



# 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 on sand with 1 and 5 % biochar additions, but that 10 % biochar removed ~50 %, and ≥25 % biochar removed ~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.

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## 1. 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 octadecane and octadecanoic acid because they have been found on natural soils and are thought to be associated with soil water repellency (Morley et al., 2005; Mainwaring et al., 2013). In previous work we found that water repellency could be induced when mixtures of octadecane/octadecanoic acid were added to acid

washed sand at levels comparable to those found in naturally water repellent soils, whereas the sand remained wettable with octadecane alone (Mainwaring et al., 2013); so our interests were also in how the non-polar octadecane behaved when alone compared to when in mixtures with octadecanoic acid.

Two questions were of interest for this study.

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

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

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

## 2. Materials and methods

Although conceptually simple, the success of the experiment required the development of analytical procedures for determining the

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amount of hydrophobic materials on sand and biochar, either directly or by extraction, and a brief account of method development and the 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<sub><2000</sub>), < 250 µm (FGB<sub><250</sub>), and < 106 µm (FGB<sub><106</sub>).

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<sub><106</sub>, the sand used was pre-sieved to > 106 µm (AWS<sub>>106</sub>).

Octadecane (GPR), hexadecane (98%) and octadecanoic acid (99%) from BDH, (Poole, UK), and CCl<sub>4</sub> (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 h.

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

To check whether sieving was effective at separating sand from biochar, three ~2 g mixtures of sand (AWS<sub>>106</sub>) and biochar (FGB<sub><106</sub>), 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 et al., 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 h 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<sub>2</sub> adsorption onto sand and biochar (FGB<sub><250</sub>) are shown in Fig. 1; analysis gives sand a specific surface area of 0.0292 ± 0.0003 m<sup>2</sup> g<sup>-1</sup>; and biochar a specific surface area of 359.1 ± 7.4 m<sup>2</sup> g<sup>-1</sup>.

In terms of compound laydowns the quantities dealt with are mass, or moles, of organics added per gram of sand (mg g<sup>-1</sup>sand, mol g<sup>-1</sup>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<sup>-15</sup> cm<sup>2</sup> molecule<sup>-1</sup> (Moore, 1972; Shaw, 1995), one monolayer equivalent of octadecanoic acid (OA) on sand corresponds to 2.42 × 10<sup>-7</sup> mol OA g<sup>-1</sup>sand, which, since octadecanoic acid has a molar mass of 284.48 g mol<sup>-1</sup>, is 0.0688 mg OA g<sup>-1</sup>sand. Octadecanoic acid and octadecane are very similar sized C<sub>18</sub> 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 octadecane (OD) on sand also corresponds to 2.42 × 10<sup>-7</sup> mol OD g<sup>-1</sup>sand, which, since octadecane has a molar mass of 254.5 g mol<sup>-1</sup>, is 0.0615 mg OD g<sup>-1</sup>sand.

It is of interest to note that based on BET N<sub>2</sub> adsorption surface area measurements, 10 monolayer equivalents of either organic on sand is equal to only ~0.0007 monolayer equivalents on the same mass of 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<sup>-1</sup>sand, 0.0615 to 6.15 mg OD g<sup>-1</sup>sand). The maximum loading rate before solid was visible on the sand or biochar surface was 50 monolayers (3.44 mg OA g<sup>-1</sup>sand, 3.08 mg OD g<sup>-1</sup>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<sup>-1</sup>), 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 detectable after extraction (see later for extraction details) using GC with no need for attenuation adjustments, and IR spectra of extracts 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<sup>-1</sup>, well within instrument limits for suitable precision (Hallin, 2013).

### 2.2.4. Sand and biochar sample preparation

Each treatment (octadecanoic acid, octadecane, and mixed octadecanoic acid and octadecane) was replicated three times on sand (AWS<sub>>106</sub>) alone. For each replicate, 200 g of sand was weighed into a flask to which 1.21 × 10<sup>-5</sup> mol g<sup>-1</sup>sand of octadecane, or an octadecanoic acid/octadecane mix, was then added as an ethanolic

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