Impact of activated carbon on the catabolism of $^{14}$C-phenanthrene in soil

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Abstract:

Activated carbon amendment to contaminated soil has been proposed as an alternative remediation strategy to the management of persistent organic pollutant in soils and sediments. The impact of varying concentrations (0%, 0.01%, 0.1% and 1.0%) of different types of AC on the development of phenanthrene catabolism in soil was investigated. Mineralisation of \(^{14}\)C-phenanthrene was measured using respirometric assays. The increase in concentration of CB4, AQ5000 or CP1 in soil led to an increase in the length of the lag phases. Statistical analyses showed that the addition of increasing concentrations of AC to the soil significantly reduced (P < 0.05) the extent of \(^{14}\)C-phenanthrene. For example, for CB4-, AQ5000- and CP1-amended soils, the overall extent of \(^{14}\)C-phenanthrene mineralisation reduced from 43.1% to 3.28%, 36.9% to 0.81% and 39.6% to 0.96%, respectively, after 120 d incubation. This study shows that the properties of AC, such as surface area, pore volume and particle size, are important factors in controlling the kinetics of \(^{14}\)C-phenanthrene mineralisation in soil.

Keywords: Catabolism; \(^{14}\)C-Phenanthrene mineralisation; Activated carbon; Soil
1. Introduction

The growing need for industrialisation based upon petroleum products has turned polycyclic aromatic hydrocarbons (PAHs) into ubiquitous contaminants in the environment. The physico-chemical characteristics of PAHs include low aqueous solubility, hydrophobicity, lipophilicity, nonpolarity and structural stability, which are responsible for their strong sorption to organic matter in soil; thereby, making the compounds less bioavailable to soil microorganisms. This ultimately leads to their persistence, as a result of diminished mobility and biodegradation.

Black carbon (BC) is a general term used to describe various forms of carbonaceous geosorbents, such as activated carbon (AC), charcoal, soot, ash, coke and char. They are widely present in the soil environment, and enhance sorption of PAHs in soils and sediments. AC is a manufactured type of BC, produced from coal peat or coconut shells, by incomplete combustion followed by either thermal, chemical or steam activation. AC possess high porosity, high specific surface area, strong hydrophobicity and a high degree of surface reactivity, making it a versatile sorbent. The strong interaction between hydrophobic organic contaminants (HOCs) and AC can greatly reduce the mobility, bioaccessibility and environmental risk of HOCs in soils and sediments, thus lowering the actual risk to terrestrial and marine organisms. Oyelami et al. reported that the addition of 1% AC to soil reduced uptake of 14C-phenanthrene in E. fetida over 100 d.

Hence, AC amendment has been proposed as a cost effective remediation technique that is less invasive than many other reclamation techniques, since AC amendment does not require digging large volumes of soil before washing and/or incineration. ACs differ in their characteristics, such as particle size, porosity, surface area and composition; it is essential to identify the affinity parameters for that may affect enhanced sequestration of HOCs to AC. Increasing soil-HOC contact time can lead to a reduction in bioavailability, this time-
dependent condition of reduced biological availability is termed ‘ageing’ \(^{16}\), and is one of the limitations for the adoption of biological approaches for the remediation of contaminated soils \(^{17}\).

Currently, there is considerable interest in the impact of BC on the bioaccessibility and reduction of risk on contaminants in soil. Therefore, the aims of this study were to (i) investigate the impact of three different AC with different properties and particle sizes on the mineralisation of \(^{14}\)C-phenanthrene in soil with varying concentrations (0, 0.01, 0.1 and 1\%); (ii) investigate the effect of prior exposure of indigenous microorganisms to AC and \(^{12}\)C-phenanthrene on catabolic development after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time.

2. Materials and methods

2.1. Materials

Non-labelled phenanthrene (> 96\%) was obtained from Sigma Aldrich, UK, and its radiolabelled analogue 9-\(^{14}\)C-phenanthrene (radio-chemical purity > 96\%, specific activity 55 mCi mmol\(^{-1}\)) was obtained from American Radiolabeled Chemical Inc. (ARC). Goldstar multipurpose liquid scintillation fluid (LSC) was obtained from Meridian, UK. Sodium hydroxide (NaOH) used for CO\(_2\) traps, and chemicals for minimal basal salts were purchased from Fisher-Scientific, UK. Activated carbon; Aquasorb CP1 PAC-F (hereinafter referred to as CP1), Aquasorb CB4 PAC-S (hereinafter referred to as CB4) and Aquasorb 5000 PAC-S (hereinafter referred to as AQ5000) were purchased from Jacobi carbons, Sri Lanka. The properties are listed in Table 1.

2.2. Soil and soil spiking
A pristine agricultural soil (Dystric Cambisol) was collected from a depth of 5-20 cm, from Myerscough College, Preston, UK. Soil physico-chemical properties are as follows: pH 6.5, organic matter 2.7%, sand 60.4%, silt 20%, and clay 19.5%. The air-dried soil was sieved with a 2 mm sieve to remove roots and stones, and then stored at 4 °C until ready for use. When ready for use, soil was rehydrated with deionised water back to original water holding capacity (WHC). A third of whole soil was first spiked with 12C-phenanthrene prepared acetone to achieve a concentration of 50 mg kg⁻¹, then mixed with an stainless steel spoon for 3 min followed by a period of venting (1–2 h). Afterwards, the amended soil was mixed with the remaining unsiked soil, following the method reported by Doick, et al. Aliquots of soil were then mixed with different concentrations of (0, 0.01, 0.1 and 1%) of CB4, AQ5000 and CP1. Soil-AC mixtures were then sealed in amber glass jars (in triplicate per treatment), left to age in the dark at 20 ± 2 °C and analysed at 1, 20, 40, 60 and 120 d. At each time point, freshly prepared 12C/14C-phenanthrene (42 Bq g⁻¹ soil) was added to each of the previously aged soils, and respirometry was carried out for 18 d. Blank soils with neither phenanthrene nor AC were also prepared.

2.3. Mineralisation of 14C-phenanthrene in soil by indigenous microorganisms

14C-Phenanthrene mineralisation was assessed using the method of Reid, et al. after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time. The evolution of 14CO₂ was determined using modified 250 ml Erlenmeyer flasks. Each respirometer incorporated a Teflon-lined screw cap and a CO₂ trap containing 1 M NaOH (1 ml) within a suspended 7 ml glass scintillation vial. Respirometers were prepared in triplicate, with 10 ± 0.2 g soil (w/w) and 30 ml sterilised minimal basal salts medium (MBS) to give a soil to liquid ratio of 1:3, following the method reported by Doick and Semple. The respirometric flasks were placed securely on an orbital shaker (IKA Laborteknik KS501 digital), incubated at 20 ± 2 °C and shaken at
100 rpm for 18 days to ensure adequate mixing of the slurry over the sampling period. The 
14C-activity in the 14CO2 traps was assessed after every 24 hours by replacing the NaOH traps 
and adding Goldstar liquid scintillation fluid (5 ml) to each spent 14CO2 trap. After storage in 
darkness overnight, trapped 14C-activity was quantified using a Canberra Packard Tricarb 
2250CA liquid scintillation analyser, using standard protocols for counting and automatic 
quench correction. An analytical blank (containing no 14C-phenanthrene) determined the 
level of background activity. The length of the lag phase (defined as the time taken for 
mineralisation to reach 5%), the maximum rate and overall extent of 14C-phenanthrene 
mineralisation were calculated over the 18 days 20.

2.4. Analysis of AC
Nuclear magnetic resonance cryoporometry (NMR-C) was used to determine the total pore 
volume and liquid per unit mass of the different AC. It is a method suitable for measuring 
pore sizes and pore size distributions. NMR-C is based on the technique of freezing a liquid 
in the pores and measuring the melting temperature by NMR. Since the melting point is 
depressed for crystals of small size, the melting point depression gives a measurement of pore 
size. The method was described by Mitchell et al 21.

2.5. Statistical Analysis
Following blank correction, statistical analysis of the results from mineralisation assays was 
accomplished by using the Sigma Stat for Windows ® (Version 3.5, SPSS Inc.). All graphs 
were presented using SigmaPlot for Windows ® (Version 10.0, SPSS Inc.). Statistical 
significance of the addition of the different types of AC, at different concentrations and soil 
contact time was determined using analysis of variance (ANOVA) followed by Tukey test at 
the 95% confidence level (P < 0.05) to assess significant differences.
3. Results

3.1. Properties of AC

The porosity and pore diameter of each AC is illustrated in Table 1. Analysis of AC showed that CP1 had a wide range of distribution from the micropore to the mesopore range, and also had a high pore volume over the distribution, while CB4 and AQ500 showed little porosity at large pore sizes. However, AQ 5000 displayed a slight but significant porosity in the 1 µm range, with a larger peak at about 10 nm. The similarity of the pore size distribution for CB4 and AQ5000, over the range 5 nm to 20 nm can be seen (micropores), but AQ5000 having a significant peak at 20 nm (larger pore volume). CP1 on the other hand showed more porosity over the 30 nm to 800 nm range, with a peak at about 200 nm (micro-macroporosity) (Figure 1).

3.2. The mineralisation of $^{14}$C-phenanthrene on AC-amended soil

The catabolism of $^{14}$C-phenanthrene to $^{14}$CO$_2$ was monitored for an incubation period of 18 days in soils spiked with various concentrations (0, 0.01, 0.1 and 1%) of CB4, AQ 5000 or CP1, at 1, 20, 40, 60 and 120 d soil-phenanthrene contact time (Figures 2 to 4). The impact of the ACs focused on changes in the lag phase, rates and extent of $^{14}$C-PAH mineralisation.

3.2.1. Lag phase

The lengths of the lag phases varied over the course of the experiment and were dependent upon the concentration, and the type of AC used. Overall, the shortest lag phases were seen in the control soils while the longest were measured in soils amended with 1% AC (P < 0.05). For example, at 1 d, the lag phases for 0% and 1% were 4.56 d and 7.71 d, respectively, in CB4-amended soils. For AQ5000-amended soils, the lag phase was 13.1 d, while CP1-
amended soil was not measurable for 1% amendment (Tables 2 to 4). However, there were no
significant differences (P > 0.05) in the length of the lag phases of 0.01% and 0.1% AC-
amended soils, when compared to control soils at 20-120 d (Tables 2 to 4). An increase in
contact time revealed that the lag phases were shorter (P < 0.05) after a 100 d soil contact
time, compared to 1 d. However, no difference (P > 0.05) was observed at consecutive time-
points after 20 d (Table 2). A comparison between CB4-, AQ5000- and CP1-amended soils
revealed that at concentrations less than 1%, CB4-amended soils consistently had shorter (P <
0.05) lag phases in comparison to AQ5000- and CP1-amended soils, respectively. For
example, in 0.1% CB4-, AQ5000-, and CP1-amended soils, at 20 d, the lag phases were 3.72
d, 5.13 d and 6.69 d, respectively (Tables 2 to 4). Furthermore, at concentrations of 0.1%, lag
phases were shorter (P < 0.05) in AQ5000-, compared to CP1-amended soils.

3.2.2. Maximum rates of $^{14}$C-phenanthrene mineralisation

Overall, maximum rates of $^{14}$C-phenanthrene mineralisation were consistently observed to be
highest in control soils, and lowest in 1% AC-amended soils (Figures 2 to 4; Tables 2 to 4).
The maximum rates of mineralisation decreased (P < 0.05) with an increase in the
concentration from, 0% to 1%. At 1 d, the maximum rates of $^{14}$C-phenanthrene mineralisation
reduced from 0.80% h$^{-1}$ to 0.02 % h$^{-1}$ in AC-amended soils (Tables 2 to 4). With an increase
in soil-phenanthrene contact time, the maximum rates of $^{14}$C-phenanthrene mineralisation
reduced with an increase in contact time after 20 d soil-contact time; this was found to be
significant (P < 0.05) at consecutive time points for CB4-, AQ5000- and CP1-amended soils
(Tables 2 to 4). CB4-amended soils had the greatest maximum rates of $^{14}$C-phenanthrene
mineralisation compared to AQ50000-and CP1-amended soils, which were similar (Table 2
to 4).
3.2.3. Overall extents of $^{14}$C-phenanthrene mineralisation in soil

Overall, the extents of $^{14}$C-phenanthrene mineralisation were observed to decline with an increase in concentration of AC (Figures 2 to 4; Tables 2 to 4). Generally, control soils had the highest extents of $^{14}$C-phenanthrene mineralisation. At 1 d contact time in 0, 0.01, 0.1 and 1% CB4-amended soils, extents of $^{14}$C-phenanthrene mineralisation were 54.1%, 43.1%, 22.8% and 12.2%, respectively (Figure 2; Table 2). An increase in soil-phenanthrene contact time resulted in significant reductions (P < 0.05) in the overall extents of $^{14}$C-phenanthrene mineralisation. The extents of $^{14}$C-phenanthrene mineralisation were higher after 1 d (P < 0.05); however, no statistical significance (P > 0.05) was observed at other time points in AC-amended soils (Figures 2 to 4). At all time-points, significantly greater (P < 0.05) extents of $^{14}$C-phenanthrene were mineralised, in CB4-, than in AQ5000- and CP1-amended soils, at concentrations greater than 0.01% (Figures 2 to 4; Tables 2 to 4). At 0.1% CB4-, AQ5000-, and CP1-amended soils, at 20 d, total extents of $^{14}$C-phenanthrene mineralisation were 36.5%, 24.31% and 15.3%, respectively. A comparison CB4, AQ5000 and CP1-amended soils showed that CB4-amended soils generally had the highest extents of $^{14}$C-phenanthrene mineralisation; this was found to be statistically significant (P < 0.001), when compared to AQ5000- and CP1-amended soils (Figures 2 to 4; Tables 2 to 4). However, $^{14}$C-phenanthrene mineralisation rates of the AQ5000- and CP1-amended soils were similar (Figures 2 to 4; Tables 2 to 4).

4. Discussion

4.1. Effect of AC addition on $^{14}$C-phenanthrene mineralisation in soil

This study investigated the impact of AC on the catabolism of $^{14}$C-phenanthrene in soil. The results obtained showed that there was an increase in lag phase, together with a reduction in
maximum rates and overall extents of $^{14}$C-phenanthrene mineralisation, with an increase in
the concentration of AC. This is consistent with results from previous studies which have
shown that an increase in AC concentration in soils may extensively reduce the rate at which
the catabolic activity of indigenous microorganisms develop in contaminated soils
consequently inhibiting biodegradation; although that study was carried out using a single
type of AC. In this study, 1% concentration impacted upon the development in catabolism as
seen in the lag phases, which was generally immeasurable. The bioavailability (maximum
rates) and bioaccessibility (overall extents) of $^{14}$C-phenanthrene were also severely reduced
in the presence of high concentrations (1%) of CB4, AQ5000 and CP1, respectively. The
concentration of AC also played an important role on the bioaccessibility of $^{14}$C-
phenanthrene, with the higher concentrations providing more sorption sites, and thus
decreasing the bioavailable and bioaccessible fractions. This indicates that the increase in
availability of active sites for adsorption resulting from the increased dose of the AC affected
the catabolism of $^{14}$C-phenanthrene. This is consistent with previous studies on the effect of
adsorbent dose on bioavailability of HOCs in soils. Rhodes, et al. determined that
the increase in lag phase and decrease in the maximum rates and extents of $^{14}$C-phenanthrene
mineralisation found with soils amended with 1% and 5% AC may be due to improved
phenanthrene sorption to AC leading to a reduction in the bioaccessible fraction, and thus a
decrease in $^{14}$C-phenanthrene mineralisation. Sorption of PAHs to AC has previously been
reported to limit mass transfer or reduce accessibility to microorganisms; hence, the
reduced extent of mineralisation $^{14}$C-phenanthrene in the present study after addition with
high concentrations of AC.

An increase in soil-phenanthrene contact time led to a reduction in the rates and extents of
$^{14}$C-phenanthrene mineralisation, although it was not significant in the lower concentrations
of AC-amended soils. This is consistent with previous studies that showed that $^{14}$C-
phenanthrene mineralisation generally decreased with increasing soil-phenanthrene contact time, in the presence of BC. A reduction in the lengths of the lag phase after 120 d could indicate an adaptation of the indigenous microflora to the presence of AC. However, the decline observed in rates and extents of 14C-phenanthrene proves otherwise. Therefore, the decline may be due to the decrease in the catabolic potential of the degrading microbial population, as a result of the presence of AC in soil. For example, Stroud et al. demonstrated that the reduction in overall extent of mineralisation may be as a result of a decrease in the catabolic potential of the degrading microbial population. In this study, it was observed that despite the addition of fresh 14C-phenanthrene at each time-point, the rates and extents of mineralisation declined subsequently. This is due to the effects of sorption of AC, as described earlier, which indicates that sorption is time-dependent. The very slow rates of desorption allow for a consistently increasing sorbed fraction over the 120 d AC-soil contact time, similar to results obtained by. This ultimately results in the development of a relatively large, recalcitrant and non-bioaccessible fraction. Hence, increasing AC concentration provides additional sites for phenanthrene adsorption. Despite decreases in the length of the lag phases in this study, indigenous soil populations did not appear to fully adapt to the addition of 14C-phenanthrene in the presence of AC.

4.2. Effect of AC type on 14C-phenanthrene mineralisation in soil

All of the types of AC used in this study were effective in reducing the bioavailability and bioaccessibility of 14C-phenanthrene in soil, with the reduction efficiencies trending in the following order; CP1 > AQ5000 > CB4. Analysis of the data suggested that there was a relation between the AC type, and its impact on 14C-phenanthrene mineralisation in soil. In this study, CB4-amended soil consistently displayed shorter lag phases, together with greater maximum rates and extents of 14C-phenanthrene mineralisation, compared to AQ5000- and
CP1-amended soils, respectively. Although the mechanism of sorption was not investigated, the decline in $^{14}$C-phenanthrene mineralisation may be attributed to sorption of AC to phenanthrene, as shown in previous studies $^{12,30}$. The higher values observed for maximum rates and overall extents of $^{14}$C-phenanthrene mineralisation in CB4-amended soils, in comparison to AQ5000- and CP1-amended soils, respectively. This indicated that the adsorption capacity of CB4 towards $^{14}$C-phenanthrene was lower than that of AQ5000 and CP1, as observed from the values of the SSA for each AC. The surface area of CP1 (1106 m$^2$ g$^{-1}$) and AQ5000 (1249 m$^2$ g$^{-1}$) were both higher than of CB4 (653 m$^2$ g$^{-1}$). This is in agreement with studies that showed that sorption capacities positively correlate with the SSA of a sorbent $^{12,23,26}$. This indicates that the characteristic of coconut shell based carbon, which has a predominance of pores in the micropore-mesopore range, accounts for 95% of the available internal surface area. Therefore, CP1 has the characteristics of being more porous than that of the AQ5000 and CB4.

Overall, AQ5000- and CP1-amended soils mineralised $^{14}$C-phenanthrene to almost identical levels. However, AQ5000-amended soils had slightly higher extents of $^{14}$C-phenanthrene mineralised than CP1-amended soils, despite AQ5000 having higher surface area. This may be explained by the differences in the pore volume and pore size distribution of both adsorbents. This agrees with earlier findings that pore volume and pore distribution is one of the most important parameters determining sorption $^{24,31}$. Jusoh et al. $^9$ reported that a larger pore volume would contribute to the higher adsorption capacity. Additionally, CP1 has a wide distribution of pore sizes. The pore size distribution has a role to play, with the micropores constituting the majority of the specific surface area or adsorption sites, whereas macropores and mesopores facilitate the mass transfer of chemicals into AC adsorption sites $^{31}$. When comparing the effectiveness of all sorbents, both sorption capacity (SSA or the abundance of micropores) and the mass transfer kinetics impact the uptake of phenanthrene.
CP1 has a higher pore volume and pore width, ranging from micropores to the macropore, compared to AQ5000. The higher sorption of CP1 than AQ5000 may be due to the higher pore volume and the narrower pores of CP1 in the micropore range. Therefore, the transfer of \(^{14}\)C-phenanthrene from accessible soil-AC compartments (macropores) into less accessible compartments (mesopores and micropores), results in a reduction in bioaccessibility, hence a reduction in overall extent of \(^{14}\)C-phenanthrene mineralisation. This implies that the entrapped phenanthrene within higher concentrations of AC will not be bioaccessible over a long period of time due to strong sorption \(^{12,32}\).

The reduction in overall extent of \(^{14}\)C-phenanthrene, observed with CP1, AQ5000 and CB4, may be attributable to differences in particle sizes instead of pore size. Both AQ5000 and CB4 had the same nominal particle sizes (65 - 85 \(\mu m\)) but different pore size distributions.

To ascertain whether the particle size of the sorbents plays a major role in determining the effectiveness of each AC in mineralisation of \(^{14}\)C-phenanthrene mineralisation, the particle sizes were studied. CP1 had the largest particle size of 95 \(\mu m\), AQ5000 had 84.6 \(\mu m\), while the smallest was CB4 with 74.8 \(\mu m\). It was observed that the result obtained also showed that the particle size of AC affects the extent of adsorption. The AC with the largest particle size (CP1) had the lowest extent of \(^{14}\)C-phenanthrene mineralisation, while that with the smallest particle size (CB4) had higher extents of \(^{14}\)C-phenanthrene mineralisation. This implies that reducing the particle size of CB4 increased the mineralisation of \(^{14}\)C-phenanthrene, which suggests that CB4 a lesser efficiency in phenanthrene adsorption. This is similar to results obtained from previous studies \(^{10,23}\).

5. CONCLUSION

The results from this study showed that the application of high concentrations of AC severely impacted the development of \(^{14}\)C-phenanthrene catabolism in the soil. One of the more
significant findings to emerge from this study is that the type of AC is important in remediation studies and plays a key role in bioavailability of organic contaminants to microorganisms. A good understanding of the impact of surface area, pore volume and pore size distribution on competitive adsorption is required as a basis for selecting the best type of AC and applying it in an optimal way. Since each AC type differs in its characteristics, it is highly relevant to identify the affinity parameters for \textit{in situ} sorption of PAHs to AC in order to be able to design and evaluate applications of AC in reducing risk. The better performance of CP1 in this study may be due to its higher porosity and wider pore size distribution which made it have a better adsorption of phenanthrene. Effectiveness of treatment increases with contact time and varies for different forms of activated carbon with similar surface areas. The importance and usefulness of AC should be considered in risk assessment and remediation of contaminated soils.
References


Table 1: Properties of AC used in this study.

Table 2: Lag phases (d), maximum rates (% h⁻¹) and overall extents (%) of ¹⁴C-phenanthrene mineralisation in Myerscough soil amended with CB4 after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time. Values are mean ± standard error (n = 3).

Table 3: Lag phases (d), maximum rates (% h⁻¹) and overall extents (%) of ¹⁴C-phenanthrene mineralisation in Myerscough soil amended with AQ5000 after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time. Values are mean ± standard error (n = 3).

Table 4: Lag phases (d), maximum rates (% h⁻¹) and overall extents (%) of ¹⁴C-phenanthrene mineralisation in Myerscough soil amended with CP1 after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time. Values are mean ± standard error (n = 3).
List of figure caption

Figure 1: Pore distribution of AC

Figure 2: Catabolism of $^{14}$C-phenanthrene by indigenous microorganisms in soil after addition of CB4 at contact time: (A) 1 d (B) 20 d (C) 40 d (D) 60 d and (E) 120 d. Error bars are SEM (n = 3). Legend key: 0% (●), 0.01% (○), 0.1% (▼) and 1% (Δ).

Figure 3: Catabolism of $^{14}$C-phenanthrene by indigenous microorganisms in soil after addition of AQ5000 at contact time: (A) 1 d (B) 20 d (C) 40 d (D) 60 d and (E) 120 d. Error bars are SEM (n = 3). Legend key: 0% (●), 0.01% (○), 0.1% (▼) and 1% (Δ).

Figure 4: Catabolism of $^{14}$C-phenanthrene by indigenous microorganisms in soil after addition of CP1 at contact time: (A) 1 d (B) 20 d (C) 40 d (D) 60 d and (E) 120 d. Error bars are SEM (n = 3). Legend key: 0% (●), 0.01% (○), 0.1% (▼) and 1% (Δ).
Table 1.

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* refers to properties obtained by NMR-cryoporometry.
Table 2:

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<td>37.9 ± 1.32</td>
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* Mineralisation did not exceed 5% over the incubation period
Table 3:

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<tr>
<th>Ageing (d)</th>
<th>Conc (%)</th>
<th>Lag time (d)</th>
<th>Max rate (% h⁻¹)</th>
<th>Extent (%)</th>
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</tbody>
</table>

* Mineralisation did not exceed 5% over the incubation period
### Table 4: 

<table>
<thead>
<tr>
<th>Ageing (d)</th>
<th>Conc (%)</th>
<th>Lag time (d)</th>
<th>Max rate (% h(^{-1}))</th>
<th>Extent (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>0.96 ± 0.13</td>
</tr>
</tbody>
</table>

* Mineralisation did not exceed 5% over the incubation period
Figure 1

Porosity [µl. Å⁻¹. g⁻¹]

Pore Diameter

- CP1
- AQ5000
- CB4
Figure 2

- A: 1 d
- B: 20 d
- C: 40 d
- D: 60 d
- E: 120 d

% 14C-Phenanthrene mineralised (%)

Time (d)

0 2 4 6 8 10 12 14 16 18 20
Figure 3

A 1 d  B 20 d  
C 40 d  D 60 d  
E 120 d
Figure 4

A 1 d  B 20 d  C 40 d  D 60 d  E 120 d

% 14C-Phenanthrene mineralised (%) vs Time (d)