



Sorption of the monoterpenes α -pinene and limonene to carbonaceous geosorbents including biochar



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HIGHLIGHTS

- Sorption of 2 monoterpenes to graphite, coal, coke, biochar and peat was quantified.
- Polyethylene (PE) passive samplers were calibrated and used.
- The sorption of α pinene followed the order: biochar \approx peat \approx coal \approx coke < graphite.
- The sorption of limonene followed the order: peat \approx biochar \approx coal < graphite \approx coke.

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ABSTRACT

The sorption of two monoterpenes, α pinene and limonene to the carbonaceous geosorbents graphite, bituminous coal, lignite coke, biochar and Pahokee peat was quantified. Polyethylene (PE) passive samplers were calibrated for the first time for these compounds by determining the PE-water partitioning coefficients and used as a tool to determine sorption to the carbonaceous geosorbents. Log $K_{PE-water}$ values were 3.49 ± 0.58 for α pinene and 4.08 ± 0.27 for limonene. The sorption of limonene to all materials was stronger than that for α pinene (differences of 0.2–1.3 log units between distribution coefficients for the monoterpenes). Placing K_d values in increasing order for α pinene gave biochar \approx Pahokee peat \approx bituminous coal \approx lignite coke < graphite. For limonene the order was: Pahokee peat \approx biochar \approx bituminous coal < graphite \approx lignite coke. Micropore (defined as pores < 1.5 nm) and nanopore surface area (defined as pores 1.5 nm to 50 nm) normalised carbonaceous geosorbent-water distribution coefficients were also calculated. There was no clear correlation of these distribution coefficients with SA. Elemental composition was used to assess the degree of condensation (or alteration) of the carbonaceous geosorbents. The degree of carbonisation increased in the order; Pahokee peat < lignite coke < bituminous coal < biochar < graphite, however this was not correlated with an increase in the experimental distribution coefficients.

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1. Introduction

Monoterpenes are biogenic compounds with the molecular formula $C_{10}H_{16}$ and can be acyclic, monocyclic or bicyclic in structure. They are formed via a C_{10} acyclic intermediate geranyl diphosphate (GPP), which is derived from the C_5 compounds isopentenyl diphosphate and dimethylallyl diphosphate by GPP synthase (Tholl et al., 2004). Monoterpenes are found in various plant fractions (Kainulainen and Holopainen, 2002; Turtola et al., 2003;

Maurer et al., 2008) and in soils of forest areas (White, 1991, 1994; Maurer et al., 2008) and are emitted into the troposphere (Tsigaridis and Kanakidou, 2002). Monoterpenes have been implicated in diverse environmental processes. They can influence rates of nitrogen and carbon cycling (White, 1994; Amaral et al., 1998) by inhibiting nitrification, reducing net N mineralisation, enhancing immobilisation of NO_3-N relative to NH_4-N and/or stimulating overall net immobilisation of N by providing a C rich source material. In addition, they are an important source of secondary organic aerosols (Yasmeen et al., 2012). Further, they can function as a chemical defence against herbivores and diseases, as well as an allelopathic inhibition of seed germination and plant

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growth (Gershenzon and Croteau, 1991). A demonstrated toxic effect of carvacrol against ticks, fleas and mosquitoes has been shown (Panella et al., 2005). Monoterpenes can also stimulate the biodegradation of ^{14}C -2,4 dichlorophenol by indigenous soil microorganisms, showing that adding monoterpenes to soil could be an effective strategy for the biotic removal of organic contaminants (Rhodes et al., 2007).

Such wide reaching environmental effects point to the need for a greater understanding of the physicochemical properties and behaviour of monoterpenes. One of the most important environmental processes related to organic pollutants is sorption as it controls their environmental mobility and bioavailability, and thus their risk. The adsorption of various organic compounds to carbonaceous geosorbents has been investigated extensively (Bucheli and Gustafsson, 2003; Khalil et al., 2006). Observations of enhanced sorption due to the presence of carbonaceous geosorbents in natural matrices such as soil and sediment (Bucheli and Gustafsson, 2000; Cornelissen et al., 2005), multiphase desorption kinetics (Cornelissen et al., 2000) as well as strong non linear sorption (Huang et al., 1997; Xia and Ball, 1999) are likely reasons for this interest. Carbonaceous geosorbents are characterised by condensed, rigid and aromatic structures, with high carbon contents and relatively few polar functional groups (Cornelissen et al., 2005) and include materials from pyrogenic sources (e.g., charcoal, soot, coke, often termed as black carbon) and also materials exposed to diagenetic alterations (e.g., coals).

However, in contrast to this, the adsorption of monoterpenes to carbonaceous geosorbents is a little explored research areas. Research in this regard would be useful in order to understand for example if the way monoterpenes influence rates of nitrogen and carbon cycling could be altered following sorption to environmental matrices. In addition, sorption of monoterpenes to carbonaceous geosorbents could be used as an abiotic method to remove these compounds from the environment. Such a mechanism could be especially important if the monoterpenes are being used as a natural pesticide and have performed their environmental function. One previous study determined soil fate model input parameters for 20 monoterpenes (van Roon et al., 2005a) and used them in order to investigate the influence of soil temperature, soil water content and soil organic carbon fraction on the mobility of these monoterpenes. The study demonstrated that by increasing soil water saturation, both the cumulative amount of monoterpenes volatilised and the cumulative amount of monoterpenes leached decreased (van Roon et al., 2005b). In addition, the study showed that the organic matter phase served as the phase that sorbed the greatest fraction of monoterpenes and was thus able to reduce the cumulative amount of monoterpenes leached and volatilised.

In order to obtain a more detailed knowledge related to the sorption behaviour of monoterpenes in the environment, the primary aim of this work was to determine the sorption of two monoterpenes, α pinene and limonene, to several carbonaceous geosorbents (graphite, bituminous coal, lignite coke, biochar and Pahokee peat). These monoterpenes were chosen as they dominate woodland soil emissions (Steinbrecher et al., 1997; Hayward et al., 2001; Isidorov and Jdanova, 2002; Isidorov et al., 2003; Lin et al., 2007), and are readily degraded by indigenous microorganisms (Misra et al., 1996; Misra and Pavlostathis, 1997; Owen et al., 2007) thus could play an active role in the environmental processes mentioned previously. The carbonaceous geosorbents were chosen as they contain variable H/C, H/O and O/C atomic ratios which is a key physicochemical property that can influence the degree of adsorption of non-ionic organic chemicals (Grathwohl, 1990). In addition, biochar, which is the solid product formed via the pyrolysis of biomass, was chosen as it has recently been proposed as a climate mitigating tool that can improve the quality of weathered or low fertility soils, particularly in tropical regions

(Lehmann, 2007). In order to achieve this aim, a novel approach using polyethylene passive samplers, calibrated for the first time for these compounds, was employed. The hypotheses of the study were that: (i) the adsorption of the monoterpenes would increase in accordance with an increasing degree of geosorbent condensation, inferred by elemental composition, (ii) the adsorption of the monoterpenes would increase with an increase in the surface area of the geosorbents and (iii) the difference in chemical structure of the two compounds affects resulting sorption.

2. Materials and methods

2.1. Reagents and materials

The monoterpenes used, (-)- α -Pinene and (S)-(-)-Limonene, were obtained as neat solutions in acetone (analytical standards with purity greater than 99%) from Sigma Aldrich. Their structures are given in the [Supplementary information](#). Stock solutions were prepared via dilutions in acetone. The carbonaceous geosorbents used in the experiments were graphite, bituminous coal, lignite coke, Pahokee peat, biochar. Bituminous coal was sampled in the Decazeville basin, France and was predominately hard coal (97% of organic particles by percent total sorbent, by volume). The lignite coke was obtained from Rheinbraun AG and is a highly porous material. The standard IHSS Pahokee Peat from the Everglades was used and contains a much lower TOC (46%) than the coal or coke (78% and 72%, respectively). Graphite was obtained from Boom BV (The Netherlands) and had the highest TOC (88%) of the materials. Biochar was produced from cacao shell in a locally constructed pyrolysis unit of 30–40 L at the Indonesian Soil Research Institute in Bogor, Indonesia. All materials have been used in previous studies (Jonker and Koelmans, 2002; Endo et al., 2009; Hale et al., 2013) and their physicochemical properties (including TOC, contribution from various organic particles and composition) as determined in these previous studies are found in [Tables S1 and S2 in the Supplementary information](#). The materials were air dried, pulverised, sieved through a 2 mm mesh and stored at room temperature before use.

2.2. Specific surface area

Specific surface area was determined according to previous methods (Kasozi et al., 2010; Mukherjee et al., 2011) by gas adsorption on a Quantachrome Autosorb 1 analyzer after degassing samples for at least 24 h at 180 °C. Micropore surface area (defined here as pores <1.5 nm) was determined using CO_2 as the probe gas at 273 K and interpreted using canonical Monte Carlo simulations of the non-local density functional theory (DFT) (Pignatello et al., 2006). The DFT model used assumed a slit-shaped carbonaceous surface. Nanopore surface area (defined here as pores 1.5–50 nm) was determined using N_2 as the probe gas at 77 K and calculated using BET theory (Brunauer et al., 1938) on multi-point adsorption data from the 0.01 to 0.3 P/Po linear segment of the adsorption isotherms.

2.3. Determination of polyethylene-water partitioning coefficients

In order to measure aqueous concentrations in the sorption batch experiments described below, polyethylene (PE) passive samplers were used. This is the first time that a passive sampling method has been used in order to measure the aqueous concentration of such compounds. Therefore several preliminary experiments were carried out to investigate: (i) the most suitable passive sampler membrane material, (ii) the most effective extraction solvent, (iii) the necessity of a clean up step and (iv)

the development of a GCMS method. Complete details of these experiments and their outcomes are given in the [Supplementary information](#). Following optimisation of the methods, a polyethylene passive sampler, an 80:20 mixture of heptane:acetone for an extraction period of 48 h and without prior clean up was selected as the method of choice.

In order to determine the polyethylene-water partitioning coefficients, pre-cleaned PE sheets (0.10 ± 0.01 g), Millipore water, α pinene or limonene (3–5000 μg spike), and sodium azide (1% by water volume from a 20 g L^{-1} stock) were added to 50 mL glass vials with glass lids. All batches were rolled end-over-end at 10 rpm for 35 d before the PE and water concentrations were quantified and PE-water partitioning coefficients $K_{\text{PE-water}}$ ($\mu\text{g kg}^{-1}$ PE) ($\mu\text{g L}^{-1}$ water) $^{-1}$ were determined. PE-water partitioning coefficients were also estimated using three methods. (1) the SPARC online calculator (<http://ibmlc2.chem.uga.edu/sparc/>, version: October 2011 release w4.6.1691-s4.6.1687, accessed 30th January 2013) which determines solute-solvent interactions using various empirical molecular descriptors derived only from the molecular structure of the solute and solvent (Hilal et al., 2004), (2) the use of a pp-LFER based on the Abraham approach (Abraham et al., 2004), where the condensed phase used was dry hexadecane. pp-LFERs estimate the partitioning of any non-ionic solute between water and another condensed phase. (3) COSMOtherm (version C3.0 Release 13.01, TZVP level), which performs solvation calculations using statistical thermodynamic approaches based on density functional quantum chemical calculations performed with Turbomole (Eckert and Klamt, 2002). Details of these methods can be found in the [Supplementary information](#).

2.4. Sorption of α pinene and limonene to carbonaceous geosorbents

A batch sorption method was used to obtain monoterpene sorption isotherms. Millipore water (40 mL), a precleaned PE sampler (0.10 ± 0.01 g), sodium azide (1% by water volume from a 20 g L^{-1} stock), and 50 mg of all carbonaceous geosorbents were added to 50 mL glass vials. Vials were spiked at up to seven different monoterpene concentrations ranging from 50 to 5000 μg for α pinene and 10–10000 μg of limonene, in duplicate. In addition, batches without sorbent served as blanks and contamination was not evident. All vials were rolled end-over-end at 10 rpm for 35 d after which PE sheets were removed, extracted and analysed as described in the [Supplementary information](#). The 35 d period was considered sufficient based on a previous study in which 10–30 d were found to suffice when a stronger sorbent (activated carbon) and more hydrophobic compounds (PAHs) were tested for establishment of equilibrium at various temperatures and for different time periods (Cornelissen et al., 2006). A description of the calculations used to obtain geosorbent-water distribution coefficients is given in the [Supplementary information](#), where a three phase mass balance was solved to obtain the concentration of monoterpene sorbed to the carbonaceous geosorbent. When comparing resulting geosorbent-water distribution coefficients, student t-tests performed in Microsoft excel were used.

3. Results and discussion

3.1. Experimental polyethylene-water partitioning coefficients ($K_{\text{PE-water}}$)

Log $K_{\text{PE-water}}$ values were 3.49 ± 0.58 for α pinene and 4.08 ± 0.27 for limonene (Table 1; Fig. 1) and owing to the error on these measurements, the sorption of both monoterpenes to PE was not significantly different ($p > 0.05$). The Freundlich isotherms were, as expected for a rubbery polymer like PE (Hale et al., 2011),

close to linear with Freundlich exponents of approximately one for both compounds (1.37 ± 0.28 for α pinene and 1.11 ± 0.07 for limonene). This is the first time that passive sampler-water partitioning coefficients have been established for α pinene and limonene, and the values were similar to those previously reported for other organic compounds of similar hydrophobicity (Perron et al., 2009; Smedes et al., 2009; Hale et al., 2010; Sacks and Lohmann, 2011). Differences in the degree of non-specific (e.g. van der Waals forces and cavity formation) and specific (or polar) interactions (e.g. hydrogen bonding) depending on functional groups and bonds present in the organic compounds affect the PE-water partitioning coefficient.

PE-water partitioning coefficients were also estimated in order to try to verify the experimental values (values in Table 1). Hexadecane was used as a surrogate for PE (values are reported as $K_{\text{hexadecane-water}}$) as it is a liquid with the same molecular structure of repeating CH_2 units (Hale et al., 2010). The similarity in partitioning coefficients for both monoterpenes was echoed in the estimated $K_{\text{hexadecane-water}}$ values (differences of 0.1 log units SPARC and COSMOtherm and differences of 0.3 log units for the pp-LFER). For all estimation methods, α pinene had the larger $K_{\text{hexadecane-water}}$ value, indicating that α pinene has weaker polar interactions in water and thus higher $K_{\text{hexadecane-water}}$ values than limonene. The estimated $K_{\text{hexadecane-water}}$ values are higher than the experimental $K_{\text{PE-water}}$ values, in agreement with previous results for organochlorine pesticides (Hale et al., 2010). The discrepancy between the values reveals the deviation between the actual cavity formation energy of PE and the predicted cavity formation energy of hexadecane. PE and hexadecane have different proportions of crystalline phases and as cavity formation in solid, partly crystalline PE is likely slightly more difficult than in liquid hexadecane, slightly lower partitioning coefficients result (Hale et al., 2011; van Noort, 2012). While the use of predictive models can be a tool to aid in obtaining partitioning coefficients, these results highlight the importance of developing and validating a passive sampling method for the compounds of interest.

3.2. Sorption of α pinene and limonene to carbonaceous geosorbents

The carbonaceous geosorbents used here vary both in their physicochemical properties and degree of environmental alteration. Lignite coke, biochar and graphite are combustion/pyrolysis products and represent porous and non porous (graphite) counterpart materials (Endo et al., 2009). Lignite coke is the intermediate stage in the diagenesis of peat to coal and is a rigid, aromatic material with a high carbon content. Pahokee peat has a high organic carbon content and contains only a minor carbonaceous geosorbent fraction (see Table S2). Bituminous coals are the thermally altered residues of high plants that remain after exposure to higher temperatures and pressures and consist of a macromolecular 3D network of condensed aromatics (polymers) and separate molecular compounds (Allen-King et al., 2002).

Fig. 2 shows the sorption isotherms of α pinene (Fig. 2a) and limonene (Fig. 2b) on graphite, lignite coke, bituminous coal, biochar and Pahokee peat. The corresponding distribution coefficients (K_d) calculated over the entire concentration range of the isotherm and calculated at an aqueous concentration of 1 ng L^{-1} are given in Table 2. At the highest spiked concentration, the aqueous solubility of α pinene was exceeded (aqueous solubility of 4.071 mg L^{-1} , EPI Suite) and thus this point was excluded from the data analysis. Both monoterpenes were sorbed to the carbonaceous geosorbents to varying degrees. The sorption of limonene to all materials was stronger than that for α pinene (differences of 0.2–1.3 log units between distribution coefficients for the monoterpenes) supporting the hypothesis that sorption is affected by molecular structure. Placing K_d values in increasing order for α pinene gave

Table 1

Experimental log $K_{PE-water}$ values, and Freundlich isotherm parameters as well as estimated values and corresponding model input data for SPARC (CAS number and SMILES string), the pp-LFER given in (Abraham et al., 2004) (compound descriptors E, S, A, B and V).

	α Pinene	Limonene
CAS number	7785-26-4	5989-54-8
Log K_{OW}^a	4.48	4.45
<i>Experimental data</i>		
Measured log $K_{PE-water}$ ($L\ kg^{-1}$)	3.49 \pm 0.59	4.08 \pm 0.27
Measured log K_{Fr} ($\mu g\ g^{-1}$)/($\mu g\ mL^{-1}$) ^{-N}	3.63 \pm 0.19	4.20 \pm 0.07
Measured N (-)	1.27 \pm 0.22	1.11 \pm 0.07
<i>Estimated data and input parameters</i>		
SPARC estimated log $K_{hexadecane-water}$ (-) ^b	5.23	5.10
pp-LFER estimated log $K_{hexadecane-water}$ (-) ^b	4.95	4.66
COSMOtherm estimated log $K_{hexadecane-water}$ (-) ^b	4.53	4.42
SMILES string	C1=C(C)C2CC(C1)C2(C)(C)	C=C(C)C1CC=C(C)CC1
E	0.438	0.501
S	0.20	0.31
A	0.00	0.00
B	0.14	0.23
V	1.2574	1.3230
L	4.256	4.688

^a Estimated with COSMOtherm.

^b Surrogate phase for PE, owing to the presence of repeating CH_2 unit.

biochar \approx Pahokee peat \approx bituminous coal \approx lignite coke < graphite. For limonene the order was: Pahokee peat \approx biochar \approx bituminous coal < graphite \approx lignite coke. When the errors on the K_d values are taken into consideration, the sorption of α pinene to all materials except graphite (showing stronger sorption, log K_d 5.31 \pm 0.16), was similar (log K_d values range from 3.87 \pm 0.18 for biochar up to 4.32 \pm 0.25 for lignite coke) and not significantly different. For limonene biochar, Pahokee peat and bituminous coal had similar sorption affinities (log K_d values from 4.10 \pm 0.36 for Pahokee peat to 4.62 \pm 0.26 for bituminous coal), while sorption to graphite and lignite coke was stronger (log K_d values of 5.43 \pm 0.12 and 5.61 \pm 0.66).

Table 2 also presents log K_{OC} values (organic carbon normalised distribution coefficients). Normalising to this fraction resulted in increasing distribution coefficients for α pinene as: bituminous coal < Pahokee peat < biochar < lignite coke < graphite. For limonene the order was: Pahokee peat < bituminous coal < biochar < graphite < lignite coke. Previously the organic matter-water partitioning coefficient was predicted to be 0.80 $L\ kg^{-1}$ for limonene, based on predicted values of the solubility of limonene in organic matter and water (van Roon et al., 2005a). The organic carbon-water partitioning coefficient was then assumed to be 1.724 times this value. These values are around three orders of magnitude smaller than those determined here, but vast variation in geosorbent properties and the use of existing physico-chemical property data used to obtain model parameters in the previous study, compared to the determination of experimental data here, is likely the reason for this.

Although statistically significant variation in the sorption of α pinene and limonene was not evident (0.05 confidence level), from a qualitative perspective a slightly stronger sorption of limonene was observed. This could be explained by the different geometry of the monoterpenes. The less sterically hindered 3D structure of limonene probably allows a more energetically favourable occupation of sorption sites. One line of evidence supporting this is that the estimated solvent-water partitioning coefficients for wet octanol, dry octanol, chloroform, acetone, methanol, acetonitrile, DMSO, hexane, benzene, toluene and diethylether (Table S3 in the Supporting information), do not differ greatly between α pinene and limonene, (variation of 0.15 log units at most). This similarity suggests that the stronger sorption of limonene could not occur because of different interaction

properties without being related to molecular structure. Another line of evidence that supports the notion that compound geometry could affect sorption, was the difference in linearity of the isotherms. For α pinene, isotherms were close to linear (N values of 0.75 \pm 0.08–1.01 \pm 0.09), while the slightly stronger sorbing limonene exhibited non linear sorption to lignite coke (N of 0.50 \pm 0.04) and more linear sorption to other geosorbents (N between 0.80 \pm 0.05 and 0.99 \pm 0.04). Due to its less sterically hindered 3D structure, limonene may have better access to the narrow pores in lignite coke that have a high sorption energy. As α pinene is sterically hindered to a greater degree than limonene, it requires a larger cavity volume in order to fill sorption sites and this becomes less favourable, for example, for the higher energy sorption sites in lignite coke. Differences in the geometry of n -octane and cyclooctane were implicated previously for the lower partitioning coefficients of cyclooctane sorbed to lignite coke, bituminous coal and Pahokee peat (Endo et al., 2009). A similar explanation was given related to the stronger adsorption of planar PCBs and PAHs compared to non planar molecules, to the graphite used here, (Jonker and Koelmans, 2002) and for a similar PAH and PCB study using a black carbon isolate (Cornelissen et al., 2004).

3.3. The influence of surface area on the sorption of α pinene and limonene to carbonaceous geosorbents

Also shown in Table 2 are micropore (defined as pores <1.5 nm and determined with CO_2 as the probe gas) and nanopore surface area (defined as pores 1.5 nm to 50 nm and determined with N_2 as the probe gas) normalised carbonaceous geosorbent-water distribution coefficients ($K_{d,micro,SA}$ and $K_{d,nano,SA}$ $mL\ m^{-2}$). The specific surface areas of the sorbents are shown in Table 3. The surface area of Pahokee peat is not relevant for such comparisons as Pahokee peat sorbs hydrophobic compounds mainly by a partition mechanism and as such is not represented by SA. For this reason the discussion focuses on the other carbonaceous geosorbents. The nanopore surface area (SA) of the reference materials decreased in the order: lignite coke > biochar > graphite > bituminous coal while the micropore SA decreased in the order: lignite coke > biochar > bituminous coal > graphite.

The data show that all sorbents had greater than 90% of their surface present within micropores, except lignite which had about half of its surface within nanopores. SA-normalised distribution coefficients (both $K_{d,micro,SA}$ and $K_{d,nano,SA}$ $mL\ m^{-2}$) for α pinene

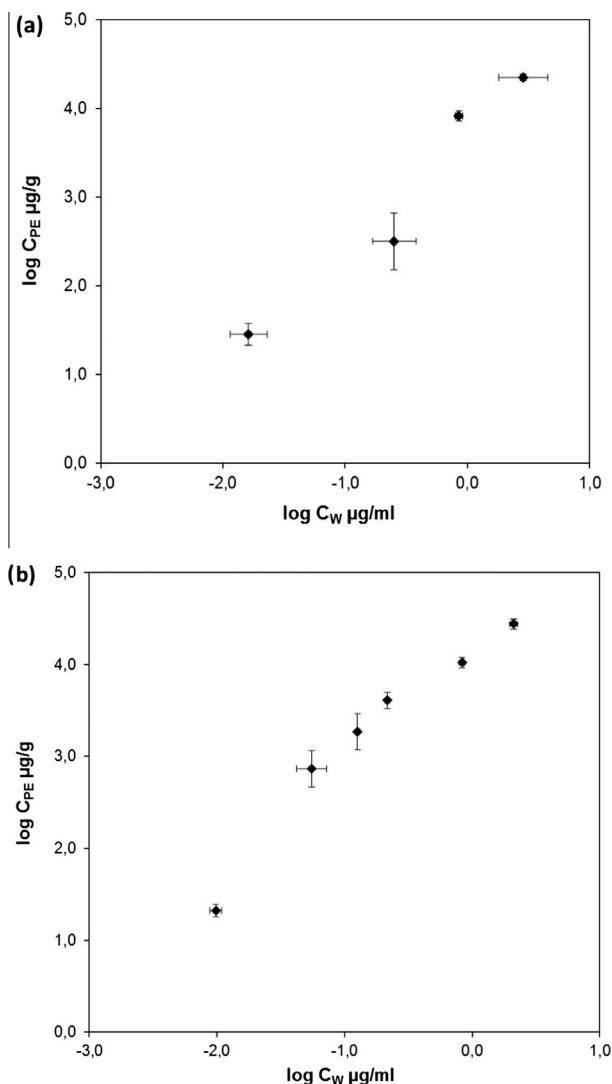


Fig. 1. 12–18-point sorption isotherms of (a) α pinene and (b) limonene on PE passive samplers. Error bars represent the average of three data points.

were largest for graphite and decreased through bituminous coal and lignite coke, and were smallest for biochar. Thus these distribution coefficients were not well correlated with SA and the hypothesis that the adsorption of the monoterpenes would increase with an increase in the surface area of the geosorbents was not correct in this case. For limonene, the micropore and nanopore SA normalised distribution coefficients followed different trends. Nanopore normalised values decreased as: graphite > bituminous coal > lignite coke > biochar. Micropore normalised values decreased in the following way: graphite > lignite coke > bituminous coal > biochar. Again these values were not well correlated with SA.

Previously sorption of organic compounds to various sorbents has been related to sorbent SA (Chen and Chen, 2009; Kasozi et al., 2010; Cornelissen et al., 2013). For example, sorption of catechol to a range of biochars was found to be directly related to micropore SA (Kasozi et al., 2010). The lack of clear correlation of sorption with SA can probably be explained by different affinities of that the monoterpenes have for the various sorbents, where SA only reflects sorption capacity. In addition; (1) Sorbates may be restricted from entering sorbent pores either due to size or kinetic restraints. For example, proteins were inhibited from

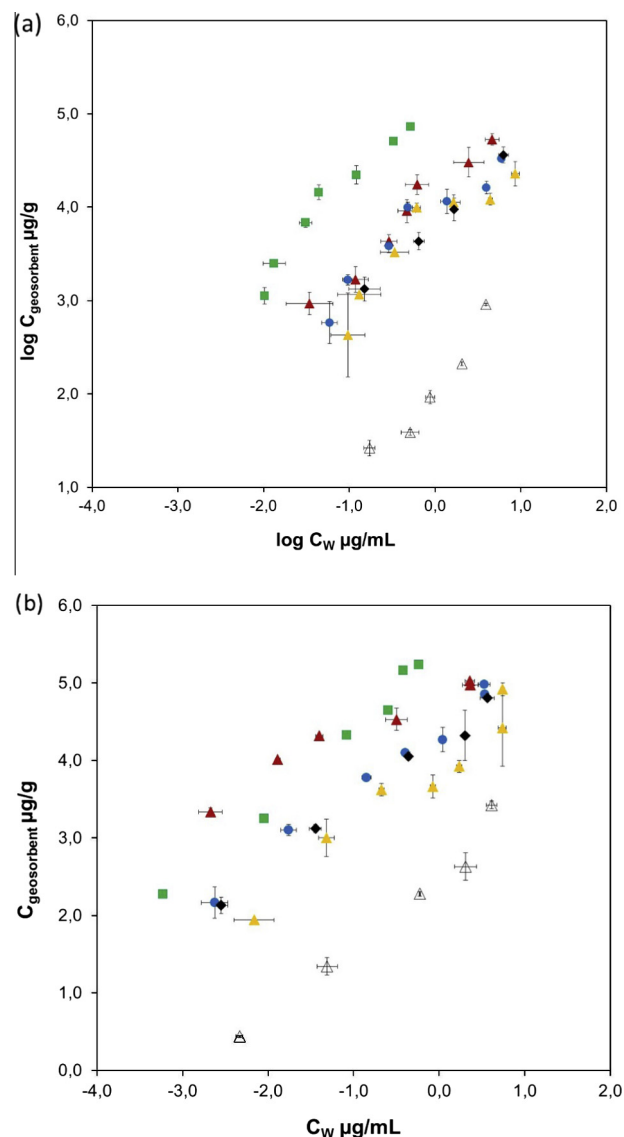


Fig. 2. 14 point sorption isotherms for (a) α pinene and (b) limonene on graphite (■, green), lignite coke (▲, red), bituminous coal (●, blue), biochar (◆, black), Pahokee peat (▲, orange) and soil (△, white). Error bars represent the average of two data points. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

sorbing to alumina and silica sorbents with nanopores of diameters similar to the protein molecular dimensions (Zimmerman et al., 2004). We estimate the molecular dimensions of the monoterpenes to be about 0.8 nm (following a previous method (Zimmerman et al., 2004)), while the molecular dimensions of the sorption sites in the carbonaceous geosorbents were found to be in the same range, but are likely to be heterogeneous (Kasozi et al., 2010). (2) The measurements made of sorbent surface areas may not reflect the actual SA seen by the sorbate in the aqueous environment. For example, graphites can be compressed, expanded or exfoliated, creating varying SA (Shornikova et al., 2009). The assumption of homogeneous surface chemistry used by the BET and DFT models to calculate SA is most likely inappropriate for all of these carbonaceous sorbents except graphite. CO₂ may also partly dissolve in organic materials and this could lead to overestimations in micropore SA, since the DFT model assumes all sorbed CO₂ is sorbed to micropore surfaces, not partitioned in a matrix.

Table 2
Carbonaceous geosorbent distribution coefficients ($\log K_d$), Freundlich isotherm parameters ($\log K_{Fr}$ ($\mu\text{g g}^{-1}$) ($\mu\text{g mL}^{-1}$)^{-N}, Freundlich exponent, N (-)), organic carbon normalised distribution coefficients ($\log K_{OC}$) and surface area normalised distribution coefficients ($\log K_{d,nano,SA}$ $\log K_{d,micro,SA}$ (mL m^{-2})) for; biochar, lignite coke, graphite, Pahokee peat and bituminous coal.

Sorbent	$\log K_{Fr}$ ($\mu\text{g g}^{-1}$) ($\mu\text{g mL}^{-1}$) ^{-N}	N (-)	$\log K_d$ (L kg^{-1})	$\log K_d$ (L kg^{-1}) calculated at $1 \mu\text{g L}^{-1}$	$\log K_{OC}$	$\log K_{d,nano,SA}$ ^a (mL m^{-2})	$\log K_{d,micro,SA}$ ^b (mL m^{-2})
<i>α pinene</i>							
Pahokee peat	3.76 ± 0.09	0.75 ± 0.12	3.91 ± 0.36	4.52	4.25	c	c
Biochar	3.82 ± 0.04	0.84 ± 0.08	3.87 ± 0.18	4.29	4.32	2.22	1.43
Lignite coke	4.19 ± 0.07	0.83 ± 0.08	4.32 ± 0.25	4.71	4.43	1.98	1.66
Bituminous coal	3.94 ± 0.06	0.75 ± 0.08	4.07 ± 0.27	4.68	4.21	3.51	1.89
Graphite	5.29 ± 0.13	1.01 ± 0.09	5.30 ± 0.16	5.25	5.35	4.21	3.22
<i>Limonene</i>							
Pahokee peat	3.94 ± 0.09	0.81 ± 0.10	4.10 ± 0.36	4.52	4.44	c	c
Biochar	4.24 ± 0.07	0.80 ± 0.05	4.49 ± 0.30	4.83	4.95	3.03	2.24
Lignite coke	4.85 ± 0.05	0.50 ± 0.04	5.61 ± 0.66	6.35	5.72	3.28	2.95
Bituminous coal	4.43 ± 0.05	0.82 ± 0.04	4.62 ± 0.26	4.97	4.77	4.08	2.45
Graphite	5.40 ± 0.06	0.99 ± 0.04	5.43 ± 0.12	5.43	5.48	4.33	3.25

^a Nanopore surface area (pores 1.5–50 nm) was determined using N₂ as the probe gas at 77 K.

^b Micropore surface area (pores <1.5 nm) was determined using CO₂ as the probe gas at 273 K.

^c Pahokee peat was not included in the discussion (see text).

Table 3
Nanopore and micropore surface areas ($\text{m}^2 \text{g}^{-1}$) and elemental composition of biochar, lignite coke, graphite, Pahokee peat and bituminous coal.

	Pahokee peat	Biochar	Lignite coke	Bituminous coal	Graphite
Nanopore surface area ($\text{m}^2 \text{g}^{-1}$) ^a	1	29	214	4	12
Micropore surface area ($\text{m}^2 \text{g}^{-1}$) ^b	48	178	458	150	121
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.016		0.13	0.046	0.004
% C	44	70	76	71	96
% H	4.5	1.6	n.d. ^d	4.8	n.d
% O	35	10	18	16	1
% N	3.0	1.4	n.d	1.4	n.d
% Ash ^c	13	10	6.8	7.3	2.4
H/C	0.10	0.022	n.d. ^e	0.068	n.d. ^e
O/C	0.80	0.14	0.23	0.22	0.012
H/O	0.13	0.16	n.d. ^e	0.30	n.d. ^e

^a Nanopore surface area (pores 1.5–50 nm) was determined using N₂ as the probe gas at 77 K.

^b Micropore surface area (pores <1.5 nm) was determined using CO₂ as the probe gas at 273 K.

^c Determined by heating to 700 °C for 6 h.

^d The carbon peak tailed into the hydrogen peak and therefore a determination of the % H could not be made.

^e Ratios could not be calculated as the % H was below detection.

3.4. The influence of elemental composition on the sorption of α pinene and limonene to carbonaceous geosorbents

Organic matter is often characterised by the H/C and O/C atomic ratios which indicate the aromaticity or degree of condensation, similarly the H/O atomic ratio can be used as an index of the degree of oxidation of the organic matter (Xing et al., 1994). A high H/O ratio indicates relatively low amounts of O containing functionalities (corresponding to a relatively low polarity and high hydrophobicity) and therefore a high sorption affinity of non-ionic organic compounds by the organic matter (Grathwohl, 1990). H/C and O/C ratios have been used previously to characterise organic matter in terms of sorption (Huang and Weber, 1997). During progressive stages of diagenesis and catagenesis, the coal carbon content increases and sorption becomes stronger and more nonlinear (Grathwohl, 1990; Huang et al., 1997; Johnson et al., 2001). The elemental composition of the geosorbents and elemental ratios are shown in Table 3 and a van Krevelen plot for H/C and O/C ratios is shown in Fig. S1 in the Supporting information. When placed in order of increasing degree of condensation (or alteration), the geosorbents displayed the following; Pahokee peat < lignite coke < bituminous coal < biochar < graphite. This order is also somewhat different to that of the experimental distribution coefficients showing that the hypothesis that an increase in degree of condensation is positively correlated to an increase in sorption.

Overall this leads to the conclusion that one single factor, be it SA or elemental composition, is not enough to explain the relative the carbonaceous geosorbent sorption.

3.5. Environmental implications

The sorption of organic compounds to environmental geosorbents is important as it implicates their fate and transport. The investigation of the sorption of monoterpenes to environmentally relevant geosorbents provides relevant information if such a method was to be used to remove these compounds from the environment. For example, the use of monoterpenes as natural pesticides provides a potential use for this strategy as the monoterpenes could be sequestered and removed from the environment after they have performed their environmental function. The presence of various carbonaceous geosorbents in soils and sediments (Cornelissen et al., 2005) also suggests that this could occur as a natural process and without the need for invasive treatment methods.

Of special interest is the sorption of the monoterpenes to the biochar used in this study, as previously monoterpenes have been implicated as one way in which the addition of biochar to soil can suppress the anaerobic formation of the strong greenhouse gas nitrous oxide (Rondon et al., 2007; Yanai et al., 2007). The sorption demonstrated here warrants further investigation into the

mechanism by which monoterpenes could reduce greenhouse gas emissions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.08.052>.

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