Environmental Science
Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Activated carbon (AC) is a modified form of carbonaceous geosorbents, which is effective at reducing organic pollutant mobility and bioavailability in soils due to its high adsorption capacity, high porosity, high specific surface area and a high degree of surface reactivity, which makes them versatile adsorbents. The amendment of AC to soils contaminated by polycyclic aromatic hydrocarbons has been proposed as a remediation strategy to reduce the risk of pollutant transfer to soil biota. Since 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 sequestration of pollutants by ACs in soil.

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

Ayodeji O. Oyelami, Uchenna Ogbonnaya, Chitom Muotoh, Kirk T. Semple*

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom.

* Author to whom correspondence should be addressed; E-Mail: k.semple@lancaster.ac.uk; Tel.: +44 1524 510554

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 [1]. The physico-chemical characteristics of PAHs include low aqueous solubility, hydrophobicity, lipophilicity, nonpolarity and structural stability [2], 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 [2, 3].

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 [4, 5].They are widely present in the soil environment, and enhance sorption of PAHs in soils and sediments [6, 7]. 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 [8, 9]. AC possess high porosity, high specific surface area, strong hydrophobicity and a high degree of surface reactivity, making it a versatile sorbent [10]. 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 [11, 12]. Oyelami et al.[12] reported that the addition of 1% AC to soil reduced uptake of ^{14}C-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 [13]. 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 [14, 15]. 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 ^{12}C-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 unspiked soil, following the method reported by Doick, et al. [18]. 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 ^{12}C/^{14}C-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 ^{14}C-phenanthrene in soil by indigenous microorganisms

^{14}C-Phenanthrenre mineralisation was assessed using the method of Reid, et al. [19], after 1, 20, 40, 60 and 120 d soil-phenanthrene contact time. The evolution of $^{14}CO_2$ was determined using modified 250 ml Erlenmeyer flasks [19]. Each respirometer incorporated a Teflon-lined screw cap and a CO_2 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 [3]. The respirometric flasks were placed securely on an orbital shaker (IKA Labortechnik 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 ^{14}C-activity in the $^{14}CO_2$ traps was assessed after every 24 hours by replacing the NaOH traps and adding Goldstar liquid scintillation fluid (5 ml) to each spent $^{14}CO_2$ trap. After storage in darkness overnight, trapped ^{14}C-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 ^{14}C-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 ^{14}C-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).

189

190 *3.2.3. Overall extents of ^{14}C-phenanthrene mineralisation in soil*

191 Overall, the extents of ^{14}C-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 ^{14}C-phenanthrene mineralisation. At 1 d contact time in 0, 0.01, 0.1 and
194 1% CB4-amended soils, extents of ^{14}C-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 ^{14}C-phenanthrene
197 mineralisation. The extents of ^{14}C-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 ^{14}C-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 ^{14}C-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 ^{14}C-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, ^{14}C-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 ^{14}C-phenanthrene mineralisation in soil*

212 This study investigated the impact of AC on the catabolism of ^{14}C-phenanthrene in soil. The
213 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 [22]; 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 [12, 22, 23]. Rhodes, et al. [22] 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 [24]; hence, the reduced extent of mineralisation ^{14}C-phenanthrene in the present study after addition with high concentrations of AC [12].

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-

239 phenanthrene mineralisation generally decreased with increasing soil-phenanthrene contact
240 time [25], 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 ^{14}C-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 ^{14}C-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 by [22]. 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 adsorption [29]. 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 ^{14}C-phenanthrene in the presence of AC.
256
257 *4.2. Effect of AC type on ^{14}C-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 ^{14}C-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 ^{14}C-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 ^{14}C-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 μm) 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 μm, AQ5000 had 84.6 μm, while the smallest was CB4 with 74.8 μm. 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 *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

1. H. Fromme, T. Lahrz, A. Piloty, H. Gebhardt, A. Oddoy and H. Ruden, *Science of the Total Environment*, 2004, 326, 143-149.
2. J. D. Stokes, G. I. Paton and K. T. Semple, *Soil Use and Management*, 2005, 21, 475-486.
3. K. J. Doick and K. T. Semple, *Fems Microbiology Letters*, 2003, 220, 29-33.
4. M. W. I. Schmidt and A. G. Noack, *Global Biogeochemical Cycles*, 2000, 14, 777-793.
5. A. A. Koelmans, M. T. O. Jonker, G. Cornelissen, T. D. Bucheli, P. C. M. Van Noort and Ö. Gustafsson, *Chemosphere*, 2006, 63, 365-377.
6. M. T. O. Jonker and A. A. Koelmans, *Environmental Science & Technology*, 2002, 36, 4107-4113.
7. G. Cornelissen, G. D. Breedveld, S. Kalaitzidis, K. Christanis, A. Kibsgaard and A. M. P. Oen, *Environmental Science & Technology*, 2006, 40, 1197-1203.
8. R. C. Brandli, T. Hartnik, T. Henriksen and G. Cornelissen, *Chemosphere*, 2008, 73, 1805-1810.
9. A. Jusoh, W. J. H. Hartini, N. Ali and A. Endut, *Bioresource Technology*, 2011, 102, 5312-5318.
10. Y. Chai, R. J. Currie, J. W. Davis, M. Wilken, G. D. Martin, V. N. Fishman and U. Ghosh, *Environmental Science & Technology*, 2012, 46, 1035-1043.
11. U. Ghosh, R. G. Luthy, G. Cornelissen, D. Werner and C. A. Menzie, *Environmental Science & Technology*, 2011, 45, 1163-1168.
12. A. Oyelami, B. Elegbede and K.T. Semple, *Environments*, 2014, 1, 137-156.
13. I. Hilber, G. S. Wyss, P. Mäder, T. D. Bucheli, I. Meier, L. Vogt and R. Schulin, *Environ. Pollut.*, 2009, 157, 2224-2230.
14. J. R. Zimmerman, U. Ghosh, R. N. Millward, T. S. Bridges and R. G. Luthy, *Environmental Science & Technology*, 2004, 38, 5458-5464.
15. K. Amstaetter, E. Eek and G. Cornelissen, *Chemosphere*, 2012, 87, 573-578.
16. P. B. Hatzinger and M. Alexander, *Environmental Science & Technology*, 1995, 29, 537-545.
17. K. M. Scow, *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*, 1993, 73-114.
18. K. J. Doick, P. H. Lee and K. T. Semple, *Environmental Pollution*, 2003, 126, 399-406.
19. B. J. Reid, C. J. A. MacLeod, P. H. Lee, A. W. J. Morriss, J. D. Stokes and K. T. Semple, *Fems Microbiology Letters*, 2001, 196, 141-146.
20. A. H. Rhodes, A. Carlin and K. T. Semple, *Environmental Science & Technology*, 2008, 42, 740-745.
21. J. Mitchell, J. B. W. Webber and J. H. Strange, *Physics Reports-Review Section of Physics Letters*, 2008, 461, 1-36.
22. A. H. Rhodes, L. E. McAllister, R. R. Chen and K. T. Semple, *Chemosphere*, 2010, 79, 463-469.
23. J. R. Zimmerman, D. Werner, U. Ghosh, R. N. Millward, T. S. Bridges and R. G. Luthy, *Environmental Toxicology and Chemistry*, 2005, 24, 1594-1601.
24. K. Nam and M. Alexander, *Environmental Science & Technology*, 1998, 32, 71-74.
25. K. T. Semple, N. M. Dew, K. J. Doick and A. H. Rhodes, *Environmental Pollution*, 2006, 140, 164-172.
26. Y. Yang, W. Hunter, S. Tao, D. Crowley and J. Gan, *Environmental Toxicology and Chemistry*, 2009, 28, 2283-2288.

27. J. L. Stroud, G. I. Paton and K. T. Semple, *Journal of Applied Microbiology*, 2007, 102, 1239-1253.
28. R. Lohmann, J. K. MacFarlane and P. M. Gschwend, *Environmental Science & Technology*, 2005, 39, 141-148.
29. E. M. Lamoureux and B. J. Brownawell, *Environmental Toxicology and Chemistry*, 2004, 23, 2571-2577.
30. A. H. Rhodes, M. J. Riding, L. E. McAllister, K. Lee and K. T. Semple, *Environmental Science & Technology*, 2012, 46, 12445-12451.
31. C. Pelekani and V. L. Snoeyink, *Water Research*, 1999, 33, 1209-1219.
32. F. Rouquerol, I. Rouquerol and K. Sing, Academic Press, London,UK, 1999, pp. 5-6.

417 **List of table caption**

418

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 ^{14}C-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 ^{14}C-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 ^{14}C-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).

432
433
434
435
436
437
438
439
440
441
442
443

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.

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.

Table 2:

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

* Mineralisation did not exceed 5% over the incubation period

Table 3:

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

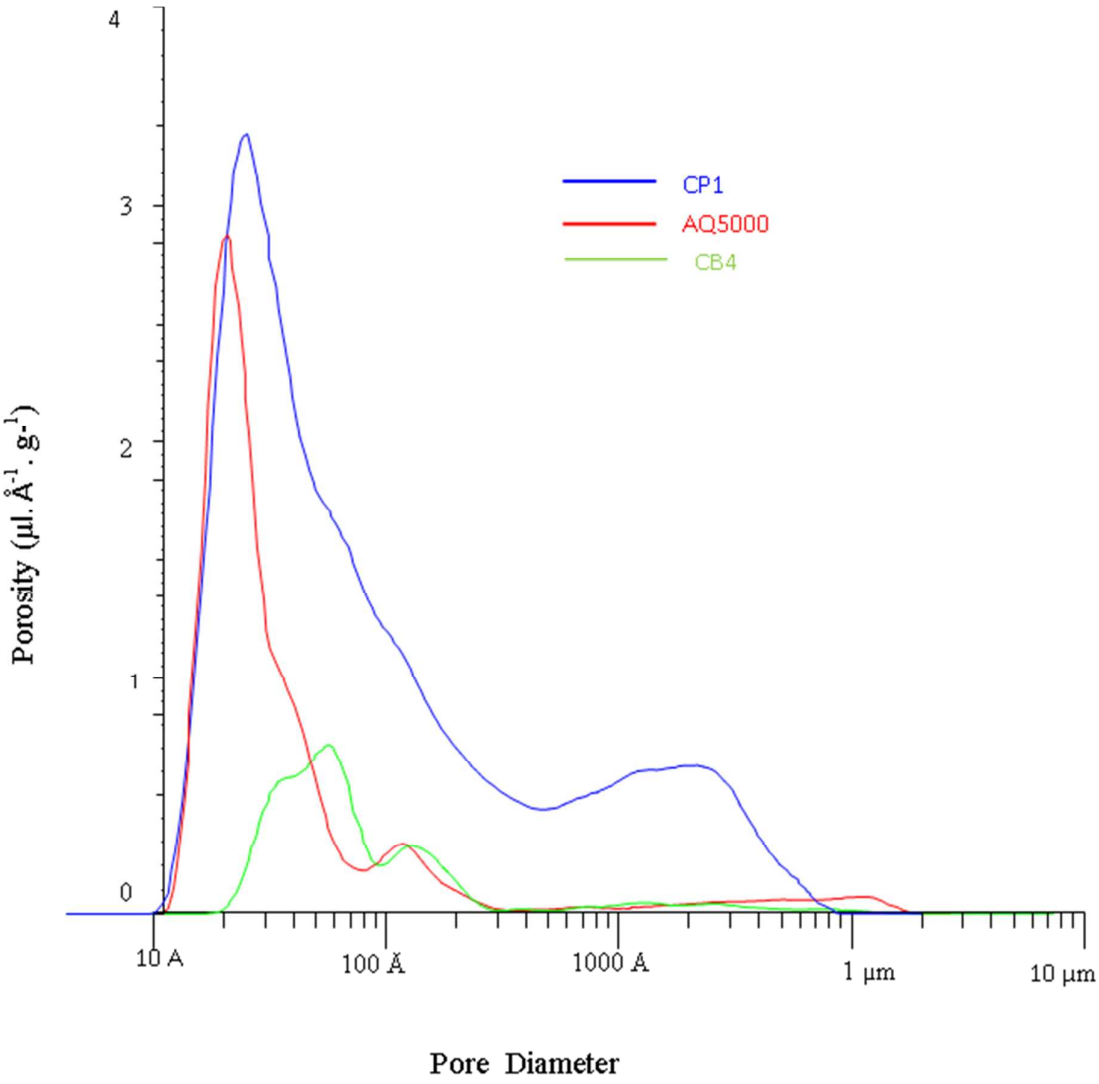
* Mineralisation did not exceed 5% over the incubation period

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

* Mineralisation did not exceed 5% over the incubation period

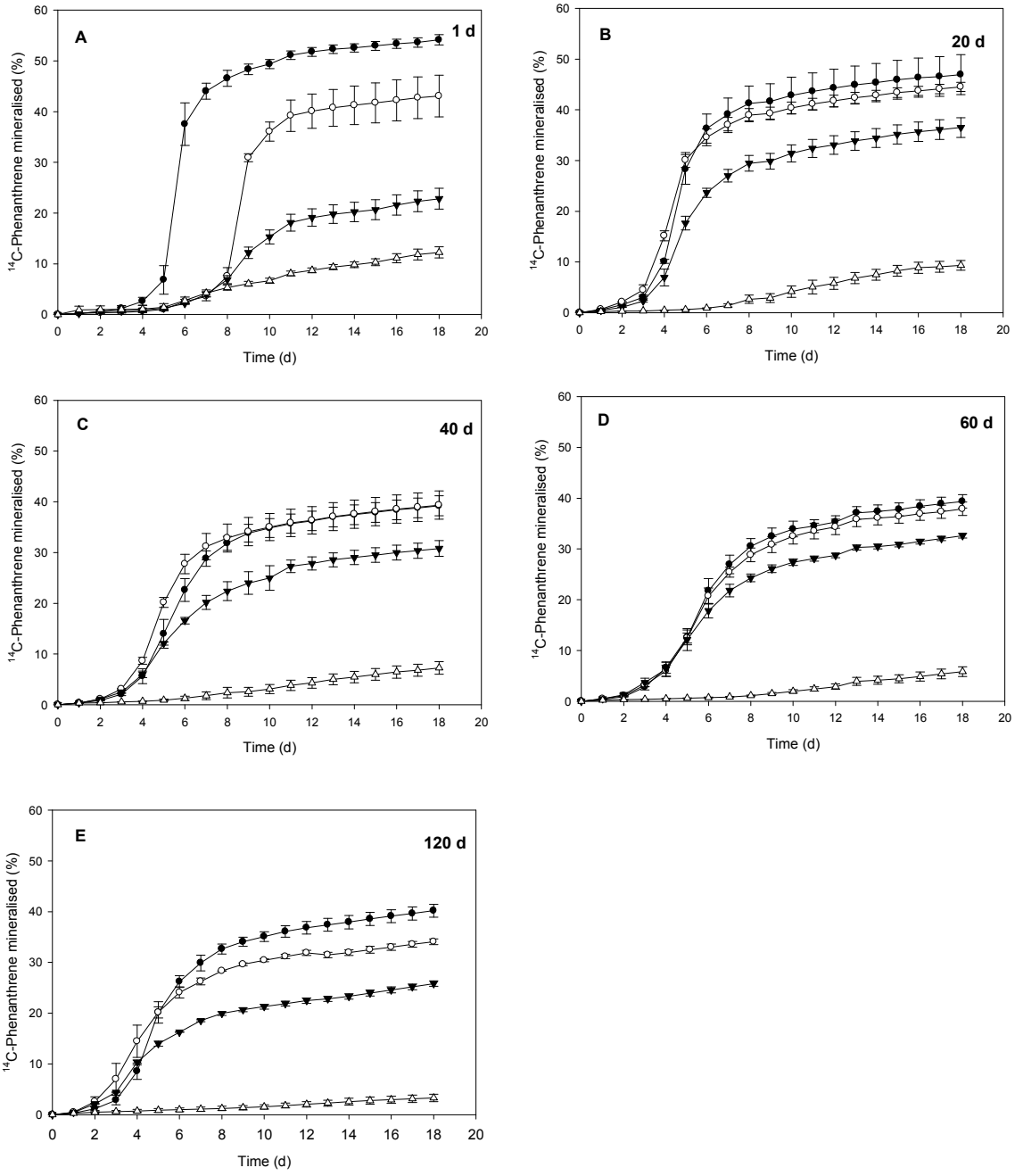
526 Figure 1



527
528
529
530
531
532
533
534
535
536

537 Figure 2

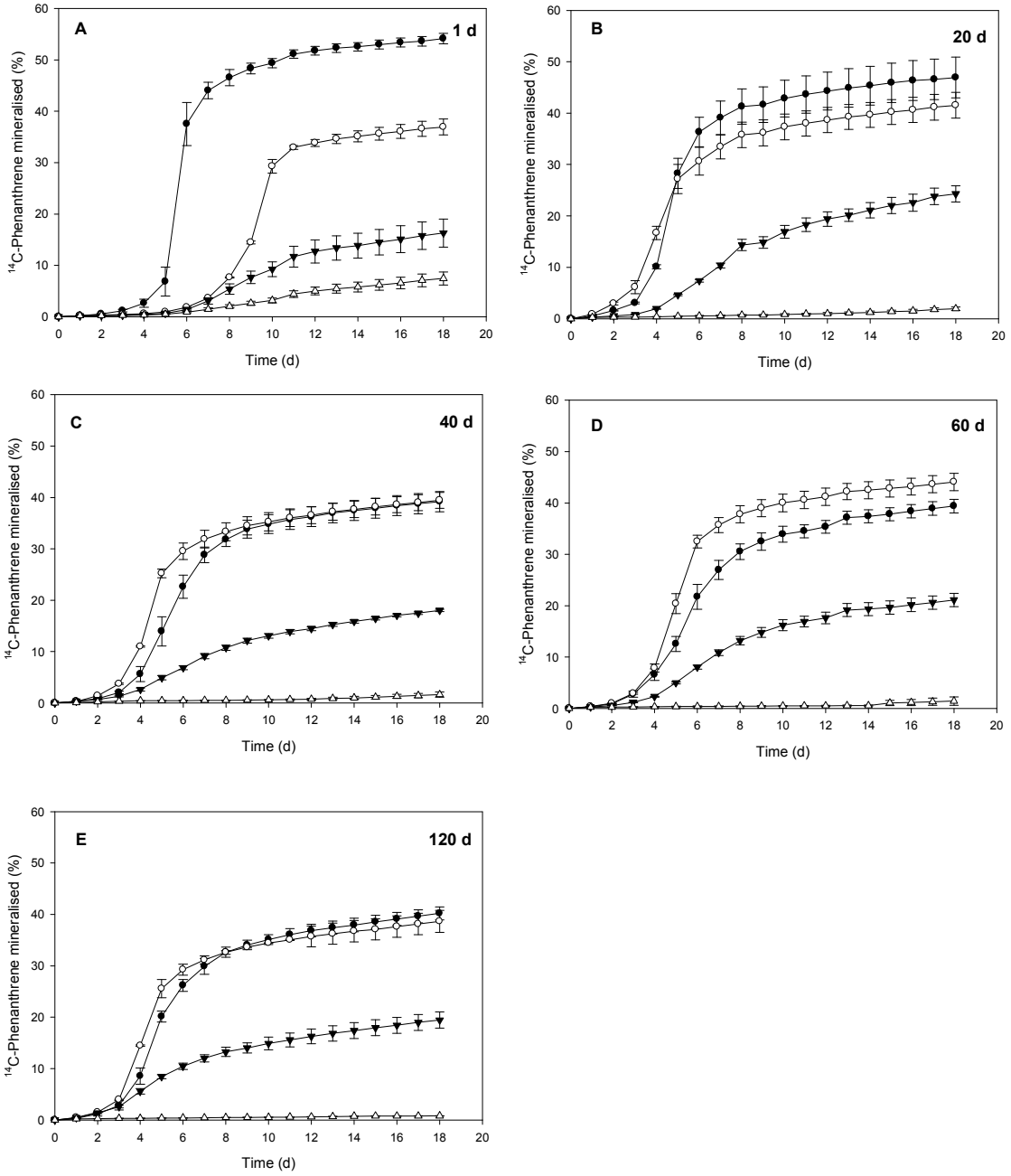
538



539
540
541
542
543

544 Figure 3

545



546

547

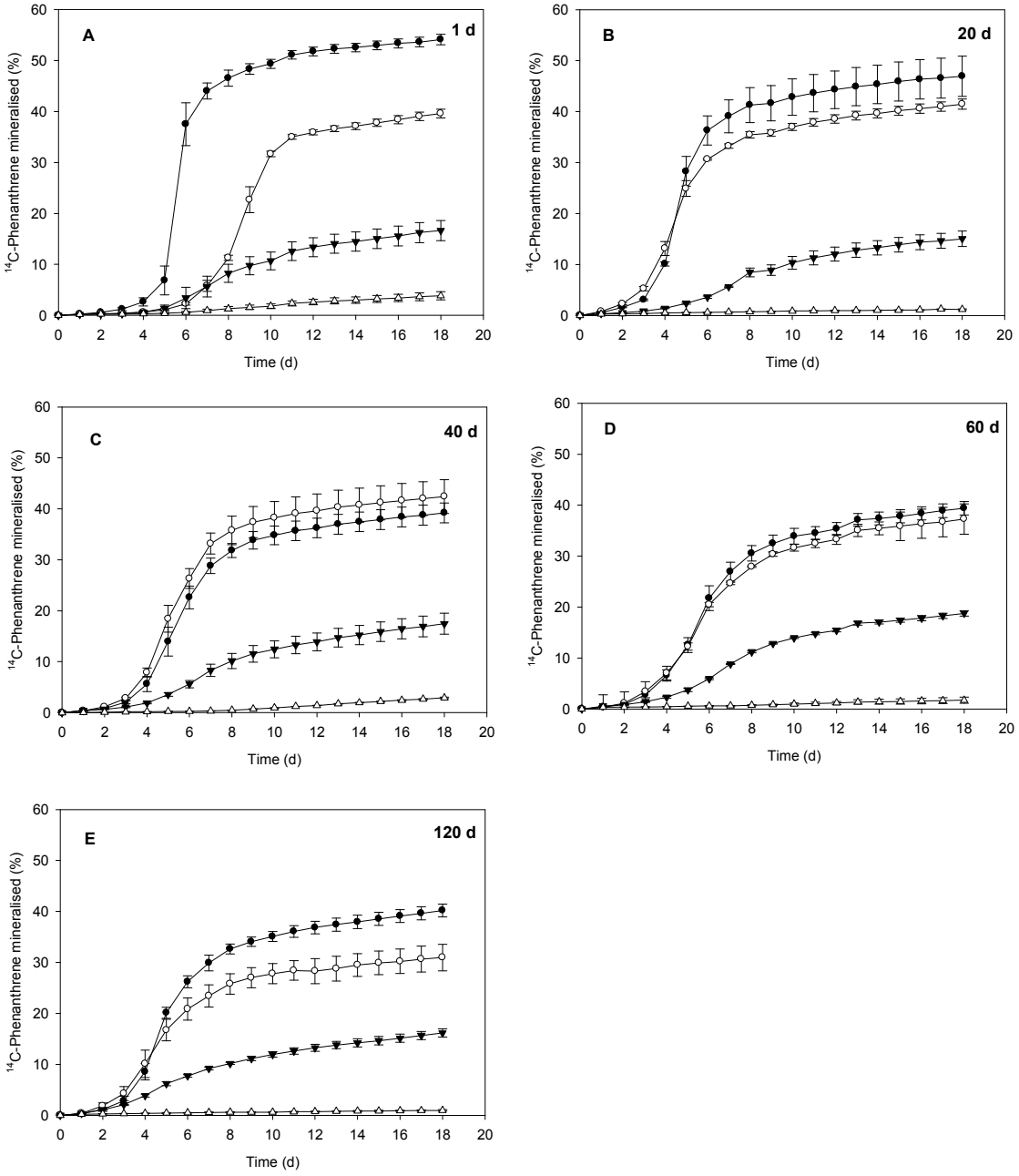
548

549

550

551 Figure 4

552



553