test this hypothesis, we developed quantitative methods for addition of two hydrophobic organic compounds (octadecane and octadecanoic acid, commonly found in naturally hydrophobic soils) to, and their subsequent extraction from, acid washed sand (as a model for sandy soil). We then measured the quantity of the organic compounds which remained on the sand after: deposition; subsequent addition of 0, 1, 5, 10, 25 or 40% wettable biochar; and storage for 1, 10, and 30 days in solutions of pH 3, 6 or 9. We found that there were small reductions in hydrophobic compound coverage of sand with 1 and 5% biochar additions, but that 10% biochar reduced coverage by 50%, and ≥ 25% biochar reduced coverage by 100%. The significance of these results in understanding the potential of wettable biochar to remove hydrophobic compounds from sandy soils, and thus act as an ameliorant of soil water repellency, is discussed.

1.0 Introduction

In previous work we showed that addition of wettable biochar to sandy soils reduced soil water repellency (Hallin et al., 2015). Since soil water repellency is generally thought to be caused by organic compounds adsorbed to soil particle surfaces (Ma'Shum et al., 1988; Doerr et al., 2005; Morley et al., 2005; Mainwaring et al., 2013), and biochar has been proven to strongly adsorb organic compounds in soil (DeLuca et al., 2009; Sohi et al., 2010; Novak and Watts, 2013), we hypothesised that one mechanism by which wettable biochar might reduce soil water repellency is by removal of hydrophobic organics. To test this hypothesis, we developed quantitative methods for the addition extraction and measurement of octadecane and octadecanoic acid onto/from acid washed sand, which is a model system commonly used to represent sandy soil. We then studied the effect of addition of wettable biochar. We chose

41 octadecane and octadecanoic acid because they have been found on natural soils and are
42 thought to be associated with soil water repellency (Morley et al., 2005; Mainwaring et al.,
43 2013). In previous work we found that water repellency could be induced when mixtures of
44 octadecane/octadecanoic acid were added to acid washed sand at levels comparable to those
45 found in naturally water repellent soils, whereas the sand remained wettable with octadecane
46 alone (Mainwaring et al., 2013); so our interests were also in how the non-polar octadecane
47 behaved when alone compared to when in mixtures with octadecanoic acid.

48 Two questions were of interest for this study.

49 1) To what degree will biochar remove hydrophobic organic compounds from a model
50 hydrophobic sandy soil (acid washed sand made repellent by adding octadecane or
51 octadecane/octadecanoic acid mixtures)?

52 2) How does the quantity of hydrophobic compound removed depend on the amount of
53 biochar added, solution pH, and exposure time?

54 To address these questions, acid washed sand (AWS) was coated with octadecane, or
55 octadecane/octadecanoic acid mixtures, and mixed with 0, 1, 5, 10, 25 or 40 w/w% finely
56 ground biochar (FGB) for 1, 10 or 30 days in solutions of either pH 3, 6, or 9. The sand and
57 biochar were then separated by sieving, and the organics remaining on the sand extracted and
58 quantified using FT-IR and GC analyses.

59 **2.0 Materials and methods**

60 Although conceptually simple, the success of the experiment required the development of
61 analytical procedures for determining the amount of hydrophobic materials on sand and
62 biochar, either directly or by extraction, and a brief account of method development and the
63 rationale for the final experimental procedure is given here. Both FT-IR and gas

chromatography (GC) were used for analysis. FT-IR offers the potential for direct measurement of material adsorbed to solids, without the need for an extraction step, and so was used when directly measuring the quantity of organics adsorbed to biochar. It is also suitable for detection of octadecanoic acid without the need for the additional derivatisation step often required for GC analysis of compounds with strongly polar functional groups, such as carboxylic acids. Since our GC equipment was well suited for the direct detection of octadecane but less suitable for octadecanoic acid, FT-IR was used for both octadecane and octadecanoic acid, and GC was used for octadecane only. The use of two independent techniques for octadecane analysis gave a useful internal check on the reliability of the results.

2.1 Materials

Biochar was provided by the UK Biochar Research Centre in Edinburgh. This was prepared from a softwood mixture of pine and spruce pellets (Puffin Pellets, Banff, Scotland), pyrolysed in a 250-mm diameter rotary kiln at a peak temperature of 700°C with intermediate mean residence time. The wettability of biochar was tested by applying water drops directly to the surface of the biochar pellets and dishes of ground biochar. All drops infiltrated on contact.

Finely ground biochar was made by grinding the pellets in a mortar and pestle and sieving to give three samples of different particle size: <2000 µm ($FGB_{<2000}$), <250 µm ($FGB_{<250}$), and <106 µm ($FGB_{<106}$).

Acid washed sand (~ 0.1 to 0.3 mm particle diameter, calcined, Supelco Analytical Reagent), was supplied by Sigma-Aldrich (Gillingham, UK). For work requiring physical separation of sand from biochar, sand was sieved to give a complementary particle size; e.g. when using $FGB_{<106}$, the sand used was pre-sieved to >106 µm ($AWS_{>106}$).

Octadecane (GPR), hexadecane (98%) and octadecanoic acid (99%) from BDH, (Poole, UK), and CCl_4 (99%, extra pure) from Acros, (Geel, Belgium), were used as received. Distilled water was used throughout.

2.2 Method

2.2.1 Sand and biochar substrate preparation and separation

To ensure that any readily suspended colloidal fractions of biochar, which might interfere with analysis, were removed, biochar was soaked in distilled water for 7 days with intermittent shaking, and then filtered 4 times under vacuum through a 47 mm Whatman (Kent, UK) borosilicate glass filter funnel fitted with GF/F filter paper. While the filtrate was still a colloidal suspension after four rinses, it was only slightly discoloured. The biochar was then collected and dried at 50°C for 24 to 48 hours.

Similarly, to ensure that no extraneous colloids < 0.1 mm were part of the sand mixture (which may have lead to inflated biochar retrieval fractions after separation), sand was soaked in distilled water for 24 hours, filtered once through the Whatman GF/F filter, then dried at 50°C for 24 to 48 hours.

To check whether sieving was effective at separating sand from biochar, three ~2 g mixtures of sand ($AWS_{>106}$) and biochar ($FGB_{<106}$), ranging from 3 to 11% biochar by weight, were prepared and then gently dry sieved at 106 μm. Sieving was very effective; recovery of sand was high from all three mixes (99.9 ± 0.1% weight recovered), and the sand returned to its initial pale colour rather than the darker colour of the biochar-sand mix. Although biochar recovery was lower (73.3 ± 4.9%), a biochar film was clearly visible on the sieve mesh and collection tray that could only be removed with a cloth or a wire brush, which likely accounted for the remaining mass.

2.2.2 Substrate surface areas

Surface areas of sand and biochar were determined by the Brunauer, Emmett and Teller (BET) method (Black, 1965), using a Micromeritics (Atlanta, USA) Tristar II 3020 Surface Area and Porosity Analyser.

Sand surface area was determined from samples weighing between 2.5 and 3.5 g, while biochar, which has a much larger surface area, was analysed from ~ 0.05 g samples. Sand samples were dried, degassed and heated in a VacPrep 041 unit to 200°C for 1 hour prior to analysis. Biochar samples were dried, degassed and heated overnight at 100°C in a VacPrep 041 unit prior to analysis.

Langmuir isotherms for N_2 adsorption onto sand and biochar ($FGB_{<250}$) are shown in Figure 1; analysis gives sand a specific surface area of 0.0292 ± 0.0003 $m^2\ g^{-1}$; and biochar a specific surface area of 359.1 ± 7.4 $m^2\ g^{-1}$.

In terms of compound laydowns the quantities dealt with are mass, or moles, of organics added per gram of sand (mg g^{-1}sand, mol g^{-1}sand). However, it is also useful to express this in a more readily accessible physically significant unit of 'monolayer equivalents', which is '*the number of monolayers the organic would form on the sand if it were distributed uniformly'*, although it should be noted we make no assumption that in reality there is uniform deposition, monolayer or otherwise.

Using the surface area of sand from BET analysis and an octadecanoic acid surface area of 2.00×10^{-15} cm^2 $molecule^{-1}$ (Moore, 1972; Shaw, 1995), one monolayer equivalent of octadecanoic acid on sand corresponds to 2.42×10^{-7} mol OA g^{-1}_{sand}, which, since octadecanoic acid has a molar mass of 284.48 g mol^{-1}, is 0.0688 mg OA g^{-1}_{sand}. Octadecanoic acid and octadecane are very similar sized C_{18} compounds with similar surface areas for the same stacking arrangements, although it is recognised that the stacking arrangement upon

adsorption of octadecane may well not be the same as for octadecanoic acid, since octadecane does not have the potentially anchoring carboxylic acid group of octadecanoic acid. Using this approach one monolayer equivalent of octadecanoic acid on sand also corresponds to 2.42×10^{-7} mol OA g^{-1}_{sand}, which, since octadecane has a molar mass of 254.5 g mol^{-1}, is 0.0615 mg OD g^{-1}_{sand}.

It is of interest to note that based on BET N_2 adsorption surface area measurements, 10 monolayer equivalents of either organic on sand is equal to only ~0.0007 monolayer equivalents on the biochar.

2.2.3 Loading rate for hydrophobic compounds

Hydrophobic compounds were deposited onto sand in increments between 1 and 100 monolayer equivalents (0.0688 to 6.88 mg OA g^{-1} sand, 0.0615 to 6.15 mg OD g^{-1} sand). The maximum loading rate before solid was visible on the sand or biochar surface was 50 monolayers (3.44 mg OA g^{-1} sand, 3.08 mg OD g^{-1} sand), and calibration data showed this to be a good maximum loading for both infrared and gas chromatography analyses using the chosen extraction method. This loading rate also falls well within the range of total organic carbon in severely water repellent dune sands (0.8 to 36.2 mg g^{-1}), as measured by Morley et al. (2005), and so these quantities could easily be found in nature. The 10, 25 and 50 octadecane monolayer equivalent deposits were all visible on the GC chromatogram with no need for attenuation adjustments, and IR spectra showed that 1 and 50 monolayers were the ideal lower and upper octadecanoic acid concentration limits, respectively, with both spectra providing measurable peaks at 2854 and 2927 cm^{-1}, well within instrument limits for suitable precision (Hallin, 2014).

158 *2.2.4 Sand and biochar sample preparation*

159 Each treatment (octadecanoic acid, octadecane, and mixed octadecanoic acid and octadecane)
160 was replicated three times on sand ($AWS_{>106}$) alone. For each replicate, 200 g of sand was
161 weighed into a flask to which 1.21×10^{-5} mol g^{-1}_{sand} of octadecane, or an octadecanoic
162 acid/octadecane mix, was then added as an ethanolic solution. Anywhere between 10 and 30
163 ml of ethanol were also added to each flask to ensure all solids were saturated before
164 evaporating the mixture to dryness using a rotary evaporator. Rotary evaporation has been
165 widely used as a deposition method; it allows good mass balance quantification and good
166 control over experimental parameters (Mainwaring et al., 2013).

167 Additional treatments were created in which sand ($AWS_{>106}$) and biochar ($FGB_{<106}$) were
168 mixed prior to the deposition of the hydrophobic compounds (identified throughout as AWS-
169 FGB mixes). Three replicates of these treatments were made by weighing 10 g sand into five
170 flasks and adding either 0.1 g (1%), 0.5 g (5%), 1 g (10%), 2.5 g (25%) or 4.0 g (40%)
171 biochar to the flask and shaking thoroughly to ensure the two substrates were well mixed
172 prior to hydrophobic compound deposition. The necessary quantity of hydrophobic solution
173 was then added along with anywhere from 5 to 10 ml of ethanol to ensure all solids were
174 saturated before evaporating the mixture to dryness using a rotary evaporator.

175 Coated sand and AWS-FGB mixes were coned and quartered into subsamples. Coated sand
176 was divided into ~ 2 g (±0.0010 g) samples and then biochar ($FGB_{<106}$) was mixed into each
177 sample to give w/w ratios of either 0%, 1%, 5%, 10%, 25% or 40%, and the mixture placed
178 in boiling tubes. Three replicates were made with 1%, 5%, 10% and 40% biochar, and six for
179 0% and 25% biochar samples. AWS-FGB mixes were each divided into 5 equal replicates ~ 2
180 g in weight.

To one replicate of each treatment was added 5 ml of either pH 3, 6 or 9 aqueous solution. Depending on the desired pH, either HCl or NaOH was added drop-wise to 1 l of distilled water until narrow-range pH paper showed the desired pH had been achieved. Nothing was added to achieve pH 6, as the distilled water available was at pH 6 before and after mixing with coated sand. To the three remaining 0% and 25% replicates, 5 ml ethanol was added as a control to observe how readily the deposited hydrophobic compounds moved from sand to solvents in which they would readily dissolve. Samples were then covered, shaken, and left to stand for 1, 10 or 30 days in a fume cupboard to keep away from direct sunlight (which could promote microbial activity).

Out of interest, three additional sample tubes were prepared in which sand coated with octadecane was mixed with 10% biochar and left dry for 10 days, rather than introduce a pH solution.

2.2.5 Sample processing and compound extraction into carbon tetrachloride

When the allocated time was reached, wet samples were filtered through GF/F filters, the solution was discarded and the sand and biochar solids were dried in desiccators for 48 hours. All sand and biochar samples were then gently dry-sieved at 106 μm; the biochar fraction was kept for KBr disk IR analysis, and the sand fraction was retained for compound extraction and analysis.

To extract the hydrophobic compounds, ~ 1 g sand was weighed into a small vial to which 2 ml CCl_4 was then added. The vial was immediately sealed, shaken and left overnight. The sand-CCl_4 mixture was then quickly (to avoid solvent loss) filtered under vacuum through a P40 sinter to separate the sand phase. A 0.500 ml subsample of CCl_4 was taken for gas chromatography analysis, and the remaining solution kept for infrared analysis.

2.2.6 Analysis

205 *2.2.6.1 Gas Chromatography*

206 A Hewlett Packard (Palo Alto, USA) 5890 Series II gas chromatograph with an HP1
207 crosslinked methyl siloxane capillary column, 10 m × 0.53 mm in diameter was used. The
208 film thickness was 2.65 μm, and N_2 was used as a carrier gas (head pressure = 34 psi). A mix
209 of air and H_2 were used for flame ionisation; head pressure for air was 37 psi, and for H_2 was
210 25 psi. All injections were kept at 150°C for 5 minutes before being heated to 220°C at a rate
211 of 10°C per minute. An integrator attenuation of 0 was used throughout.

212 For calibration, octadecane solutions were made in CCl_4 in concentrations equivalent to what
213 would be expected for complete extraction into 2 ml of CCl_4 from 1, 10, 25 and 50
214 monolayer equivalents of octadecane on 1 g AWS>106. The 10, 25 and 50 octadecane
215 monolayer equivalent solutions were all visible on the GC chromatogram with no need for
216 attenuation adjustments. Hexadecane (HD, $C_{16}H_{34}$) was chosen as GC internal standard
217 because it is soluble in CCl_4, is of similar but slightly shorter carbon chain length to
218 octadecane, and allowed use of a temperature ramp setting that kept each run relatively short
219 (< 20 minutes), while providing consistently clear, distinct peaks for both hexadecane and
220 octadecane.

221 The response factor (RF) of octadecane to hexadecane was found by taking the average result
222 of 6 samples of 0.001 M [OD] [HD], according to Equation (1), where M_{HD} and M_{OD} are the
223 masses (mg) of hexadecane and octadecane, respectively, present in solution, and A_{HD} and
224 A_{OD} are the hexadecane and octadecane peak areas from the chromatogram.

225 $$RF = (A_{HD} \times M_{OD})/(A_{OD} \times M_{HD}) \quad (1)$$

226 For GC analysis, a known amount of hexadecane was added to the 0.500 ml subsample and
227 the mass of octadecane present in the sample was found using Equation (2).

$$M_{\mathrm{OD}} = (RF \times M_{HD} \times A_{OD})/A_{HD} \quad (2)$$

2.2.6.2 Infrared Spectroscopy

A Perkin-Elmer (Waltham, USA) Spectrum One FT-IR spectrometer was used. There were two main regions of interest within a spectrum (Figure 2): 2850 - 3000 cm^{-1}, where there are four peaks that correspond to the stretching of C-H bonds present in both carboxylic acids and in alkanes (at 2962 and 2872 cm^{-1} for $-CH_3$ groups and at 2927 and 2855 cm^{-1} for $-CH_2$ groups); and 1700 - 1725 cm^{-1}, where carboxylic acids, but not alkanes, show a strong peak corresponding to C=O bonds (at 1711 cm^{-1}) (Bellamy, 1960).

For solution work, carbon tetrachloride (CCl_4) was used, as it is transparent in the regions of interest (Figure 2). Both a 1 mm pathlength UV/Visible quartz cell and a NaCl IR flow cell of 1 mm nominal pathlength were used. NaCl is transparent throughout the spectrum, while quartz has a window in the 3400 - 2400 cm^{-1} region, well placed for studies of the $-CH_2$ and $-CH_3$ bands of interest (Figure 2). However, it was considerably less efficient to use the NaCl cell than the quartz cell for the large number of samples analysed. Therefore, the quartz cell was used for samples from experiments using octadecane only, and the NaCl cell was used for samples from experiments using mixtures of octadecane/octadecanoic acid. For calibration purposes, some octadecane samples were also analysed in the NaCl cell.

For calibration purposes, stock solutions of 1, 10, 25, 50 and 100 equivalent octadecanoic acid monolayers on sand were prepared in ethanol and deposited onto sand ($AWS_{>106}$). From each sand sample, 1 g was taken and added to 5 ml CCl_4. The mix was stoppered, shaken and allowed to equilibrate overnight.

Absorption coefficients (ε) for both octadecanoic acid and octadecane in CCl_4 were obtained from calibration curves from solutions made up to give concentrations equivalent to 100%

extraction of 0, 0.5, 1, 10, 50 and 100 equivalent monolayers from 1 g of sand (Fig. 3). Peak areas (absorbances) between 3000 - 2800 cm^{-1} and 1850 - 1650 cm^{-1} and peak heights at 2927 cm^{-1} and 1711 cm^{-1} were measured. Beer's Law (A=εcl) was used to calculate extinction coefficients, where A is the absorbance, c is the concentration of solution at that absorbance, and l is the cell path length (Osland, 1985). Absorption coefficient data (εl) from Beer's Law plots (A vs. c) are provided in Table 1.

For FT-IR analysis, the CCl_4 solutions were placed in either the UV/Vis quartz cell (octadecane alone), or the NaCl cell (octadecane/octadecanoic acid mix). The quantity of hydrophobic compound remaining on sand was then calculated using Equation (3), where (using octadecane as an example): $M_{\mathrm{AWS(OD)}}$ = mass octadecane remaining on sand (mg OD g^{-1}_{sand}); A = absorbance peak height, as measured by FT-IR at 2927 or 1711 cm^{-1}; ε = molar absorption coefficient (l mol^{-1} cm^{-1}); ℓ = path length (cm); V = volume of CCl_4 used for extraction; and M_{W} = molecular weight of octadecane (284.48 g mol^{-1}).

$$M_{\mathrm{AWS(OD)}} = \frac{\left(\frac{A}{\varepsilon \times \ell}\right) \times \mathrm{V}}{M_{\mathrm{AWS}}} \times M_{\mathrm{W}} \times 1000 \quad (3)$$

2.2.6.3 Calculation of the percentage of compound removed

Once the mass of hydrophobic compound in solution was determined by FT-IR and/or GC analysis, the percentage of compound removed from sand by biochar was calculated using Equation (4), where (using octadecane as an example): B_{OD} = proportion of octadecane removed from sand by biochar (%); M_{OD_0}= average initial mass of octadecane deposited on sand (mg g^{-1}); and M_{OD_1} = average mass of octadecane remaining on sand (mg g^{-1}) (from Equation 2 or 3).

$$B_{\mathrm{OD}} = \frac{M_{\mathrm{OD}_0} - M_{\mathrm{OD}_1}}{M_{\mathrm{OD}_0}} \times 100 \quad (4)$$

2.2.6.4 In situ infrared analysis of organics on biochar

Using the Spectrum One FT-IR spectrometer, Diffuse Reflectance Infrared Fourier Transform (DRIFT), Attenuated Total Reflectance (ATR), and transmission IR using KBr disks were examined as methods to quantify organics adsorbed to biochar *in situ*. Of the three, KBr disks proved best; biochar baseline spectra for both DRIFT and ATR were too noisy to observe small quantities of octadecanoic acid, while KBr disks made with biochar coated with the equivalent of 1 sand monolayer of octadecanoic acid provided peaks visible above the baseline (Figure 4, inset) (Hallin, 2013).

KBr disks were made by finely grinding 0.01 g biochar in an agate mortar and pestle before mixing with 1.5 g dry, ground KBr (Harwood and Moody, 1989). A disk was made by compressing 0.100 ± 0.001 g of the KBr-biochar mixture in a KBr disk press for 5 minutes at 8 tonnes of pressure. Disks were inspected to ensure even mixing of biochar and KBr and a Roebuck (Buck & Hickman, Wythenshawe, UK) Digimatic Caliper (150 mm range ± 0.01 mm error) was used to measure disk thickness. Disks were analysed in transmission, with each collected scan the average of 32 scans, at 4 cm^{-1} resolution. The average of four of these averaged scans obtained with the disk turned 90° after each run was used. A disk of untreated KBr-biochar was used as the background.

To determine whether octadecanoic acid would be visible on the KBr-biochar spectra, and ultimately to determine a quantifiable range at which hydrophobic compounds should be deposited onto the biochar, octadecanoic acid was deposited onto 1 g of biochar ($FGB_{<106}$) in quantities equivalent to 1, 10, 25, 50, 75 and 100 octadecanoic acid monolayers on sand (i.e. 0.688, 6.88, 17.2, 34.4, 51.6, 68.8×10^{-3} mg OA g^{-1} FGB) and the absorbance at each peak was recorded (Figure 4).

2.2.7 Descriptive statistics

Unless otherwise stated, descriptive statistics (means, standard deviation, and variance) are for normal distributions. Error estimates are quoted as ± 1 standard deviation from the mean, except when only one sample is available, in which case the sample value is reported with no error bars. Analyses with fewer than three samples available from which to calculate the mean are always identified.

3.0 Results

pH was found to have no effect on compound transfer, therefore in the following sections and associated figures the data from all three pHs tested are combined.

3.1 Deposition efficiency

Both gas chromatography and infrared results indicated that the third sand-octadecane replicate contained much less octadecane than the first two replicates (~ 0.65 mg OD g^{-1}_{sand}, compared to ~ 3.06 mg OD g^{-1}_{sand} for replicates 1 and 2); this difference was attributed to gross error in preparation, and results from the third replicate were omitted from further analysis.

Previous work by Mainwaring et al. (2013) has shown the method used to give efficiencies for octadecanoic acid and octadecane deposition onto acid washed sand, as measured by total organic carbon content after addition, of 84±8% and 86±5% respectively. Mass balance analysis of the organic material left adhering to the inside of the flasks following deposition, combined with the quantity of organics extracted from samples with 0% biochar addition, showed that for this work, octadecanoic acid and octadecane were deposited with 97±4% and 98±15% efficiency, respectively.

318 *3.2 GC and FT-IR measurements of octadecane removal from sand by biochar*

319 Both GC and FT-IR results show that 100% of octadecane deposited was removed within 1
320 day by 25% biochar; GC results, but not FT-IR, show increased octadecane removal with
321 time for mixtures with less biochar (Figure 5).

322 GC and FT-IR results show high variability in octadecane removed with 0%, 1%, and 5%
323 biochar, and less variability with 10% or 25% biochar (Figure 5). Depending on the exposure
324 time, between 0 and 5% octadecane was removed from sand with no biochar added, and
325 between 1 and 20% octadecane was removed with 1% biochar additions. However, for all
326 exposure times and pH levels, 5% biochar removed ~ 25%, 10% biochar ~ 50%, and 25%
327 biochar ~ 100% of the octadecane coating the sand. Results from GC analyses (Figure 5a)
328 show that more octadecane was removed by biochar in 30 days than in 1 or 10 days, but the
329 results from the three different exposure times are not statistically different from each other.
330 FT-IR results do not show this trend (Figure 5b), and again, FT-IR results are not statistically
331 different between exposure times.

332 For the three 10% biochar samples left dry after being mixed with octadecane-coated sand for
333 10 days, GC shows 32.8% ± 9.4% octadecane removed (Figure 5a, Dry Mix), while IR
334 results show 52.9% ± 12.1% octadecane was removed (Figure 5b, Dry Mix). Again, more
335 variability is seen in the IR results than in the GC, but overall the results are not significantly
336 different to each other.

337 It is worth noting that the high recovery of octadecane and octadecanoic acid from sand at
338 low biochar levels shows that sieving does not, of itself, remove these organics from sand.

339 *3.3 GC and FT-IR measurements of mixed octadecanoic acid and octadecane removal from*
340 *sand by biochar*

341 The behaviour of octadecanoic acid and octadecane when added as a mixture was similar to
342 that of octadecane alone. Assuming uniform distribution throughout the 200 g sand sample, a
343 total 6.52 mg material was initially deposited per g AWS: 3.08 mg OD g^{-1}sand and 3.44 mg
344 OA g^{-1}sand.

345 Table 2 shows the quantities of octadecanoic acid and octadecane removed from sand
346 according to pH and time. Typically, only a small amount of organic material was removed
347 with 1% biochar, whereas the addition of 10% biochar removed approximately 35-75% of
348 material.

349 Octadecanoic acid results are more variable than those for octadecane: between 0 and 25%
350 octadecanoic acid was removed when 1% biochar was present, while the same quantity of
351 biochar removed, on average, 0% octadecane. Similarly, 10% biochar removed anywhere
352 from 40 to 75% octadecanoic acid and approximately 35% octadecane. While neither
353 compound exhibited statistically significant trends proportional to the quantity of biochar
354 added, removal was consistently highest with the addition of 10% biochar. No statistical
355 differences exist between exposure times. Amounts of octadecane removed after 1, 10, and
356 30 days were essentially the same within each biochar quantity.

357 *3.4 Hydrophobic compound removal when deposited on mixed sand and biochar*

358 The quantities of octadecane and mixed octadecanoic acid/octadecane remaining on sand
359 over time after being deposited directly onto mixed sand and biochar are shown in Figure 6.
360 As previously seen, the quantity of octadecane or octadecanoic acid/octadecane on sand
361 decreased with increasing biochar; sand mixed with only 1% biochar retained more
362 hydrophobic compounds than mixtures with greater proportions of biochar. There was no
363 selective removal of either octadecane or octadecanoic acid. But it is surprising to see how
364 little effect the biochar, which has such a large specific surface area, had on the amount of

organics deposited and retained on sand. Even at 1% biochar addition, the biochar surface area by BET was greater than one hundred times that of the sand, and yet when deposited from ethanol, most of the organics added were found on the sand.

3.5 Infrared analysis of biochar as KBr disks

In a somewhat surprising result, neither organic compound could be detected on the biochar samples after separation; no FT-IR absorption bands were observed in any of the biochar samples. Assuming all octadecane was transferred to the biochar in a 25% biochar sample, we would expect the IR peak absorptions to be four times greater than that for the 50 monolayer KBr calibration disk, and thus we had expected to detect it.

4.0 Discussion

4.1 KBr disk analysis

One possible explanation for the lack of peaks from KBr disk analysis lies in the difference in deposition conditions between the calibration and the samples, and the nature of the biochar IR measurement. The calibration curve was prepared by depositing hydrophobic compounds directly onto biochar through rotary evaporation, whereas the experimental samples would probably have transferred octadecane either directly by contact, or perhaps by close migration through solution. Since biochar absorbs in the infrared region and a transmission IR measurement was made, it is possible that the IR result was influenced by the distribution of hydrophobic compound on the biochar. The IR measurement could have been affected if the compound was adsorbed to biochar external or internal pore space, or if sorption was evenly distributed or localised on the biochar surface.

4.2 The potential of biochar to remove hydrophobic compounds from sandy soils, and thus act as an ameliorant of soil water repellency

Both octadecane and octadecanoic acid were removed from sand by biochar. Between pH 3 and 9, pH was not an important factor in determining the quantity of hydrophobic compound removed from sand. Nor did time, within the 1 to 30-day window, appear to influence the removal of octadecane or octadecanoic acid from sand; removal was complete within one day. The limiting factor in the removal of hydrophobic compounds from sand was the quantity of biochar present. The behaviour of octadecanoic acid and octadecane when added as a mixture was similar to that of octadecane alone, and there was no evidence of selective removal of one compound over the other.

Previous work by Hallin et al. (2015) found that the addition of 10% biochar by weight reduced the WDPT in naturally water repellent soils by 50%, and that 25% biochar by weight eliminated water repellency altogether. Similar trends were observed here. When only small quantities (1%, 5% by weight) of biochar were added to sand coated with hydrophobic material, results tended to be quite variable, but 10% biochar consistently removed approximately 50% of the hydrophobic material, and 25% biochar removed 100% of the material present. The effects of biochar on both WDPT and the removal of organics can therefore be correlated, which lends support to the idea that removal of organics is one way in which biochar may influence soil water repellency.

That the presence of biochar reduced the amount of octadecane on sand particles even in dry conditions suggests that it was removed through direct contact, most likely through abrasion. The observation that biochar removed more material in solution than in dry mixtures may be because both biochar and sand can move more freely when in solution than when dry, allowing biochar to encounter more sand than it would in dry conditions. This contact

410 transfer idea seems sensible given that hydrophobic compounds have low solubility in water.
411 It would also explain why pH had no significant impact on the quantity of octadecanoic acid
412 or octadecane removed, and if essentially all contact transfer is made reasonably quickly, i.e.
413 within one day, it would also explain why exposure time did not have any significant effect.

414 Our previous work has shown that the same wettable biochar used here (low pyrolysis
415 temperature biochar) reduced the WDPT of soil/biochar mixes. The results presented here
416 suggest what may be at least a partial mechanism to explain those findings, i.e. removal of
417 hydrophobic organics. Adding biochar to dry, severely water repellent soil would perhaps
418 serve two functions: the biochar would provide a wettable surface for water to infiltrate,
419 reducing runoff and evaporation; and biochar would concurrently remove some hydrophobic
420 compounds and thus help reduce the severity of water repellency of individual soil grains.

421 **5.0 Conclusions**

422 Quantitative analytical procedures for addition, extraction and measurement (by both GC and
423 FT-IR) of organics on sand/biochar mixtures were developed to determine the effect biochar
424 might have on hydrophobised sand. Results showed that octadecane and octadecanoic acid
425 were removed from an acid washed sand by biochar, even when the mixture was left dry,
426 although removal was greater in wet environments. Neither pH (between 3 and 9) nor
427 exposure time (1-30 days) affected the quantity of compound removed.

428 The quantity of biochar present determined the quantity of the organic compound removed
429 from sand: small reductions were evident with 1% and 5% biochar additions, approximately
430 50% of material initially deposited onto sand was removed by 10% biochar, and $\geq$ 25%
431 biochar was able to remove 100% of the material present.

432 Our previous work has demonstrated that wettable biochar is capable of reducing water
433 repellency in soils, and we have shown here that wettable biochar removes organics from a

model system of octadecane and octadecanoic acid deposited on acid washed sand. More work is necessary to understand the sorption mechanism(s) involved in both the dry and wet transfer of hydrophobic compounds to biochar, and the next stage of work should focus on the exploration of the fundamental principles established here using natural soils.

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