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

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18 **Abstract:**

19 Activated carbon amendment to contaminated soil has been proposed as an alternative
20 remediation strategy to the management of persistent organic pollutant in soils and sediments.
21 The impact of varying concentrations (0%, 0.01%, 0.1% and 1.0%) of different types of AC
22 on the development of phenanthrene catabolism in soil was investigated. Mineralisation of
23 ¹⁴C-phenanthrene was measured using respirometric assays. The increase in concentration of
24 CB4, AQ5000 or CP1 in soil led to an increase in the length of the lag phases. Statistical
25 analyses showed that the addition of increasing concentrations of AC to the soil significantly
26 reduced ($P < 0.05$) the extent of ¹⁴C-phenanthrene. For example, for CB4-, AQ5000- and
27 CP1-amended soils, the overall extent of ¹⁴C-phenanthrene mineralisation reduced from
28 43.1% to 3.28%, 36.9% to 0.81% and 39.6% to 0.96%, respectively, after 120 d incubation.
29 This study shows that the properties of AC, such as surface area, pore volume and particle
30 size, are important factors in controlling the kinetics of ¹⁴C-phenanthrene mineralisation in
31 soil.

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36 **Keywords:** Catabolism; ¹⁴C-Phenanthrene mineralisation; Activated carbon; Soil

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40 **1. Introduction**

41 The growing need for industrialisation based upon petroleum products has turned polycyclic
42 aromatic hydrocarbons (PAHs) into ubiquitous contaminants in the environment ¹. The
43 physico-chemical characteristics of PAHs include low aqueous solubility, hydrophobicity,
44 lipophilicity, nonpolarity and structural stability ², which are responsible for their strong
45 sorption to organic matter in soil; thereby, making the compounds less bioavailable to soil
46 microorganisms. This ultimately leads to their persistence, as a result of diminished mobility
47 and biodegradation ^{2,3}.

48 Black carbon (BC) is a general term used to describe various forms of carbonaceous
49 geosorbents, such as activated carbon (AC), charcoal, soot, ash, coke and char ^{4,5}. They are
50 widely present in the soil environment, and enhance sorption of PAHs in soils and sediments
51 ^{6,7}. AC is a manufactured type of BC, produced from coal peat or coconut shells, by
52 incomplete combustion followed by either thermal, chemical or steam activation ^{8,9}. AC
53 possess high porosity, high specific surface area, strong hydrophobicity and a high degree of
54 surface reactivity, making it a versatile sorbent ¹⁰. The strong interaction between
55 hydrophobic organic contaminants (HOCs) and AC can greatly reduce the mobility,
56 bioaccessibility and environmental risk of HOCs in soils and sediments, thus lowering the
57 actual risk to terrestrial and marine organisms ^{11,12}. Oyelami et al. ¹² reported that the addition
58 of 1% AC to soil reduced uptake of ¹⁴C-phenanthrene in *E. fetida* over 100 d.
59 Hence, AC amendment has been proposed as a cost effective remediation technique that is
60 less invasive than many other reclamation techniques, since AC amendment does not require
61 digging large volumes of soil before washing and/or incineration ¹³. ACs differ in their
62 characteristics, such as particle size, porosity, surface area and composition; it is essential to
63 identify the affinity parameters for that may affect enhanced sequestration of HOCs to AC ¹⁴,
64 ¹⁵. Increasing soil-HOC contact time can lead to a reduction in bioavailability, this time-

65 dependent condition of reduced biological availability is termed 'ageing'¹⁶, and is one of the
66 limitations for the adoption of biological approaches for the remediation of contaminated
67 soils¹⁷.

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

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76 **2. Materials and methods**

77 *2.1. Materials*

78 Non-labelled phenanthrene (> 96%) was obtained from Sigma Aldrich, UK, and its
79 radiolabelled analogue 9-¹⁴C-phenanthrene (radio-chemical purity > 96%, specific activity 55
80 mCi mmol⁻¹) was obtained from American Radiolabeled Chemical Inc. (ARC). Goldstar
81 multipurpose liquid scintillation fluid (LSC) was obtained from Meridian, UK. Sodium
82 hydroxide (NaOH) used for CO₂ traps, and chemicals for minimal basal salts were purchased
83 from Fisher-Scientific, UK. Activated carbon; Aquasorb CP1 PAC-F (hereinafter referred to
84 as CP1), Aquasorb CB4 PAC-S (hereinafter referred to as CB4) and Aquasorb 5000 PAC-S
85 (hereinafter referred to as AQ5000) were purchased from Jacobi carbons, Sri Lanka. The
86 properties are listed in Table 1.

87

88 *2.2. Soil and soil spiking*

89 A pristine agricultural soil (Dystric Cambisol) was collected from a depth of 5-20 cm, from
90 Myerscough College, Preston, UK. Soil physico-chemical properties are as follows: pH 6.5,
91 organic matter 2.7%, sand 60.4%, silt 20%, and clay 19.5%. The air-dried soil was sieved
92 with a 2 mm sieve to remove roots and stones, and then stored at 4 °C until ready for use.
93 When ready for use, soil was rehydrated with deionised water back to original water holding
94 capacity (WHC). A third of whole soil was first spiked with ¹²C-phenanthrene prepared
95 acetone to achieve a concentration of 50 mg kg⁻¹, then mixed with an stainless steel spoon for
96 3 min followed by a period of venting (1–2 h). Afterwards, the amended soil was mixed with
97 the remaining unspiked soil, following the method reported by Doick, et al. ¹⁸. Aliquots of
98 soil were then mixed with different concentrations of (0, 0.01, 0.1 and 1%) of CB4, AQ5000
99 and CP1. Soil-AC mixtures were then sealed in amber glass jars (in triplicate per treatment),
100 left to age in the dark at 20 ± 2 °C and analysed at 1, 20, 40, 60 and 120 d. At each time
101 point, freshly prepared ¹²C/¹⁴C-phenanthrene (42 Bq g⁻¹ soil) was added to each of the
102 previously aged soils, and respirometry was carried out for 18 d. Blank soils with neither
103 phenanthrene nor AC were also prepared.

104

105 2.3. Mineralisation of ¹⁴C-phenanthrene in soil by indigenous microorganisms

106 ¹⁴C-Phenanthrene mineralisation was assessed using the method of Reid, et al. ¹⁹, after 1, 20,
107 40, 60 and 120 d soil-phenanthrene contact time. The evolution of ¹⁴CO₂ was determined
108 using modified 250 ml Erlenmeyer flasks ¹⁹. Each respirometer incorporated a Teflon-lined
109 screw cap and a CO₂ trap containing 1 M NaOH (1 ml) within a suspended 7 ml glass
110 scintillation vial. Respirometers were prepared in triplicate, with 10 ± 0.2 g soil (w/w) and 30
111 ml sterilised minimal basal salts medium (MBS) to give a soil to liquid ratio of 1:3, following
112 the method reported by Doick and Semple ³. The respirometric flasks were placed securely
113 on an orbital shaker (IKA Labortechnik KS501 digital), incubated at 20 ± 2 °C and shaken at

114 100 rpm for 18 days to ensure adequate mixing of the slurry over the sampling period. The
115 ^{14}C -activity in the $^{14}\text{CO}_2$ traps was assessed after every 24 hours by replacing the NaOH traps
116 and adding Goldstar liquid scintillation fluid (5 ml) to each spent $^{14}\text{CO}_2$ trap. After storage in
117 darkness overnight, trapped ^{14}C -activity was quantified using a Canberra Packard Tricarb
118 2250CA liquid scintillation analyser, using standard protocols for counting and automatic
119 quench correction. An analytical blank (containing no ^{14}C -phenanthrene) determined the
120 level of background activity. The length of the lag phase (defined as the time taken for
121 mineralisation to reach 5%), the maximum rate and overall extent of ^{14}C -phenanthrene
122 mineralisation were calculated over the 18 days²⁰.

123

124 *2.4. Analysis of AC*

125 Nuclear magnetic resonance cryoporometry (NMR-C) was used to determine the total pore
126 volume and liquid per unit mass of the different AC. It is a method suitable for measuring
127 pore sizes and pore size distributions. NMR-C is based on the technique of freezing a liquid
128 in the pores and measuring the melting temperature by NMR. Since the melting point is
129 depressed for crystals of small size, the melting point depression gives a measurement of pore
130 size. The method was described by Mitchell et al²¹.

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132 *2.5. Statistical Analysis*

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

139

140 **3. Results**

141 *3.1. Properties of AC*

142 The porosity and pore diameter of each AC is illustrated in Table 1. Analysis of AC showed
143 that CP1 had a wide range of distribution from the micropore to the mesopore range, and also
144 had a high pore volume over the distribution, while CB4 and AQ500 showed little porosity at
145 large pore sizes. However, AQ 5000 displayed a slight but significant porosity in the 1 µm
146 range, with a larger peak at about 10 nm. The similarity of the pore size distribution for CB4
147 and AQ5000, over the range 5 nm to 20 nm can be seen (micropores), but AQ5000 having a
148 significant peak at 20 nm (larger pore volume). CP1 on the other hand showed more porosity
149 over the 30 nm to 800 nm range, with a peak at about 200 nm (micro-macroporosity) (Figure
150 1).

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152 *3.2. The mineralisation of ¹⁴C-phenanthrene on AC-amended soil*

153 The catabolism of ¹⁴C-phenanthrene to ¹⁴CO₂ was monitored for an incubation period of 18
154 days in soils spiked with various concentrations (0, 0.01, 0.1 and 1%) of CB4, AQ 5000 or
155 CP1, at 1, 20, 40, 60 and 120 d soil-phenanthrene contact time (Figures 2 to 4). The impact of
156 the ACs focused on changes in the lag phase, rates and extent of ¹⁴C-PAH mineralisation.

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158 *3.2.1. Lag phase*

159 The lengths of the lag phases varied over the course of the experiment and were dependent
160 upon the concentration, and the type of AC used. Overall, the shortest lag phases were seen in
161 the control soils while the longest were measured in soils amended with 1% AC (P < 0.05).
162 For example, at 1 d, the lag phases for 0% and 1% were 4.56 d and 7.71 d, respectively, in
163 CB4-amended soils. For AQ5000-amended soils, the lag phase was 13.1 d, while CP1-

164 amended soil was not measurable for 1% amendment (Tables 2 to 4). However, there were no
165 significant differences ($P > 0.05$) in the length of the lag phases of 0.01% and 0.1% AC-
166 amended soils, when compared to control soils at 20-120 d (Tables 2 to 4). An increase in
167 contact time revealed that the lag phases were shorter ($P < 0.05$) after a 100 d soil contact
168 time, compared to 1 d. However, no difference ($P > 0.05$) was observed at consecutive time-
169 points after 20 d (Table 2). A comparison between CB4-, AQ5000- and CP1-amended soils
170 revealed that at concentrations less than 1%, CB4-amended soils consistently had shorter ($P <$
171 0.05) lag phases in comparison to AQ5000- and CP1-amended soils, respectively. For
172 example, in 0.1% CB4-, AQ5000-, and CP1-amended soils, at 20 d, the lag phases were 3.72
173 d, 5.13 d and 6.69 d, respectively (Tables 2 to 4). Furthermore, at concentrations of 0.1%, lag
174 phases were shorter ($P < 0.05$) in AQ5000-, compared to CP1-amended soils.

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176 3.2.2. Maximum rates of ^{14}C -phenanthrene mineralisation

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

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190 3.2.3. Overall extents of ¹⁴C-phenanthrene mineralisation in soil

191 Overall, the extents of ¹⁴C-phenanthrene mineralisation were observed to decline with an
192 increase in concentration of AC (Figures 2 to 4; Tables 2 to 4). Generally, control soils had
193 the highest extents of ¹⁴C-phenanthrene mineralisation. At 1 d contact time in 0, 0.01, 0.1 and
194 1% CB4-amended soils, extents of ¹⁴C-phenanthrene mineralisation were 54.1%, 43.1%,
195 22.8% and 12.2%, respectively (Figure 2; Table 2). An increase in soil-phenanthrene contact
196 time resulted in significant reductions ($P < 0.05$) in the overall extents of ¹⁴C-phenanthrene
197 mineralisation. The extents of ¹⁴C-phenanthrene mineralisation were higher after 1 d ($P <$
198 0.05); however, no statistical significance ($P > 0.05$) was observed at other time points in
199 AC-amended soils (Figures 2 to 4). At all time-points, significantly greater ($P < 0.05$) extents
200 of ¹⁴C-phenanthrene were mineralised, in CB4-, than in AQ5000- and CP1-amended soils, at
201 concentrations greater than 0.01% (Figures 2 to 4; Tables 2 to 4). At 0.1% CB4-, AQ5000-,
202 and CP1-amended soils, at 20 d, total extents of ¹⁴C-phenanthrene mineralisation were
203 36.5%, 24.31% and 15.3%, respectively. A comparison CB4, AQ5000 and CP1-amended
204 soils showed that CB4-amended soils generally had the highest extents of ¹⁴C-phenanthrene
205 mineralisation; this was found to be statistically significant ($P < 0.001$), when compared to
206 AQ5000- and CP1-amended soils (Figures 2 to 4; Tables 2 to 4). However, ¹⁴C-phenanthrene
207 mineralisation rates of the AQ5000- and CP1-amended soils were similar (Figures 2 to 4;
208 Tables 2 to 4).

209

210 4. Discussion

211 4.1. Effect of AC addition on ¹⁴C-phenanthrene mineralisation in soil

212 This study investigated the impact of AC on the catabolism of ¹⁴C-phenanthrene in soil. The
213 results obtained showed that there was an increase in lag phase, together with a reduction in

214 maximum rates and overall extents of ^{14}C -phenanthrene mineralisation, with an increase in
215 the concentration of AC. This is consistent with results from previous studies which have
216 shown that an increase in AC concentration in soils may extensively reduce the rate at which
217 the catabolic activity of indigenous microorganisms develop in contaminated soils
218 consequently inhibiting biodegradation ²²; although that study was carried out using a single
219 type of AC. In this study, 1% concentration impacted upon the development in catabolism as
220 seen in the lag phases, which was generally immeasurable. The bioavailability (maximum
221 rates) and bioaccessibility (overall extents) of ^{14}C -phenanthrene were also severely reduced
222 in the presence of high concentrations (1%) of CB4, AQ5000 and CP1, respectively. The
223 concentration of AC also played an important role on the bioaccessibility of ^{14}C -
224 phenanthrene, with the higher concentrations providing more sorption sites, and thus
225 decreasing the bioavailable and bioaccessible fractions. This indicates that the increase in
226 availability of active sites for adsorption resulting from the increased dose of the AC affected
227 the catabolism of ^{14}C -phenanthrene. This is consistent with previous studies on the effect of
228 adsorbent dose on bioavailability of HOCs in soils ^{12, 22, 23}. Rhodes, et al. ²² determined that
229 the increase in lag phase and decrease in the maximum rates and extents of ^{14}C -phenanthrene
230 mineralisation found with soils amended with 1% and 5% AC may be due to improved
231 phenanthrene sorption to AC leading to a reduction in the bioaccessible fraction, and thus a
232 decrease in ^{14}C -phenanthrene mineralisation. Sorption of PAHs to AC has previously been
233 reported to limit mass transfer or reduce accessibility to microorganisms ²⁴; hence, the
234 reduced extent of mineralisation ^{14}C -phenanthrene in the present study after addition with
235 high concentrations of AC ¹².

236 An increase in soil-phenanthrene contact time led to a reduction in the rates and extents of
237 ^{14}C -phenanthrene mineralisation, although it was not significant in the lower concentrations
238 of AC-amended soils. This is consistent with previous studies that showed that ^{14}C -

239 phenanthrene mineralisation generally decreased with increasing soil-phenanthrene contact
240 time²⁵, in the presence of BC^{12, 22, 26}. A reduction in the lengths of the lag phase after 120 d
241 could indicate an adaptation of the indigenous microflora to the presence of AC. However,
242 the decline observed in rates and extents of ¹⁴C-phenanthrene proves otherwise. Therefore,
243 the decline may be due to the decrease in the catabolic potential of the degrading microbial
244 population, as a result of the presence of AC in soil. For example, Stroud et al.²⁷
245 demonstrated that the reduction in overall extent of mineralisation may be as a result of a
246 decrease in the catabolic potential of the degrading microbial population. In this study, it was
247 observed that despite the addition of fresh ¹⁴C-phenanthrene at each time-point, the rates and
248 extents of mineralisation declined subsequently. This is due to the effects of sorption of AC,
249 as described earlier, which indicates that sorption is time-dependent. The very slow rates of
250 desorption allow for a consistently increasing sorbed fraction over the 120 d AC-soil contact
251 time, similar to results obtained by²². This ultimately results in the development of a
252 relatively large, recalcitrant and non-bioaccessible fraction^{11, 28}. Hence, increasing AC
253 concentration provides additional sites for phenanthrene adsorption²⁹. Despite decreases in
254 the length of the lag phases in this study, indigenous soil populations did not appear to fully
255 adapt to the addition of ¹⁴C-phenanthrene in the presence of AC.

256

257 *4.2. Effect of AC type on ¹⁴C-phenanthrene mineralisation in soil*

258 All of the types of AC used in this study were effective in reducing the bioavailability and
259 bioaccessibility of ¹⁴C-phenanthrene in soil, with the reduction efficiencies trending in the
260 following order; CP1 > AQ5000 > CB4. Analysis of the data suggested that there was a
261 relation between the AC type, and its impact on ¹⁴C-phenanthrene mineralisation in soil. In
262 this study, CB4-amended soil consistently displayed shorter lag phases, together with greater
263 maximum rates and extents of ¹⁴C-phenanthrene mineralisation, compared to AQ5000- and

264 CP1-amended soils, respectively. Although the mechanism of sorption was not investigated,
265 the decline in ^{14}C -phenanthrene mineralisation may be attributed to sorption of AC to
266 phenanthrene, as shown in previous studies ^{12, 30}. The higher values observed for maximum
267 rates and overall extents of ^{14}C -phenanthrene mineralisation in CB4-amended soils, in
268 comparison to AQ5000- and CP1-amended soils, respectively. This indicated that the
269 adsorption capacity of CB4 towards ^{14}C -phenanthrene was lower than that of AQ5000 and
270 CP1, as observed from the values of the SSA for each AC. The surface area of CP1 (1106 m^2
271 g^{-1}) and AQ5000 ($1249\text{ m}^2\text{ g}^{-1}$) were both higher than of CB4 ($653\text{ m}^2\text{ g}^{-1}$). This is in
272 agreement with studies that showed that sorption capacities positively correlate with the SSA
273 of a sorbent ^{12, 23, 26}. This indicates that the characteristic of coconut shell based carbon, which
274 has a predominance of pores in the micropore-mesopore range, accounts for 95% of the
275 available internal surface area. Therefore, CP1 has the characteristics of being more porous
276 than that of the AQ5000 and CB4.

277 Overall, AQ5000- and CP1-amended soils mineralised ^{14}C -phenanthrene to almost identical
278 levels. However, AQ5000-amended soils had slightly higher extents of ^{14}C -phenanthrene
279 mineralised than CP1-amended soils, despite AQ5000 having higher surface area. This may
280 be explained by the differences in the pore volume and pore size distribution of both
281 adsorbents. This agrees with earlier findings that pore volume and pore distribution is one of
282 the most important parameters determining sorption ^{24, 31}. Jusoh et al. ⁹ reported that a larger
283 pore volume would contribute to the higher adsorption capacity. Additionally, CP1 has a
284 wide distribution of pore sizes. The pore size distribution has a role to play, with the
285 micropores constituting the majority of the specific surface area or adsorption sites, whereas
286 macropores and mesopores facilitate the mass transfer of chemicals into AC adsorption sites
287 ³¹. When comparing the effectiveness of all sorbents, both sorption capacity (SSA or the
288 abundance of micropores) and the mass transfer kinetics impact the uptake of phenanthrene.

289 CP1 has a higher pore volume and pore width, ranging from micropores to the macropore,
290 compared to AQ5000. The higher sorption of CP1 than AQ5000 may be due to the higher
291 pore volume and the narrower pores of CP1 in the micropore range. Therefore, the transfer of
292 ^{14}C -phenanthrene from accessible soil-AC compartments (macropores) into less accessible
293 compartments (mesopores and micropores), results in a reduction in bioaccessibility, hence a
294 reduction in overall extent of ^{14}C -phenanthrene mineralisation. This implies that the
295 entrapped phenanthrene within higher concentrations of AC will not be bioaccessible over a
296 long period of time due to strong sorption ^{12, 32}.

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

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

310

311 **5. CONCLUSION**

312 The results from this study showed that the application of high concentrations of AC severely
313 impacted the development of ^{14}C -phenanthrene catabolism in the soil. One of the more

314 significant findings to emerge from this study is that the type of AC is important in
315 remediation studies and plays a key role in bioavailability of organic contaminants to
316 microorganisms. A good understanding of the impact of surface area, pore volume and pore
317 size distribution on competitive adsorption is required as a basis for selecting the best type of
318 AC and applying it in an optimal way. Since each AC type differs in its characteristics, it is
319 highly relevant to identify the affinity parameters for *in situ* sorption of PAHs to AC in order
320 to be able to design and evaluate applications of AC in reducing risk. The better performance
321 of CP1 in this study may be due to its higher porosity and wider pore size distribution which
322 made it have a better adsorption of phenanthrene. Effectiveness of treatment increases with
323 contact time and varies for different forms of activated carbon with similar surface areas. The
324 importance and usefulness of AC should be considered in risk assessment and remediation of
325 contaminated soils.

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417 **List of table caption**

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419 Table 1: Properties of AC used in this study.

420

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

424

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

428

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

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444 **List of figure caption**

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446 Figure 1: Pore distribution of AC

447

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

451

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

455

456 Figure 4: Catabolism of ^{14}C -phenanthrene by indigenous microorganisms in soil after
457 addition of CP1 at contact time: (A) 1 d (B) 20 d (C) 40 d (D) 60 d and (E) 120 d. Error bars
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Table 1.

Specification	CB4	CP1	AQ5000
Surface Area (m ² g ⁻¹)	653	1106	1249
Moisture content (%)	3.1	4.8	4.7
Ash content (%)	9.8	2.8	12.9
-325 mesh	74.8 (65-85)	95 (90-100)	84.6 (65-85)
Iodine number	603	1056	1199
Pore volume / unit dry mass (ml g ⁻¹)*	0.29	2.5	0.80
Liquid quantity / unit dry mass (μl g ⁻¹)*	151	422	253

* refers to properties obtained by NMR-cryoporometry.

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490 Table 2:

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Ageing (d)	Conc (%)	Lag time (d)	Max rate (% h ⁻¹)	Extent (%)
1	0	4.56 ± 0.02	0.80 ± 0.03	54.1 ± 1.01
	0.01	6.96 ± 0.57	0.74 ± 0.06	43.1 ± 4.12
	0.1	7.35 ± 0.21	0.23 ± 0.02	22.8 ± 2.06
	1	7.71 ± 0.13	0.06 ± 0.01	12.2 ± 1.12
20	0	3.82 ± 0.04	0.76 ± 0.01	46.9 ± 3.95
	0.01	3.34 ± 0.02	0.70 ± 0.04	44.5 ± 0.89
	0.1	3.72 ± 0.01	0.47 ± 0.02	36.5 ± 1.96
	1	11.2 ± 1.79	0.07 ± 0.01	9.34 ± 0.96
40	0	3.81 ± 0.03	0.46 ± 0.02	39.2 ± 1.97
	0.01	3.95 ± 0.06	0.48 ± 0.04	39.3 ± 2.80
	0.1	3.92 ± 0.02	0.30 ± 0.01	30.8 ± 1.52
	1	11.5 ± 0.30	0.06 ± 0.01	7.25 ± 1.22
60	0	3.27 ± 0.02	0.47 ± 0.01	39.4 ± 1.31
	0.01	3.69 ± 0.02	0.38 ± 0.03	37.9 ± 1.32
	0.1	3.60 ± 0.04	0.28 ± 0.01	32.6 ± 0.47
	1	N/A*	0.04 ± 0.01	4.82 ± 0.94
120	0	3.03 ± 0.01	0.48 ± 0.02	40.2 ± 1.26
	0.01	3.31 ± 0.09	0.31 ± 0.04	34.1 ± 0.56
	0.1	3.49 ± 0.04	0.28 ± 0.03	25.8 ± 0.54
	1	N/A	0.01 ± 0.01	3.28 0.74

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493 * Mineralisation did not exceed 5% over the incubation period

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502 Table 3:

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Ageing (d)	Conc (%)	Lag time (d)	Max rate (% h ⁻¹)	Extent (%)
1	0	4.56 ± 0.02	0.80 ± 0.03	54.1 ± 1.01
	0.01	6.96 ± 0.36	0.47 ± 0.06	36.9 ± 1.54
	0.1	8.00 ± 0.73	0.10 ± 0.02	16.3 ± 2.73
	1	13.1 ± 0.23	0.05 ± 0.01	7.46 ± 1.27
20	0	3.82 ± 0.04	0.76 ± 0.01	46.9 ± 3.95
	0.01	3.17 ± 0.08	0.50 ± 0.07	41.5 ± 2.52
	0.1	5.13 ± 0.02	0.17 ± 0.03	24.3 ± 1.57
	1	N/A*	0.01 ± 0.01	1.95 ± 0.35
40	0	3.81 ± 0.03	0.46 ± 0.02	39.2 ± 1.97
	0.01	3.64 ± 0.01	0.59 ± 0.05	39.4 ± 1.56
	0.1	5.04 ± 0.02	0.11 ± 0.01	18.0 ± 0.23
	1	N/A	0.01 ± 0.01	1.63 ± 0.49
60	0	3.27 ± 0.02	0.47 ± 0.01	39.4 ± 1.31
	0.01	3.44 ± 0.02	0.52 ± 0.05	44.1 ± 1.68
	0.1	5.00 ± 0.08	0.13 ± 0.01	21.1 ± 1.29
	1	N/A*	0.01 ± 0.01	1.45 ± 0.82
120	0	3.03 ± 0.01	0.48 ± 0.02	40.2 ± 1.26
	0.01	3.38 ± 0.02	0.44 ± 0.01	38.6 ± 2.15
	0.1	3.64 ± 0.04	0.12 ± 0.01	19.4 ± 1.56
	1	N/A*	0.01 ± 0.01	0.81 ± 0.03

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505 * Mineralisation did not exceed 5% over the incubation period

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Table 4:

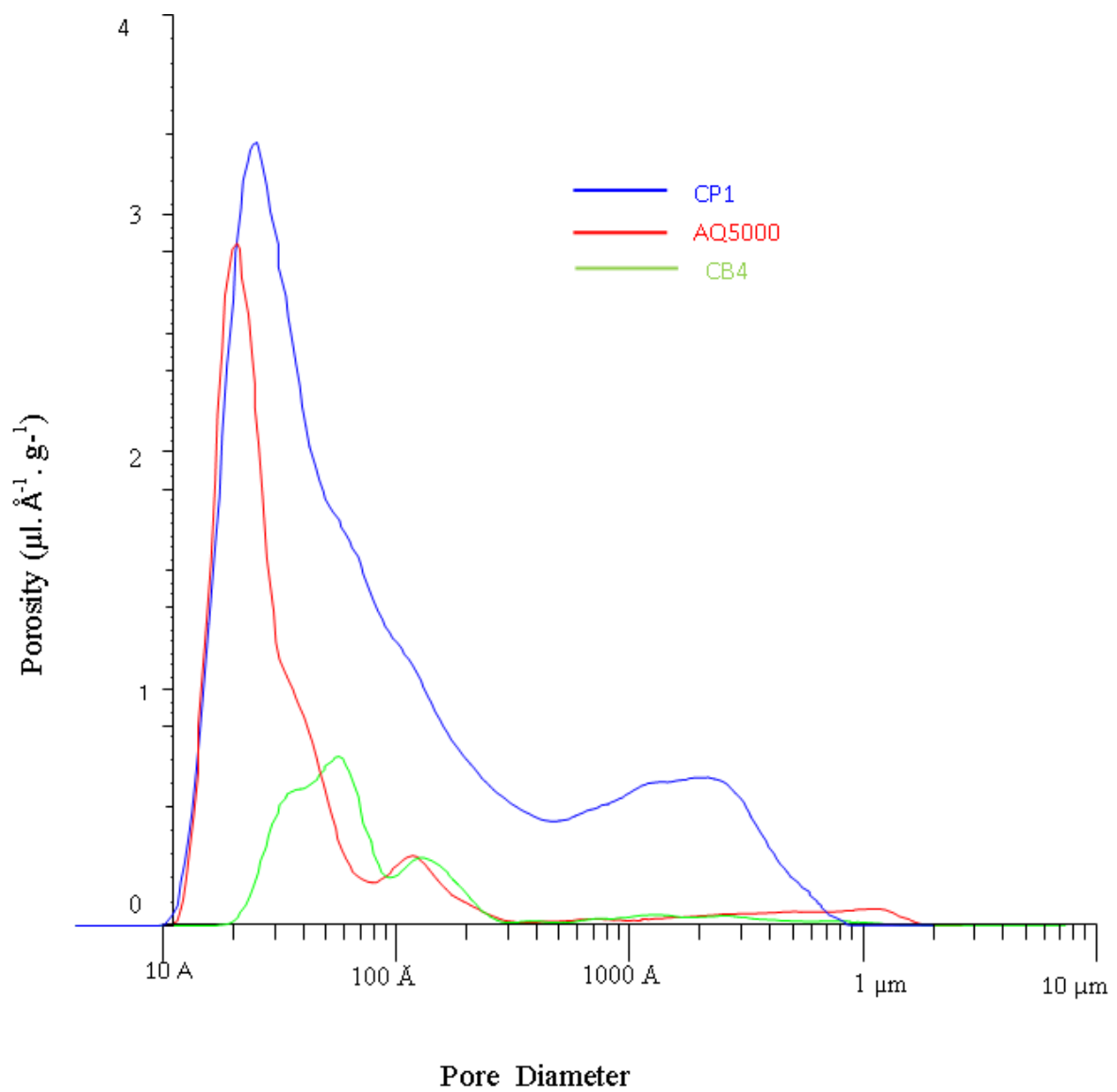
Ageing (d)	Conc (%)	Lag time (d)	Max rate (% h ⁻¹)	Extent (%)
1	0	4.56 ± 0.02	0.80 ± 0.03	54.1 ± 1.01
	0.01	6.78 ± 0.06	0.63 ± 0.04	39.6 ± 0.85
	0.1	6.71 ± 0.02	0.18 ± 0.03	16.6 ± 1.98
	1	N/A*	0.02 ± 0.01	3.82 ± 0.80
20	0	3.82 ± 0.04	0.76 ± 0.01	46.9 ± 3.95
	0.01	3.91 ± 0.02	0.49 ± 0.01	41.5 ± 0.99
	0.1	6.69 ± 0.07	0.18 ± 0.03	15.0 ± 1.53
	1	N/A	0.01 ± 0.01	1.19 ± 0.10
40	0	3.27 ± 0.02	0.46 ± 0.02	39.2 ± 1.97
	0.01	3.43 ± 0.09	0.44 ± 0.09	42.4 ± 3.30
	0.1	5.70 ± 0.02	0.14 ± 0.02	19.4 ± 2.05
	1	N/A*	0.03 ± 0.01	2.90 ± 0.13
60	0	3.27 ± 0.02	0.47 ± 0.01	39.4 ± 1.31
	0.01	3.24 ± 0.08	0.34 ± 0.03	31.8 ± 2.98
	0.1	5.56 ± 0.04	0.12 ± 0.01	18.8 ± 0.51
	1	N/A*	0.01 ± 0.01	1.72 ± 0.61
120	0	3.03 ± 0.01	0.48 ± 0.02	40.2 ± 1.26
	0.01	3.51 ± 0.02	0.36 ± 0.04	30.9 ± 2.61
	0.1	3.89 ± 0.04	0.10 ± 0.01	16.2 ± 0.78
	1	N/A*	0.02 ± 0.01	0.96 ± 0.13

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* Mineralisation did not exceed 5% over the incubation period

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526 Figure 1



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