ORIGINAL ARTICLE

The influence of solid-phase organic carbon on the sorption of hydrophobic organic pollutants in landfill barriers, UK

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Abstract

The Oxford Clay from Bletchley, the Kimmeridge Clay from Kimmeridge Bay, Dorset, and Tertiary mud (Wittering Formation) from Whitecliff, Isle of Wight, United Kingdom were used as sorbent samples because of their distinctive organic material characteristics (Amorphous organic matter rich and/or phytoclast rich). Organic material was isolated for identification and analysis using a non-acid extraction method (heavy liquid) extraction and traditional methods involving HF digestion. These organic materials were then used to determine influences of extraction on hydrophobic organic contaminants, (toluene and naphthalene) sorption. Organic petrology classification was applied to identify the various types of isolated organic material. Amorphous organic matter from the Kimmeridge Clay displayed a higher sorption capacity (Sorption–desorption distribution coefficient (K_d), $K_d = 6{,}481$, 59, 670; for toluene and naphthalene, respectively) compared to literature values. Amorphous organic matter-rich sorbent extracts demonstrated a higher absorption capacity than the phytoclast-rich sorbents (e.g., Wittering Formation, $K_d = 219$, 10, 134; for toluene and naphthalene, respectively). Implications of results in landfill design/risk assessment and modelling are discussed.

Keywords HOCs · SOM · Sorption · Risk assessment

Introduction

Modern landfills are designed with engineered barriers to prevent pollution of surface and groundwater. Low permeability barriers such as engineered clay liners may be used to limit transport of leachate or attenuate the concentration of pollutants by processes such as sorption (Fishman et al. 2012; Simoes et al. 2011). The potential for attenuation of leachate contaminants by landfill liners may be taken into account in regulatory risk assessment. Sorption may be estimated from easily measurable parameters such as f_{oc} (the fraction of organic matter in the sorbent) and contaminant sorption coefficient values, (e.g., K_{OC} is the sorption coefficient normalized to the sorbent f_{oc}), which are commonly available in the literature (Delle Site 2001). However, greater than expected sorption capacity combined with apparently non-linear sorption isotherms have been reported in the literature and is considered to be due to the heterogeneous nature of the organic matter (Chi 2014; Chiou et al. 2000; Cornelissen et al. 2005; Huang et al. 2003; Weber et al. 2001). Simoes et al. (2011) found that hydrophobic organic contaminants (HOCs) present in landfill leachate (such as naphthalene, toluene and tetrachloromethane) sorbed to clay materials used as barriers in landfills. In their study, sorption of HOCs to Oxford Clay (OxC) was much stronger than predicted from contaminant hydrophobicity and this was attributed to the organic matter characteristics of the clay barrier material.

HOCs will sorb to different soil or sedimentary components including solid phase minerals, plant debris and organic matter, and majorly to the latest (Cornelissen et al. 2005; Trellu et al. 2016). The aromaticity and polarity of biochemical molecules are controlling factors and chemical elements such as organic carbon, oxygen, and hydrogen are important (Cornelissen et al. 2005; Delle Site 2001). The composition and the structure of the soil OM (SOM) is influenced by its source, type, age and

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alteration history (Cornelissen et al. 2005; Huang et al. 2003). These properties will influence the sorption affinity for non-ionic organic compounds and the residence time of organic carbon in sediments (Han et al. 2016; Kennedy et al. 2002; Perez et al. 2011).

The impact of sediment diagenetic changes after burial on the attachment of HOCs to SOM has been investigated through experiments simulating diagenesis through the use of high temperature and pressure (Guo et al. 2013). Treated samples were found to have an increased surface area and number of pores (Guo et al. 2013; Han et al. 2018). This was believed to provide substantial additional voids for HOCs. Additionally, after simulated diagenesis, treated samples show greater sorption nonlinearity and increased sorption capacity (Han et al. 2018).

The examination of OM can be achieved by chemical methods or changes in morphology. Chemical methods are capable of measuring elemental composition, whereas organic petrological techniques can give structural OM compositional information. Organic petrology can be used to examine components such as coal and charcoal, from the remains of microorganisms, plants and animals, which can predetermine the heterogeneous character of the resultant OM (Lichtfouse et al. 2005; Ligouis et al. 2005) and can also provide a visual interpretation of the interface between HOCs and OM. Karapanagioti and Sabatini (2000) and Huang et al. (2006), suggested estimations for sorption capacity by organic petrology analysis quantification.

As stated in Simoes et al. (2011), the selection of appropriate sorption parameters for use in landfill risk assessment is difficult because of the wide range of values available in the literature and because the types of OM found in clay-rich sediments used in landfill barriers may be significantly different to soils and sediments previously studied. Simoes et al. (2011) demonstrated through petrological examination that OxC had a high concentration of amorphous organic matter and excess sorption was attributed to the presence of this type of OM in the clay barrier material. This research is extended here by considering sorption of HOCs to other types of sediments which have different OM compositions and have undergone varying degrees of diagenesis. The overall aim of the study was to determine the influence of different types of sedimentary OM on the sorption of HOCs through chemical and petrological methods and determine whether petrology can be used to predict sorption. The study investigated the sorption of two HOCs (toluene, naphthalene) commonly found in landfill leachate onto the following: [1] three different formations and [2] the OM extracted from these sediments/clays.

Materials and methods

Materials

Barrier materials (sorbent)

Three barrier materials were chosen to present different and distinct types of OM, this because of their high variability in terms of character and maturation due to the sedimentary history (i.e., Tertiary or Jurassic). These include Kimmeridge Clay (KC) from Kimmeridge Bay, Dorset, UK which is a bituminous shale (SY91916 77760), the Wittering Formation (WF) is from sandy clay with lignitic logs scattered among it (SZ63899 86027), and the Oxford Clay (OxC) from Bletchley, UK is from mudstone with well-preserved OM and fossils. Figure 1 in the supplementary material shows the geographical distribution of the three sediments/clays in the UK. Both KC and OxC were deposited during the Jurassic, and it could be expected that these would have similar geological history. Conversely, the WF provided sandy material and abundant phytoclasts (plant debris) from a younger geological time, the Tertiary. KC and OxC sediments have been used as clay barrier materials in landfills; the WF was used in the study to provide a sample with significantly different OM.

The KC Formation was deposited in a series of basin that are distributed across the North Atlantic area. Though the KC is the source rock for most North Sea oil fields, the burial depth is shallower in Dorset, consequently there was insufficient pressure and heat for the type II kerogen to mature (Fishman et al. 2012). The average TOC is 8 wt%, but varies between 3 and 26 wt% (Morgans-Bell et al. 2001). The Blackstone Bed among four lithological units has an abundant TOC of over 35 wt%, with typical contents between 8 and 15 wt%; this material was selected for the study because the kerogen can be extracted more efficiently. The majority of the KC OM is amorphous organic matter of marine origin (75% and 95%, in) The OM of the KC has been classified as Type II kerogen.

The OxC OM is also immature in terms of petroleum generation potential (Delle Site 2001). Petrographic analysis (Delle Site 2001) divides the Peterborough Member into an organic-rich group (TOC 12.2 ~ 14.2%) and the medium content TOC Peterborough Member (TOC 5.2 ~ 5.6%) that was used in this study. The reason for using a medium-TOC rather than the organic-rich is that it is more typical of the TOC in OxC. The two groups exhibit different palynofacies characteristics: the higher organic carbon content group has a greater AOM component of type II kerogen than the other, and the remaining components are plant fragments, pollen, spores, microplankton and lignitic debris.

The Eocene sediments at Whitecliff Bay is a reference section for the global chronostratigraphical and eustatic schemes. The estuarine laminated sandy clays in the Wittering Formation include rooted coals (Huggett et al. 2005).

All three sampling sites were outcrop and composed of loose components compared to the underlying rock. After documenting the location of the site [photographically and with global positioning system (GPS) tracking] and removal of allogenic material, samples were extracted from the exposed solid rock using shovels, chisels and geological hammers and placed in ziploc bags and plastic box containers for storage. At least two kilograms of each sediment was taken for analysis and organic matter extraction.

Leachate

To simulate landfill conditions, a synthetic leachate is used in the sorption experiments. This was used rather than real leachate to maintain a stable and repeatable composition throughout the sorption testing (Cornelissen et al. 2005). The synthetic leachate was designed to represent a typical UK municipal solid waste (MSW) leachate (Table 1 in supplementary material) (Environment Agency 2009; Simoes et al. 2011).

As a surrogate, the level of aromaticity, molecular weight, carbon/nitrogen ratio and reactivity of artificial materials (tannic acid) may not be representative of either leachate humic or fulvic acid (Simoes et al. 2011). However, in this research it was considered to be the best surrogate for DOC (dissolved organic carbon) in leachate. The synthetic leachate was found to react with oxygen such that darkening and precipitation of DOC were observed. As such the solution was stored in an anaerobic cabinet in an atmosphere of 90% N_2, 5% CO_2 and 5% H_2 (Wolflabs Model A Vinyl cabinet) to prevent precipitation of tannic acid. The batch sorption tests were also prepared in the anaerobic glovebox.

Analytical compounds

Naphthalene and toluene were chosen as examples of HOC pollutants to be used in this study because they are often found in landfill leachate. They have different hydrophobicities with the Log K_{OW} of naphthalene being 3.17 and that of toluene 2.54 (Mackay and Gschwend 2000).The physicochemical properties of the hazardous substances are shown in supplementary material Table 2. Analytical-grade naphthalene (solid) from Sigma Aldrich Chemical Co. (Ebukanson and Kinghorn) and analytic grade toluene from Fisher Scientific (Ebukanson and Kinghorn) were used as HOCs.

Petrology analysis

Sediment samples were dried and milled and the TOC determined on a Carlo-Erba EA1108 elemental analyser as total carbon [TC] and then on decarbonated sediments/clays using the HCl fumigation method (Harris et al. 2001; Yamamoto et al. 2001). The elemental analysis (N, C, O, S, H) of the sediments and isolated OM was measured by OEA Ltd (Organic Elemental Analysis Laboratories Limited). The elemental analysis determined total carbon, hydrogen, nitrogen and sulphur simultaneously. The detection limits were 0.01% for C, N, O and H, and 0.05% for sulphur.

The samples of the OxC, KC and WF were air-dried, crushed and then sieved to a ≤ 3 μm particle size and stored in air-tight containers. Mineral contents were determined by X-ray diffraction (XRD) using a Philips PW 3040/60 X-ray Diffractometer and linked X'Pert software. Precision values and detection limits for mineral analysis of crystalline materials are generally of the order of ± 0.5–2%, and for total clay precision values of ± 15%.

Microscopic methods were used for determination of kerogen type and maturity of that portion of kerogen which was microscopically recognizable, or structured. The HF digestion residues and heavy liquid floating OM were mounted in Elvacite 2044™ to make transmitted light slides for point counting. This gave a percentage of the different OM types. These types were identified by using a transmitted light microscope based on microfossil morphology.

Methods of extraction of SOM from clay barrier materials

Dried material was treated by two different extraction methods: [1] HF acid digestion (Yule et al. 2000), and [2] heavy liquid separation (Riding and Kyffin-Hughes 2009).

1. HF digestion

   The sediment/clay was weighed and placed into plastic beakers for acid digestion in a fume cupboard. First, 30% HCl was added to remove the carbonate. The sample was then washed to neutral pH. 60% HF was then added to dissolve the majority of the silicates, then decanted and the residue washed to neutral pH. The sample was then treated with hot concentrated HCl to dissolve fluorides which had formed during the HF digestion. The solution was then neutralized by dilution with water. Slides of the residue were again mounted in Elvacite 2044 for point counting using a transmitted light microscope.

2. Heavy liquid separation

   This was carried out on samples which were initially dispersed, using Calgon ($NaPO_3)_6$, neutral, non-oxide) to remove the silicate clay (Riding and Kyffin-

Hughes 2009). The samples were then placed in an ultra-sonic tank, disaggregated and sieved at 15 µm (Riding and Kyffin-Hughes 2009). This deflocculation and sieving method was repeated until no cloudy suspension remained.

In this study, instead of using heavy liquid zinc bromide ($ZnBr_2$), LST Fastfloat (Pangea UK) was used. Fastfloat (hydrated sodium heteropolytungstate (Li_mNa_m ($W_{12}O_{40}$), 80 wt% dissolved in water) has a low-toxicity and is a low-viscosity heavy liquid and has the advantage of being reusable. Taking into account the density of the OM [i.e., vitrinite ($1.25 \sim 1.4$ g/cm^3) and semifusinite ($1.4 \sim 1.7$ g/cm^3), kerogen type II ($1.15 \sim 1.25$ g/cm^3)] (Okiongbo et al. 2005; Pilawa et al. 2002; Tyson 2012), a 2.0-g/cm^3 density Fastfloat was prepared because the majority of the silicates in the rocks was clay, and the density demarcation between OM and minerals was 2.0 g/cm^3. After putting the dried sample in the Fastfloat, a sonication bath was used to ensure thorough mixing. The sample was then centrifuged for 3 min at a speed of 1400 rpm. The floating particles were then decanted to separate them from the heavier fraction. Deionised water was added to reduce the solution density until the suspension started to sink. Further centrifugation was then used until the Fastfloat had been removed. The OM was collected by filtering with a glass microfibre filter paper (Whatman, pore size 0.1 µm).

Sorption tests

The batch sorption method used in this study followed the procedure of Simoes et al. (2011). Amounts of solid samples (either extracted OM or sediments/clays, Table 3 and Table 4) were prepared for interaction with leachate. After the HOC contaminants were added, the glass bottles (122 ml internal volume, Sigma Aldrich, UK) were sealed immediately with aluminium caps and Teflon®-coated septa. These have been reported to cause loss of solute (Cornelissen et al. 2005) but no significant losses were found using a 7-day contact time. The sorbent and sorbate were mixed by horizontal rotary agitation, at 20 ± 2 °C in a constant temperature room. After 7 days of rolling, solids were separated from the aqueous solutions by centrifugation at 1500 rpm for 40 min (naphthalene) or 1 h (toluene). Sodium chloride (3 g) and sample (9.9 ml) were added to headspace vials (Sigma-Aldrich, UK) together with internal standard dichlorobenzene(1,4-DCB) and 1,4difluorobenzene(1,4-DFB) (100 µl), followed by analysis using Gas chromatography-mass spectrometry (GC–MS).

Initial tests were carried out to determine the solid/liquid (S/L) ratio required to allow measurable changes in aqueous contaminant concentration during sorption (20–80%). The resultant S/L ratios used for the clay barrier materials and

extracts are shown in Tables 3, 4. Subsequent tests allowed the generation of sorption isotherms. The concentration ranges used in this study were limited to match those found in landfill leachate (Environment Agency 2001, 2003): toluene from 60 to 400 µg /l, naphthalene from 0.25 to 50 µg/l.

Results and discussion

Abbreviations to those samples used in this study are listed below as follows

OM_{HF}: Organic matter extracted by HF digestion from KC, OxC and WF

KC_{HF}: HF digestion residues from the KC

OxC_{HF}: HF digestion residues from the OxC

WF_{HF}: HF digestion residues from the WF

OM_{HL}: Organic matter extracted by heavy liquid from KC, OxC and WF

KC_{HL}: OM separated from the KC by heavy liquid

OxC_{HL}: OM separated from the OxC by heavy liquid

WF_{HL}: OM separated from the Wittering Formation by heavy liquid

Characterization of sorbent

Mineral quantified analysis of the sediments/ clays and organic matter

Table 1 provides the mineralogy compositions, sediments/clay and of their heavy- liquid- extracted OM. The KC has median clay mineral proportion (51.4%) of the three sediments/clays; the non-clay minerals were mainly quartz with minor calcite and accessory mineral pyrite. The OxC had the largest clay mineral proportion (58.2%); non-clay minerals included quartz, feldspars, calcite, gypsum, and accessory mineral pyrite. The WF, which is a siltstone with dispersed lignite, contained the highest percentage of sand-sized quartz (40.6%) and clay minerals (30.2%) with feldspars, minor calcite, and accessory mineral pyrite. The clay components of the free sediments were major illite with minor kaolinite. The missing part of the total mineral sum (100%) is attributed to residual OM and/or water.

The advantage of SOM gathered from demineralised sediments/clays using hydrofluoric acid (HF) is the higher purity of SOM which enables the investigation to focus on the SOM contribution to sorption of HOCs. However, the heavy-liquid-enriched SOM is less subject to chemical alteration (Riding and Kyffin-Hughes 2009). Through XRD analysis, the heavy-liquid-separated organic matter was found detectable minerals remains. This finding indicates not only organic matter involved in the sorption process but also remaining minerals (Table 1). Those remaining minerals could involve and/or interfere the sorption process of HOCs. This could

Table 1 Mineral composition and moisture contents of the Kimmeridge Clay [KC], Wittering Fm [WF] and Oxford Clay [OxC] and mineral composition of OM separated by heavy liquid HL

Mineral (wt%)	KC	OxC	WF	KC$_{HL}$	OxC$_{HL}$	WF$_{HL}$
Illite	36.3	42.4	24.7	46.9	10–25	–
Kaolinite	15.1	13.8	5.5	17.5	2–3	–
Smectite	–	1.5	–	–	–	–
Chlorite	–	0.5	–	–	–	–
Feldspars	–	2.9	5.3	–	–	–
Quartz	14.8	16.1	40.6	10.1	50	7.9
Calcite	7.0	9.2	0.2	0.1	–	1.1
Gypsum	–	5.1	–	–	–	–
Pyrite	1.3	0.7	1.7	1.5	2–3	5.2
Total	74.5	92.2	77.9	76.1	64–81	14.2
TOC (%)	21.4 ± 0.2	5.5 ± 0.2	2.8 ± 0.1			
Moisture content (%)	4.8 ± 1.9	19.5 ± 0.1	20.8 ± 0.0			

The detection limitation of X-ray Diffraction (XRD) is 0.5%. –: Not detected, OxC$_{HL}$: qualitative analysis because of limited sample availability

result in variation in sorption characteristics between the two extraction methods: HF digestion and LST separation. However, the efficacy of heavy liquid separation OM for chemical elements analysis is open to question, while this LST separation could be efficacy for kerogen morphological observation (Riding and Kyffin-Hughes 2009).

Geochemical analysis of sediments/clays and organic matter

The TOC contents of the sediments/clays decreased in the following order: KC > OxC > WF (Table 1). Polarity of the sediments (Table 2) increased in the following order: KC < OxC < WF, the H/C and O/C atomic ratios /clays followed the same trend (Table 2). The reason we study the atomic ratio is that increasing H/C and O/C atomic ratios

have been found to be indicative of enhanced sorption capacity (Cornelissen et al. 2005; Jin and Zimmerman 2010; Weber et al. 2001; Zhang and He 2010) and that increasing O/C ratio has also been found to be correlated to increasing isotherm linearity (Cornelissen et al. 2005; Weber et al. 2001).

The polarity index (PI) of the sediments was higher than the corresponding extracted OM. For example, the polarity of KC decreased in the following order: KC (0.4) > KC$_{HL}$ (0.2) > KC$_{HF}$ (0.1) (Table 2). Similarly, the H/C and O/C atomic ratios of the sediments were generally higher than their corresponding extracted OM. In this study, the O/C atomic ratio of OM$_{HL}$ and OM$_{HF}$ decreased in the order WF > OxC > KC. The H/C atomic ratios behaved differently; the acid-extracted H/C atomic ratios decreases as OxC$_{HF}$ = KC$_{HF}$ > WF$_{HF}$, whereas the ratios

Table 2 Summary of the elemental compositions polarity index (PI), H/C and O/C ratios in sediments/clays for the Kimmeridge Clay [KC], Wittering Fm [WF] and Oxford Clay [OxC] and their corresponding heavy liquid (HL) and hydrofluoric acid (HF) extracted OM

	N	C	H	S	O	Total	PI	H/C	H/O	O/C
	wt%						Atomic ratio			
KC	0.6 ± 0.02	21.4 ± 0.01	2.7 ± 0.09	3.6 ± 0.06	9.4 ± 0.09	37.7 ± 0.07	0.4	1.50	4.60	0.33
OxC	0.2 ± 0.00	8.1 ± 0.00	1.5 ± 0.05	1.5 ± 0.01	10.9 ± 0.09	22.1 ± 0.03	1.0	2.12	2.20	1.00
WF	0.1 ± 0.01	4.0 ± 0.05	1.0 ± 0.02	3.3 ± 0.06	8.6 ± 0.20	17.0 ± 0.32	1.6	2.89	1.86	1.62
KC$_{HL}$	0.8 ± 0.00	30.8 ± 0.04	3.8 ± 0.00	4.3 ± 0.03	7.8 ± 0.05	47.5 ± 0.06	0.2	1.47	7.79	0.19
OxC$_{HL}$	0.6 ± 0.00	32.5 ± 0.07	3.8 ± 0.11	4.2 ± 0.00	11.3 ± 0.11	52.5 ± 0.07	0.3	1.39	5.38	0.26
WF$_{HL}$	0.5 ± 0.00	30.0 ± 0.36	4.0 ± 0.11	7.2 ± 0.18	29.6 ± 0.15	71.4 ± 0.58	0.8	1.59	2.16	0.74
WF$_{HL}$*	0.5 ± 0.00	29.9 ± 0.36	4.0 ± 0.11	6.4 ± 0.18	24.9 ± 0.15	65.6 ± 0.58	0.6	1.39	2.57	0.62
KC$_{HF}$	1.9 ± 0.01	67.8 ± 0.38	7.2 ± 0.08	9.0 ± 0.01	8.8 ± 0.03	94.7 ± 0.51	0.1	1.27	13.09	0.10
OxC$_{HF}$	1.3 ± 0.07	62.4 ± 0.04	6.9 ± 0.05	7.8 ± 0.09	15.3 ± 0.17	93.7 ± 0.31	0.2	1.31	7.22	0.19
WF$_{HF}$	9.5 ± 0.04	52.7 ± 0.09	4.1 ± 0.02	9.9 ± 0.04	23.6 ± 0.00	99.8 ± 0.00	0.5	0.93	2.78	0.34

Polarity index (PI) [(O + N)/C] of OM was calculated from the atomic ratio of (O + N) and C (Cornelissen et al. 2005). H/C and O/C were calculated from the corresponding atomic ratios. *Data with minerals content removed

of OM$_{HL}$ decreased as KC$_{HL}$ > WF*$_{HL}$ = OxC$_{HL}$ (Table 2). Among OM extracted by HF acid digestion, AOM dominated samples (KC$_{HF}$) had the lowest O/C atomic ratio and the phytoclast dominated samples (WF$_{HF}$) had the lowest H/C ratio.

The reduced H/C and O/C values of OM extracted by HF digestion compared to heavy- liquid- extracted OM were mainly due to the mineral component contribution to H and O in the OM$_{HL}$ samples. Although OM$_{HL}$ still has calcite which contributes C, the amount is comparatively small compared to the H and O content in clay mineral and quartz. Hence, H/C and O/C values of OM$_{HL}$ were not suitable for the Van Krevelen diagram.

Characterization of the organic matter

Geochemical characterization and classification of OM

The average H/C and O/C atomic ratios of OM$_{HF}$ are plotted on the Van Krevelen diagram in Fig. 1. The total weight percentage of the HF digestion-extracted OM ranged from 93.4 to 99.8%. In contrast, the total weight percentages of the heavy- liquid- extracted OM were found to range from 47.5 to 71.4%. As these samples may contain other minerals over 15% by weight, they are not plotted on the Van Krevelen plot. Inspection of the plot (Fig. 1) reveals that kerogen samples from the KC (Fishman et al. 2012; Morgans-Bell et al. 2001) and the OxC (Delle Site 2001) are immature Type II kerogens, consistent with previous studies of these samples, and that the

woody kerogen from WF are Type III kerogen (Huggett et al. 2005).

Microscopic observation on quantification, characterization and classification of extracted organic matter

In the petrological analyses of samples, 100 kerogen particles were counted at ×400 on a transmitted light slide using. Optical observation showed AOM with a sharp edge in the KC$_{HF}$ which is predominantly palynofacies (79% and 89%) and a minor maceral component of phytoclasts (6% and 7%) (Figs. 2a, 3). The phytoclast component in the KC$_{HF}$ was measured by the reflectivity show mainly low-rank (<0.5%) vitrinite with very little higher rank fusinite (>1.6%) (Fig. 4).

The WF$_{HF}$ consists mainly of phytoclasts (61%, Figs. 2c, 3), with entirely low-rank vitrinite (Fig. 4). The heavy- liquid- extracted OM from KC (Fig. 2d), OxC (Fig. 2e) and WF (Fig. 2f) observed under microscope was similar to the kerogen extracted by HF digestion. The preservation of OM is prominent in the HF- extracted OxC (Fig. 2b). Microscopic examination identified amorphous kerogen (58% and 73%), marine microplankton (31% and 8%) (dinoflagellate cysts, acritarchs) and black opaque tissue from land plants (11% and 9%) (Figs. 2b, 3). Details of the OxC kerogen have been described in a previous work (Simoes et al. 2011).

Sorption of organic contaminants

Linear sorption isotherms for sediments/clays, heavy-liquid-extracted OM, and HF-extracted OM are shown in Fig. 5. All sorption equilibrium data measured for the three sediments/

Fig. 1 Van Krevelen atomic diagram with superimposed elementary composition ratios (H/C and O/C) of kerogen extracted OM by HF digestion from the Kimmeridge Clay [KC$_{HF}$], the Oxford Clay [OxC$_{HF}$] and the Wittering Fm [WF$_{HF}$]
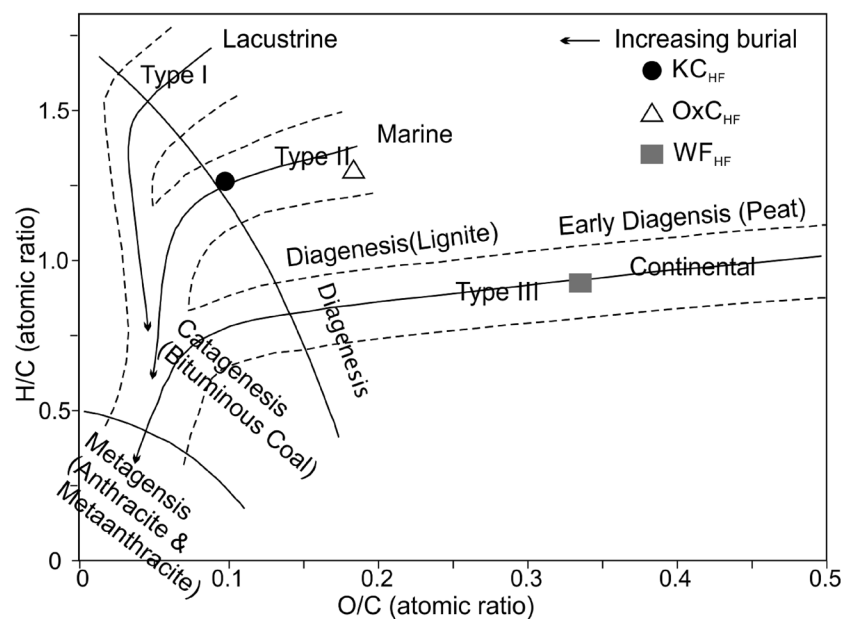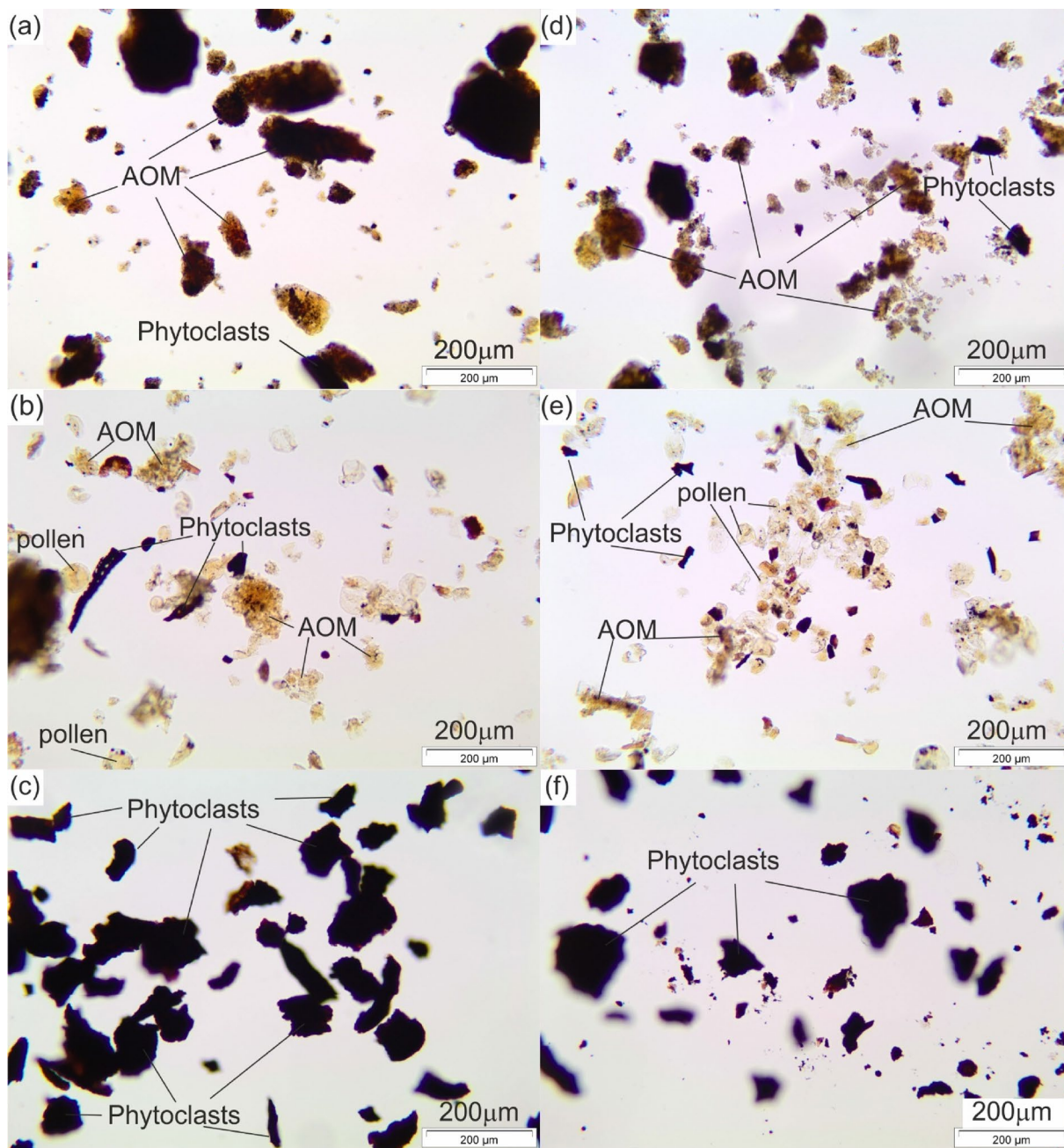
Fig. 2 OM isolated from sediments/clays viewed under incident light microscopy. **a** KC_{HF}, **b** OxC_{HF}, **c** WF_{HF}, **d** KC_{HL}, **e** OxC_{HL}, **f** WF_{HL}. *AOM (Amorphous OM)

clays and extracted OM were fitted to both the linear sorption isotherm model and the Freundlich sorption isotherm model (Tables 3, 4). Non-linearity has been shown to exist typically over three orders of magnitude or more at concentrations up to 10 or 20% of the compound's water solubility (Cornelissen et al. 2005). The concentration range in this study was narrow, less than three orders of magnitude and

thus the Freundlich model linearity index was close to 1 in most cases.

The linear sorption coefficient (K_d, ml/g) for naphthalene (388 ml/g − 8073 ml/g) was found to be greater than for toluene (37 ml/g − 887 ml/g) (Tables 3, 4). The aqueous solubility of naphthalene (142.1 mg/l) is less than that for toluene (573.1 mg/l). Similar results were also found by Jin and Zimmerman (2010) and Headley et al. (2001). The K_d values of the HOCs on the corresponding
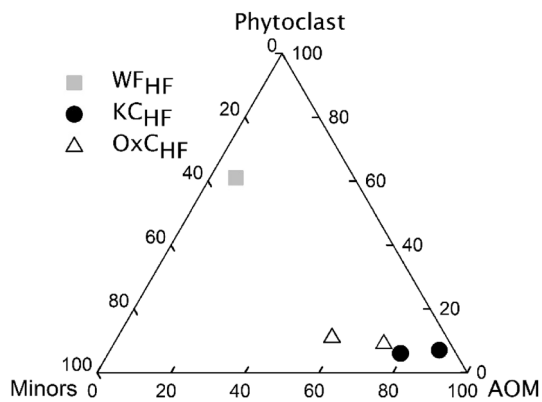
Fig. 3 Microfossil component ternary plot of the extracted OM (HF) from the Wittering, Kimmeridge Clay and Oxford Clay formations

extracted OM have the same decreasing order, i.e., KC > OxC > WF which corresponds to the TOC content.

Sorption capacity of the barrier clay for toluene and naphthalene

The linear sorption coefficients for the two HOCs and three sediments/clays were compared to literature values (supplementary material Table 3). Values for toluene K_d ranged from 0.1 to 153.6 ml/g. In this study, the toluene K_d measured from the OxC (94 ml/g) and the WF (37 ml/g) were within this range, but KC was significantly higher at 887 ml/g (Supplementary material Table 3a). Similarly, the naphthalene sorption coefficient derived in this study for KC (8073 ml/g) was high but still within the range of literature values, from 0.2 ml/g to 8530 ml/g. This extraordinarily high sorption capacity of KC could be due to the high TOC in comparison to the other sediments described in the literature and/or a function of the type of OM present.

Published log K_{OC} values (K_d normalised to the OM content) of toluene range from 1.52 to 3.8 (ml/g), (supplementary material Table 3a), whereas the log K_{OC}

values measured in this study ranged from 2.62 to 3.98 ml/g (Table 4). Published log K_{OC} values of naphthalene ranged from 1.28 to 4.64 ml/g (supplementary material Table 3b); here the log K_{OC} values of naphthalene ranged from 3.91 to 4.94 ml/g. In both cases K_{OC} values obtained in this study were higher than the literature values indicating that the sorption capacity was influenced by intrinsic OM structural properties. The log K_{OC} of naphthalene measured from KC_{HF} is the highest among literature.

To facilitate direct comparisons of sorption affinities amongst the samples tested, log K_{OC} values were plotted against TOC% (Fig. 6). Sediments/clays and extracted OM had K_{OC} values for both toluene and naphthalene that decreased in the following order: KC > OxC > WF. The apparent differences indicate different sorption capacity amongst the different types of OM and the sediments/clays. The microfossil component combination shown in Fig. 3 shows that the major component of OM in KC was AOM (79%) whilst OxC had a content of 58%. The toluene and naphthalene sorption was greater in KC_{HF} where AOM dominated the OM assemblage and phytoclasts contributed only 6%. Sorption was reduced in WF_{HF} where phytoclasts dominated the OM assemblage (61%) and AOM only contributed 7%. From this, it can be concluded that where AOM is the dominant component of the OM, which is clearly evident in KC and OxC, there is a much greater sorption capability than in phytoclast-dominated OM in WF.

The heavy-liquid-extracted OM produced comparatively similar K_{OC} values to the original sediments/clays (Fig. 6) in most cases. This suggests that this method did not alter the sorption capacity. However, the naphthalene K_{OC} value for Oxford Clay heavy-liquid-extracted OM was approximately three times less than the K_{OC} of the original clay: OxC_{HL} (12,213 ml/g) compared to OxC (38,855 ml/g). It is not clear why the heavy-liquid treatment affected naphthalene sorption in this way.

All the HF digestion-enriched OM showed greater K_{OC} values than the heavy-liquid-enriched OM (Fig. 6), except

Fig. 4 Histograms of phytoclast reflectivity from the extracted OM (HF) from the Wittering, Kimmeridge Clay and Oxford Clay formations
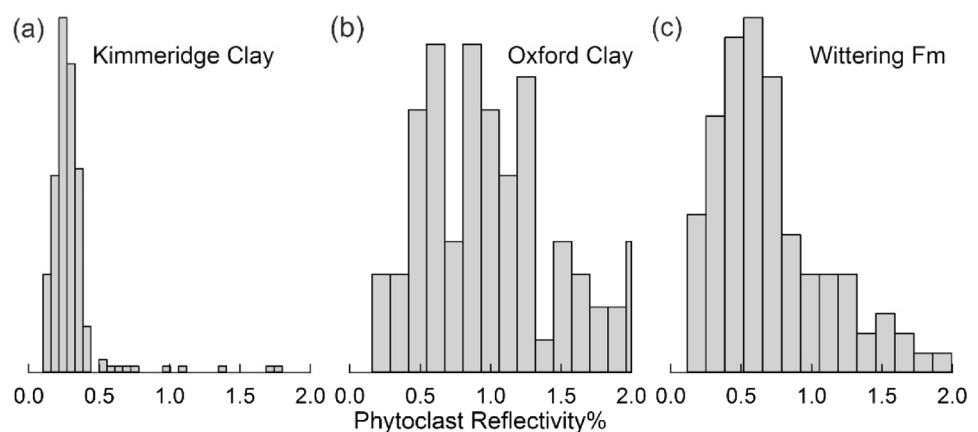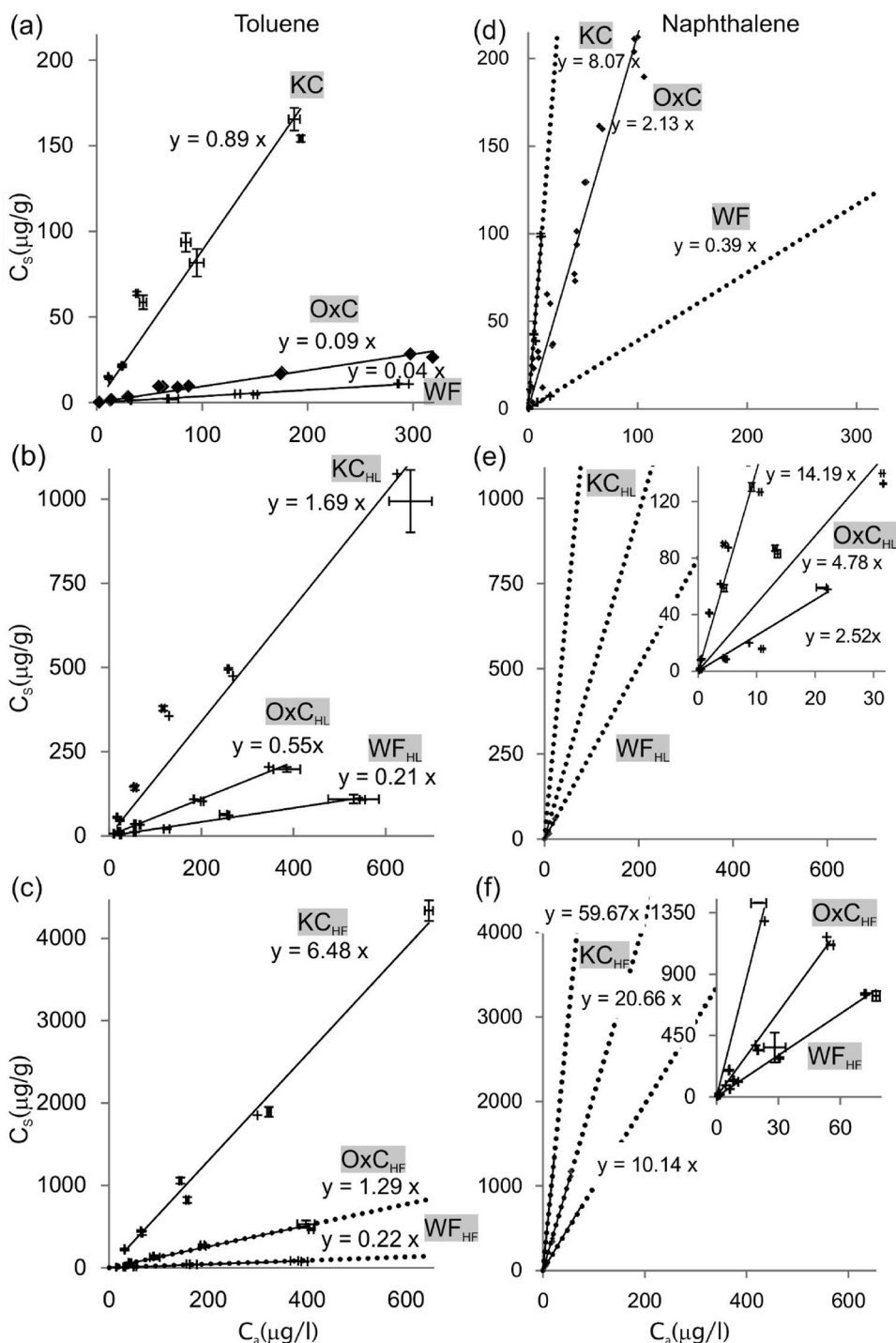
Fig. 5 HOC sorption on Kimmeridge Clay [KC], Oxford Clay [OxC] and the Wittering Formation [WF]; and their corresponding heavy liquid (HL) and hydrofluoric acid (HF) extracted OM. C_s = concentration of HOC sorbed on the solid, C_a = concentration of HOC in solution. The OxC data are from Simoes et al. (2011)

for sorption of toluene on WF where the value was lower. A previous study showed that demineralization of soil altered the functional groups of the humic acids during extraction (Sun et al. 2013). Where K_{OC} values increased after HF digestion could be attributed to the silicate coat on the OM surface (Jin and Zimmerman 2010) being dissolved by the HF. The characteristics of the OM may also have been changed by the HF digestion method, potentially the increasing number and size of the contact area resulting in higher capacity to sorb HOCs.

Table 3 Linear and Freundlich model fits for sorption data for toluene on Kimmeridge Clay [KC], the Oxford Clay [OxC] and the Wittering Fm [WF] and their corresponding heavy liquid (HL) and hydrofluoric acid (HF) extracted OM

Barrier material	Toluene								
	S/L	Linear model		Freundlich model					
	g/l	$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ (mg^{1-n}l^n/g)	N	R^2	Log K_{OC} (ml/g)	K_{OC} (ml/g)	
Kimmeridge Clay									
KC$_{HF}$	0.07	6481	0.99	8423	0.95	0.99	3.98	9565	
KC$_{HL}$	0.50	1695	0.94	4561	0.85	0.97	3.74	5433	
KC	0.42	887	0.93	1724	0.88	0.95	3.61	4069	
Oxford Clay									
OxC$_{HF}$	0.42	1286	0.97	1899	0.94	0.99	3.35	2264	
OxC$_{HL}$	4.17	548	0.99	709	0.95	0.99	3.16	1438	
OxC[a]	13.22	94	0.96	150	0.93	0.99	3.23	1709	
Wittering Fm									
WF$_{HF}$	0.42	219	0.97	380	0.91	0.99	2.62	416	
WF$_{HL}$	4.17	208	0.98	131	1.08	0.99	2.84	697	
WF	44.17	37	0.99	23	1.09	0.96	2.89	771	

[a]Simoes et al. (2011), S/L = solid sorbent and leachate used in the sorption experiment. K_d = The linear sorption coefficient (ml/g), $C_S = K_d C_a$, C_s = Sorbed contaminant concentration (mass of contaminant/mass of solid, mg/g), C_a = dissolved contaminant concentration (mg/l), K_F = Freundlich isotherm equilibrium coefficient for the sorption reaction (mg^{1-n}l^n/g), n = chemical specific constant to take account of heterogeneity, isothermal non-linearity

$C_S = K_F C_a^n$, Log$K_{OC} = K_d / F_{OC}$

Table 4 Linear and Freundlich model fits for sorption data for naphthalene on Kimmeridge Clay [KC], the Oxford Clay [OxC] and the Wittering Fm [WF] and their corresponding heavy liquid (HL) and hydrofluoric acid (HF) extracted OM

Barrier Material		Naphthalene							
		S/L	Linear Model		Freundlich Model				
		g/l	$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ (mg^{1-n}l^n/g)	N	R^2	Log K_{OC} (ml/g)	K_{OC} (ml/g)
Kimmeridge Clay	KC$_{HF}$	0.01	59,670	0.96	25,480	1.23	0.99	4.94	88,061
	KC$_{HL}$	0.25	14,198	0.92	14,664	1.09	0.96	4.66	45,506
	KC	0.50	8073	0.98	7161	1.03	0.97	4.57	37,032
Oxford Clay	OxC$_{HF}$	0.03	20,661	0.99	15,986	1.04	0.96	4.59	39,212
	OxC$_{HL}$	0.17	4653	0.95	5391	1.01	0.97	4.09	12,213
	OxC[a]	4.07	2137	0.95	3142	0.91	0.89	4.59	38,855
Wittering Fm	WF$_{HF}$	0.05	10,134	0.99	10,663	1.01	0.99	4.25	17,838
	WF$_{HL}$	0.50	2525	0.96	2672	0.91	0.98	3.93	8459
	WF	4.17	388	0.96	386	1.09	0.94	3.91	8083

Influence of organic matter characteristics on sorption capacity

The K_{OC} of sorption of naphthalene and toluene decreased with increasing effective polarity (Table 5) which corresponds to trends seen in earlier work (Chen et al. 2005; Guo et al. 2013; Kang and Xing 2005; Wang et al. 2007). It has been suggested that polar functional groups provide areas for water clusters to form through hydrogen bonding, thus causing a steric hindrance to the sorption of HOC molecules in the matrix. (Wang et al. 2007). The correlation coefficient of log K_{OC} plot with PI (Table 5) using OM$_{HF}$ has demonstrated a higher correlation than OM$_{HL}$ implying that the HF extraction method was more efficient than the HL method leading to higher purity OM.

Cornelissen et al. (2005) observed that a high H/O ratio correlates to OM which contains comparatively few oxygen-bearing functional groups, decreased polarity and increased hydrophobicity and high sorption capacity for non-polar

Fig. 6 Log K_{OC} (mg/l) vs TOC% of sorption data for toluene and naphthalene on the Kimmeridge Clay [KC], the Oxford Clay [OxC] and the Wittering Fm [WF] and their corresponding heavy liquid (HL) and hydrofluoric acid (HF) extracted OM
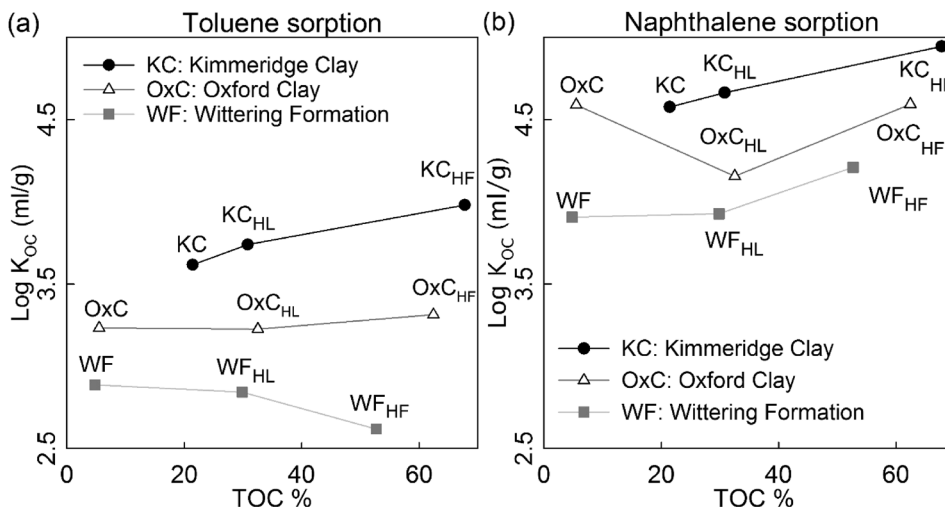
Table 5 Regression equations between Log K_{OC} and polarity index (PI): (O+N)/C atomic ratio, AOM % and phytoclast % of extracted OM*

	Toluene	Naphthalene
OM_{HF}	Log $K_{OC} = -3.38$ PI $+4.24$ $R^2 = 0.93$	Log $K_{OC} = -1.69$ PI $+5.06$ $R^2 = 0.90$
OM_{HL}	Log $K_{OC} = -1.27$ PI $+3.77$ $R^2 = 0.70$	Log $K_{OC} = -0.96$ PI $+4.62$ $R^2 = 0.56$
OM_{HF}	Log $K_{OC} = 1.99$ Log (H/O) $+1.70$ $R^2 = 0.99$	Log $K_{OC} = 1.07$ Log (H/O) $+3.7191$ $R^2 = 0.99$
OM_{HL}	Log $K_{OC} = 1.84$ Log (H/O) $+2.03$ $R^2 = 0.95$	Log $K_{OC} = 1.48$ Log (H/O) $+3.25$ $R^2 = 0.88$
OM_{HF}	Log $K_{OC} = 0.018$ AOM % $+2.450$ $R^2 = 0.97$	Log $K_{OC} = 0.008$ AOM % $+4.1647$ $R^2 = 0.91$
OM_{HL}	Log $K_{OC} = 0.011$ AOM % $+2.706$ $R^2 = 0.85$	Log $K_{OC} = 0.009$ AOM % $+3.800$ $R^2 = 0.73$
OM_{HF}	Log $K_{OC} = -0.021$ phy % $+3.856$ $R^2 = 0.85$	Log $K_{OC} = -0.010$ phy % $+4.86$ $R^2 = 0.79$
OM_{HL}	Log $K_{OC} = -0.012$ phy % $+3.562$ $R^2 = 0.67$	Log $K_{OC} = -0.009$ phy % $+4.463$ $R^2 = 0.53$

*Derived from three sources (Oxford Clay, Kimmeridge Clay and the Wittering Formation that have been treated either by hydrofluoric acid (HF) or heavy- liquid- extraction (HL))

chemicals. Similarly, in this study, log H/O has a strong positive relationship with log K_{OC}.

Karapanagioti and Sabatini (2000) proposed that the K_{OC} of a sediment could be predicted from the sum of sorption capacities of different fractions described by their organic matter subgroup (AOM, phytoclasts, and opaque particles). In their study they measured the K_{OC} of samples at a range of depths in the Canadian River alluvial aquifer material, alluvium and terrace deposits of Quaternary Holocene age. The K_{OC} values for organic subgroups at shallow depths were successfully used to predict K_{OC} values for composite samples from greater depths. Whereas, Karapanagioti and Sabatini (2000) used samples within same layer but from different depths, in this study, sediments with different geological histories were isolated. The isolated KC was predominately AOM (84%) and the isolated WF was

predominantly phytoclasts. The K_{OC} of these isolates was used in the summative model of Karapanagioti and Sabatini (2000) to predict K_{OC} values for OxC. The result considerably over estimated the observed K_{OC} of toluene and naphthalene sorption on this sediment.

Only three different sediments were tested, two of which are the main geological formations used for landfill sites in the southern UK. There appeared to be a positive correlation between the K_{OC} values for these contaminants and the proportion of AOM in the sediment (Table 5), whereas there is a negative correlation with the percentage of phytoclasts. Further tests on a range of sediments with different AOM and phytoclast concentrations would result in greater confidence in the relationship between K_{OC} and these sediment components. However, the application of the model suggests that other factors are influencing HOC sorption. AOM is

morphologically without any obvious internal or external structure that gives a clue as to its origin or properties. It is found within high productivity/preservation environments where organic matter from the otherwise non-resistant cellular material has been preserved under anaerobic or euxinic conditions in a stratified water column than can be a marine or lacustrine environment. Typical high TOC bearing sediment is a distinctive black or brown laminated sediment with a high framboidal pyrite content. The high preserved organic matter often caused by the stratified euxinic water column rises into the photic zone where microbial production thrives, and the euxinic water could rapidly cause mass mortality and preserved the bacterial remains from decomposed. Following deposition AOM forms a non-particulate network within the sediments often making up a significant component of the rock by volume. During burial this AOM can then significantly alter during diagenesis. This suggests, therefore, that sorption of HOCs by sediments of different diagenetic histories cannot be predicted solely on the basis of petrological methods.

Conclusion

In this study, the sorption capacity measured by the linear sorption coefficients (K_d) for toluene and naphthalene on KC were significantly higher than other natural sorbents in the literature. The study used only a low concentration range, reflecting the low concentrations of toluene and naphthalene found in landfill leachate in the UK. Further studies, at higher concentrations would enable direct comparison with literature studies. It is possible that non-linear sorption may be observed in these sediments over a higher concentration range, as has been found in other studies. When K_{OC} values for the different sediments were compared it was found that the AOM content in the KC and OxC strongly influenced sorption capacity, whereas the limited amount of AOM in the WF combined with a greater proportion of phytoclasts showed less sorption capacity. While polarity, H/C and log H/O were also factors affecting HOC sorption, this study demonstrated that the proportion of AOM was also a major influence. However, the proportion of AOM determined by petrological methods could not be used to predict sorption capacities in sediments from different sources. AOM extracted from the KC appeared to have a higher sorption capacity than AOM from the OxC indicating that diagenesis also plays a part. While AOM is considered as the major controlling factor, the degree of diagenesis may also influence on AOM sorption capacity.

In this study, AOM found in KC and OxC resulted in high sorption of toluene and naphthalene. When these materials are used as landfill barriers, there will be a greater retardation of leachate pollutants than might be expected from the OM content of these sediments. This demonstrates the importance of using site-specific data in risk assessments rather than relying on literature values. Petrological determinations of OM were shown to be an indicator of the mechanisms and potential magnitudes of sorption processes for HOCs. However, further work is needed to confirm the relationship between AOM, degree of diagenesis, and sorption of a range of HOCs of differing hydrophobicity to enable landfill operators to base their risk assessments on petrological examination of sediments.

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