



Study of PAH dissipation and phytoremediation in soils: Comparing freshly spiked with weathered soil from a former coking works

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ABSTRACT

A comparison was made between the dissipation of polycyclic aromatic hydrocarbons (PAHs) in soil freshly spiked with pure PAHs, soil spiked with a coal tar mixture and a contaminated soil from a former coking works where the PAHs had been present for more than a century. The potential of five selected plant species for phytoremediation was investigated. The levels of all 7 PAHs in chemically amended soil, both planted and unplanted, fell significantly (>80% reduction) over the 12 weeks of the growing trial. In the coal tar treated soils all PAHs were significantly reduced. In both the planted and unplanted soils the 2–3 ringed compounds demonstrated much greater loss (>77%) than the 4–6 ringed (16–39%). The 3–4 ringed compounds demonstrated strong evidence of phytoremediation but not the 5–6 ringed. The coking soil showed limited reduction (7–24%) of all 12 PAHs present. There was little difference in dissipation between the PAHs and little evidence of a phytoremediation effect in coking soil. The results demonstrated that the form in which PAHs were added to soil influenced their susceptibility to dissipation. Therefore, predictions of PAH dissipation from laboratory amended soil do not reflect the true situation in the field.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are found in high levels in the soil of former gas and coking works. They are by-products of the process used to produce gas for domestic and industrial consumption from the late 19th century up until the 1970s in the UK, when its use was replaced with natural gas. Residual contamination of soils with PAHs is of concern because of their toxicity; several are potential carcinogens and mutagens [1]. The major pathways of PAH dissipation are volatilization, irreversible sorption by soil, leaching, accumulation by plants and biodegradation (possibly enhanced by the presence of plant roots). In greenhouse studies it is often not possible to distinguish between these mechanisms. Volatility is an unlikely mechanism for the dissipation of PAHs with 3 or more rings [2] due to their low vapour pressures, for example naphthalene has a vapour pressure of 11,000 mPa at 25 °C whereas phenanthrene has a vapour pressure of 18 mPa. Park et al. [3] found naphthalene to be the only PAH which exhibited volatilization from soils while others lost less than 0.1% or were not detected in the vapour phase. There is little evidence of phytoextraction of PAHs. Although some studies [4] have shown

uptake or adsorption by plant roots, translocation of PAHs with 4 or more rings from root to foliar portions of plants is negligible [5]. PAHs with 3 or more rings have limited water solubility, naphthalene and phenanthrene have water solubilities at 25 °C of 30 and 1.3 mg L⁻¹ respectively, which results in low susceptibility to leaching.

Several methods of PAH treatment such as containment, incineration, thermal desorption, physical and chemical degradation and microbial degradation [6] have been used, but are often prohibitive mainly due to cost. Soil incineration is a rapid method but it is costly, thermal desorption is less expensive [7], as are physical and chemical treatment methods but these still require considerable engineering or end disposal costs. Much work has been carried out in order to determine the ability of plants to enhance microbial degradation of PAHs in soil. Investigations in the last two decades have suggested that phytoremediation could be used as an alternative technique to reduce PAHs levels in soils [7–10].

PAH degradation in the soil and sediment is slow; however, PAHs may be degraded through properly stimulated soil microorganisms by mineralization, co-metabolic degradation and non-specific radical oxidation [2]. PAHs are less phytotoxic in the short term than monoaromatics [6] and so it has been suggested if plant growth can be established and maintained in contaminated areas, the dissipation of these contaminants could be increased

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[11]. Plant roots increase the contact surface between microorganisms, soils and pollutants and so the development of a healthy root system is essential for optimum degradation. Thus grasses are an obvious choice due to their fibrous root system leading to a large surface area and intensive penetration into the soil. They should be native to the area to which they are being used and they should be tolerant to the conditions of the soil [12].

Natural attenuation of pollutants should be favoured by mixed swards including nitrogen-fixing plants to provide nitrogen, which is often limiting for both plant growth and microbial degradation of organic pollutants [13]. As translocation of PAHs with 4 or more rings from root to foliar portions of the plants is negligible, neither food chain effects nor volatilization through leaves should be a concern for phytoremediation of aged PAH contaminated soil [14].

The greening of land is a relatively cheap alternative to removing soil from a contaminated site. Polluted soils may be poorly vegetated or completely void of vegetation and planting may be desirable to reduce wind erosion and/or to enhance the degradation of organic pollutants through rhizosphere technology [13]. Not only does phytoremediation have a positive effect on contaminants, even if limited, there are wider environmental benefits as it also offers protection against wind erosion, reduction of surface water run-off, reinforcement of soil by roots and increased water infiltration. It also improves the aesthetics of the area [15]. This physical process is frequently described as phytostabilisation.

Dissipation studies have, however, tended to investigate losses from soils freshly spiked with PAHs [2,11,13,16]. Fewer studies have been carried out on land where long-term PAH contamination has occurred. Robinson et al. [5] investigated the impact of tall fescue on creosote-contaminated soil. Ahn et al. [17] studied the susceptibility of PAHs in coke-plant soil to phytoremediation. Erickson et al. [18] reported on the PAH loss during bioremediation of manufactured gas plant site works. Lu et al. [4] used goosegrass (*Eleusine indica*) to phytoremediate petroleum contaminated soil. Contradictory findings in the literature may be related to the ways in which the studies have been carried out.

Therefore the objectives of this study were investigation of how the form in which the PAHs are added to soil affects their dissipation rate, whether plants increase the dissipation of PAHs and what are the differences in dissipation between the PAHs using five plant species, which were grown in three contaminated soils (soil freshly spiked with a mixture of pure PAHs; soil freshly spiked with a natural coal tar mixture and soil from a former coking works containing aged PAHs).

2. Materials and methods

2.1. Soil and PAHs

Soil from a former coking plant (sampling depth 0–25 cm) was supplied by CPL, Chesterfield, UK. It was dried in the laboratory then passed through a 4 mm sieve and stored in sealed bags and kept in the dark for four weeks to stabilize. It contained 12 of the 16 priority PAHs specified by the United States environmental protection agency (US-EPA) and the European Union (EU) as well as some other unidentified hydrocarbons and derivatives. Metals analysis was carried out on this soil by Nobel Enterprises, Ardeer, Stevenage, UK and the pH and sulphate measurements were carried out by CPL Products Ltd., Chesterfield, UK (Table 1).

The soil used in the spiking trials was obtained from Barassie, Ayrshire Scotland. This soil belongs to the Dreghorn series, which has been classed as a freely drained brown forest soil. The soil was selected because it had a neutral pH, high level of organic content and a good structure providing good physical conditions for plant growth. Its characteristics are shown in Table 1. The soil was air

Table 1
Properties of Barassie and coking works soils.

	Dreghorn series soil	Coking works soil
pH	7.0	6.5
Loss on ignition (%)	5.6	33
Texture	loamy sand	sandy clay loam
Arsenic (mg kg ⁻¹)	16	18
Cadmium (mg kg ⁻¹)	1	2
Chromium (mg kg ⁻¹)	74	59
Copper (mg kg ⁻¹)	18	36
Mercury (mg kg ⁻¹)	ND	ND
Nickel (mg kg ⁻¹)	22	49
Lead (mg kg ⁻¹)	72	174
Zinc (mg kg ⁻¹)	113	193
Sulphate (mg kg ⁻¹)	12	53

ND not detectable (<1 mg kg⁻¹).

dried and passed through a 4 mm sieve, stored in sealed bags and kept in the dark until required.

A sample of coal tar was provided by CPL, Chesterfield, UK. Pure PAHs; naphthalene, fluorene, acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene (>96% purity) were obtained from Aldrich, UK.

The air dried Dreghorn series soil was laid out thinly and the PAHs or coal tar were dissolved in acetone and added to the soil. Acetone was utilized as the carrier solvent as it solubilizes the PAHs and is easily evaporated [2]. The soil was turned repeatedly during the additions and then left for 3 days to ensure evaporation of the acetone. The soil used for the main growing trials was then stored in open glass vessels, to a depth of 150 mm, for 4 weeks at ambient temperature in the dark to age and stabilize the mixture. It also served to allow some adsorption and mimic the action of tilling. During this period the soil was mixed at weekly intervals to ensure a homogenous distribution of PAHs. The pure PAHs were added at a rate of 1000 mg kg⁻¹ of total PAHs. The coal tar was added at a rate of 6 g per kg of soil and this resulted in approximately 1000 mg kg⁻¹ total PAHs. The levels of PAHs in each of the soils were determined at the beginning of the growing period and then at the completion of the 12 week trial.

2.2. Quantitative analysis of PAHs

Soils were extracted using 20 g sub samples. This was done by Soxhlet using a 1:1 dichloromethane acetone mixture for 6 h. Analysis was carried out using a gradient high pressure liquid chromatography (HPLC) system with a UV diode array detector. The Merck–Hitachi HPLC system comprised: L-7200 autosampler, L-7100 gradient pump, Supelcosil LC-PAH 15 cm column, L-7350 column oven, L-4500 diode array detector and L-7000 HPLC system manager software. A gradient program was developed to enable full resolution of the 16 US-EPA priority PAHs. The diode array detector enhanced limits of quantification by allowing compound specific detection wavelengths plus assessment of peak purity and confirmation of peak identity using spectral comparison with standards. From an initial eluent concentration of 60% acetonitrile and 40% water, acetonitrile was increased linearly to 70% at 10 min, to 100% acetonitrile at 20 min and maintained at 100% acetonitrile for a further 10 min. A shorter gradient program was set up to analyze the soil spiked with the 7 pure PAHs.

2.3. Growth trials

Plant seeds for the growing trials were purchased from Emorsgate Seeds, Kings Lynn, Norfolk, UK. Five plant species including three grasses and two legumes were used in these trials; *Festuca arundinacea* (tall fescue), *Festuca rubra* (red fescue), *Lolium perenne*

Table 2
PAH levels in Barassie soil amended with pure PAHs and coal tar, initially and after 4 weeks stabilization period, and the coking works soil.

PAH	Pure PAH spike		Coal tar spike		Coking works (mg kg ⁻¹)
	Spike (mg kg ⁻¹)	Aged (mg kg ⁻¹)	Spike (mg kg ⁻¹)	Aged (mg kg ⁻¹)	
Naphthalene	500	113 ± 8	411 ± 23.0	120 ± 3.0	<1
Acenaphthylene			96 ± 0.1	56 ± 2.2	<1
Acenaphthene	50	25 ± 2	<1	<1	<1
Fluorene	50	28 ± 2	100 ± 0.5	81 ± 1.5	<1
Phenanthrene	200	139 ± 10	246 ± 2.9	227 ± 5.4	222 ± 8
Anthracene	50	22 ± 2	66 ± 0.4	57 ± 1.7	117 ± 2
Fluoranthene	100	72 ± 5	154 ± 1.5	146 ± 2.6	858 ± 16
Pyrene	50	34 ± 3	95 ± 0.9	89 ± 2.1	578 ± 13
Benzo[a]anthracene			53 ± 0.6	51 ± 1.4	624 ± 8
Chrysene			41 ± 0.9	40 ± 0.9	535 ± 3
Benzo[b]fluoranthene			41 ± 0.7	39 ± 0.7	645 ± 3
Benzo[k]fluoranthene			20 ± 0.8	20 ± 0.8	322 ± 3
Benzo[a]pyrene			34 ± 0.6	34 ± 0.6	502 ± 7
Dibenzo[a,h]anthracene			7 ± 0.9	7 ± 0.3	118 ± 9
Benzo[g,h,i]perylene			18 ± 0.7	18 ± 1.0	266 ± 4
Indeno[1,2,3-c,d]pyrene			21 ± 0.4	22 ± 1.1	333 ± 24

Mean of 3 replicate (± standard deviation).

(perennial ryegrass), *Trifolium pratense* (red clover) and *Trifolium repens* (white clover).

200 g of soil was added to a 75 mm diameter pot. A disc of filter paper was placed in the bottom of each pot to prevent the dry soil escaping out from the drainage holes and the pots were placed in saucers. To each pot 0.2 g of seed from each species were spread evenly across the surface of the soil. The pots were put in the greenhouse and watered from the top using deionised water to no greater than field capacity to avoid leaching. They were then covered with black polyethylene to exclude light and encourage germination. After germination the polyethylene was removed. The plants were checked daily and similarly kept watered to just below field capacity throughout the duration of the trial. At the 2 week time-point all pots were given a nutrient feed of nitrogen, phosphorus and potassium in the ratio 100:50:100 mg kg⁻¹.

The trials were carried out over one year. During the late autumn, winter and spring the conditions in the greenhouse were controlled with a 16 h daylight cycle and a greenhouse heater was used to keep the greenhouse frost free. During the summer months no light or heating was used in the greenhouse. To prevent overheating it was coated with 'Coolglass' over this period. As a consequence overnight temperature minimum varied from 6 °C to 10 °C and daily maximum from 26 °C to 40 °C during the course of the experiment. The plants were grown for 12 weeks. At the conclusion of each growing trial the shoots were cut close to the soil. The soil was air dried and roots removed by sieving.

Three growing trials were carried out. The first growing trial compared PAH degradation in soil spiked with a mixture of 7 PAHs 1000 mg kg⁻¹ total PAHs. The second trial compared PAH degradation in soil treated with 1000 mg kg⁻¹ PAH as coal tar. The third trial compared PAH degradation in soil from a former coking works. In each trial untreated Barassie soil was used as a planted control to assess the growth of each species in uncontaminated soil.

2.4. Data analysis

Statistical analysis was carried out using the Minitab statistical package. For the PAH degradation a randomised block design was used with 4 replicates of each treatment. Comparisons of the plant species were made using one-way analysis of variance separately for each PAH. Where a significant ($p < 0.05$) F test was obtained PAH levels for each plant species were compared to the initial PAH level and to the unplanted soil using a Tukey HSD (5%).

3. Results

3.1. PAH levels in coal tar and coking works soil

The PAH levels in the coal tar treated soil and the coking works soil are shown in Table 2. The coal tar contained 15 of the 16 US-EPA priority PAHs; acenaphthene was not detectable. The lower molecular weight PAHs naphthalene, acenaphthylene, acenaphthene and fluorene were not detected in the coking works soil. The 12 PAHs that were detected, were present in substantial quantities ranging from 117 mg kg⁻¹ for anthracene to fluoranthene at 858 mg kg⁻¹.

3.2. PAH levels in treated soil at zero time

Table 2 shows the proportions of each PAH added and the levels found at zero time in the soil treated with pure PAHs. There was a decrease of the more volatile PAHs over the 4 weeks with naphthalene dropping to 20% of its original value. Acenaphthene, fluorene and anthracene were all reduced to approximately 50%, while phenanthrene, fluoranthene and pyrene fell to 70% of their original values. In general, as would be expected, as the molecular weight of the PAH increases and the saturation vapour pressure reduces, dissipation is less. These losses were considered to be mainly volatilization or irreversible sorption onto the soil. The coal tar amended soil was also quantitatively analyzed after 4 weeks ageing. The values found are also shown in Table 2. Again there were losses of the lighter molecular weight PAHs, naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene and to a lesser extent pyrene over this period. The recoveries were higher in the coal tar amended soil than from the soil amended with the pure PAHs. This can be attributed to the physical effects of the coal tar on the pore system and vapour movement. The PAHs with higher molecular weights, benzo[a]anthracene to indeno[1,2,3-c,d]pyrene showed no significant loss.

The soil from the former coking works was quantitatively analyzed at the beginning of the growing trial. It contained 12 of the 16 of the priority PAHs (as specified by the US-EPA and EU) as well as some other unidentified hydrocarbons and derivatives. Table 2 shows the values of each PAH found. The soil was also analyzed for inorganic contaminants and Table 1 shows the results. The soil had a wide range of PAHs but had low levels of inorganic contaminants, all at acceptable levels, thus the inorganic contaminants would not have a detrimental effect on growth.

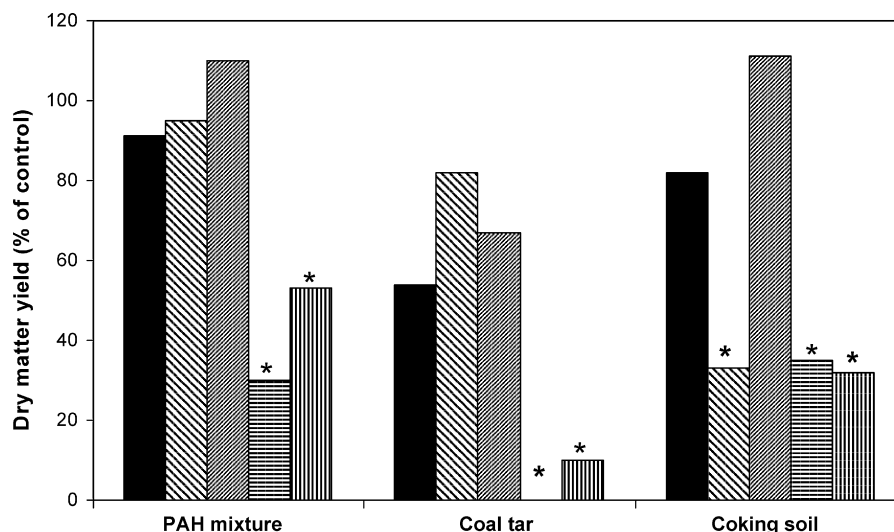


Fig. 1. Yields of vegetation in PAH treated soil as percentage of yield in untreated Dreghorn series soil ■ *Festuca arundinacea*, ▨ *Festuca rubra*, ▩ *Lolium perenne*, ▪ *Trifolium pratense* and ▫ *Trifolium repens*. Values indicated with an * are significantly different ($p < 0.05$) from their respective untreated control soil, Tukey HSD.

3.3. Effect of PAH treatments on vegetation growth

The yields of the 5 plant species in the PAH treatments are shown in Fig. 1. Because of the differences in the growth of the species the results are presented as percentages of the growth in the respective untreated control soils. The effect of the PAH treatments on yield varied considerably amongst the plant species; relative to their growth in untreated soils the legumes grew more poorly than the grasses which grew well in the majority of treatments. Coal tar had the greatest impact of the PAH treatments. In some cases where low growth was recorded at 12 weeks the plants germinated and developed but at a slower rate than the untreated soils and in the case of one of the legumes, *T. pratense*, it subsequently died so that no yield was recorded.

3.4. PAH levels in soil after plant growth

After each growing trial the soil was quantitatively analyzed for PAH levels. The levels of PAHs in soil amended with the pure PAHs all fell significantly over the 12 weeks of the growing trial (Table 3). All of the 7 PAHs detected had dropped to less than 20% of the value at the beginning of the trial. These losses were probably principally due to microbial degradation due to the ready availability of the freshly applied PAHs and irreversible sorption, though volatile losses will have contributed to the loss of the lower molecular weight PAHs. There was no significant difference in PAH levels between the unplanted and planted soils. Levels remaining in the unplanted soil were so low that no evidence could be seen of phytoremediation.

Despite the high variability in the soils treated with coal tar, after the 12 week growing trial, all the PAHs were significantly

reduced compared to the initial level in both the planted and the unplanted soils (Table 4). In the unplanted control soil the 2 and 3 ringed compounds demonstrated much greater dissipation than those with 4, 5 and 6 rings. Naphthalene and acenaphthylene were lost extremely rapidly and there was no evidence of any effect of phytoremediation. The 3 and 4 ringed compounds from fluorene to chrysene demonstrated stronger evidence of phytoremediation. However, in the case of benzo[a]anthracene and chrysene not all of the plant species showed this. For the 5 and 6 ringed compounds and also anthracene there was no evidence of phytoremediation effects (Table 4) or indeed loss of any kind. It should be borne in mind that generally the two factors which contribute to persistence of PAHs are an increase in the size and the angularity of PAH molecules which result in a concomitant increase in hydrophobicity and electrochemical stability [19].

Table 5 shows the levels of PAHs found in the coking soil after 12 weeks growth. The first four more volatile PAHs naphthalene, acenaphthylene, acenaphthene and fluorene were not present in the coking soil. After the 12 weeks of the growing trial it was found that not all of the PAHs were significantly lower than the level found at zero time. This was mainly shown in the last eight in the series, from benzo[a]anthracene to indeno[1,2,3-c,d]pyrene where the vast majority in this section demonstrated a significant difference between the initial levels and after the treatment. However, there was very little evidence of planting causing a phytoremediation effect with only two species (*F. rubra* and *T. repens*) demonstrating a small but significant effect when compared to the unplanted despite the fact that the plants had grown relatively well in the coking soil (Fig. 1). However, PAH degradation occurred to a much lesser extent than when they were added in their pure form or in the coal tar.

Table 3
PAH percentage recoveries after 12 weeks plant growth in soil treated with a mixture of pure PAHs.

PAH (rings)	Unplanted	<i>Festuca arundinacea</i>	<i>Festuca rubra</i>	<i>Lolium perenne</i>	<i>Trifolium pratense</i>	<i>Trifolium repens</i>
Naphthalene(2)	2.0	17.8	0.9	19.5	17.1	3.0
Acenaphthene(3)	<1	<1	<1	<1	<1	<1
Fluorene(3)	4.4	8.7	3.6	9.9	11.8	3.5
Phenanthrene(3)	3.6	4.4	3.3	4.4	4.7	3.3
Anthracene(3)	2.8	3.6	4.0	3.6	3.7	4.4
Fluoranthene(4)	8.7	9.4	7.9	9.8	10.7	7.2
Pyrene(4)	7.5	14.8	7.9	13.1	11.9	7.5

There was a significant difference ($p < 0.05$) between the treatment and the initial level in all cases. There was no significant difference ($p < 0.05$) between planted and unplanted treatments.

Table 4
PAH percentage recoveries after 12 weeks plant growth in soil treated with coal tar.

PAH (rings)	Unplanted	<i>Festuca arundinacea</i>	<i>Festuca rubra</i>	<i>Lolium perenne</i>	<i>Trifolium pratense</i>	<i>Trifolium repens</i>
Naphthalene(2)	5	6	6	8	6	5
Acenaphthylene(3)	<1	<1	<1	<1	<1	<1
Fluorene(3)	23	<1	<1	<1	<1	<1
Phenanthrene(3)	23	7 ^a	5 ^a	8 ^a	7 ^a	4 ^a
Anthracene(3)	18	15	12	9	19	6 ^a
Fluoranthene(3)	61	21 ^a	11 ^a	20 ^a	22 ^a	11 ^a
Pyrene(4)	62	24 ^a	16 ^a	21 ^a	23 ^a	18 ^a
Benzo[a]anthracene(4)	67	45 ^a	36 ^a	47	56	33 ^a
Chrysene(4)	75	55 ^a	51 ^a	61	64	47 ^a
Benzo[b]fluoranthene(5)	84	67 ^a	95	81	71 ^a	90
Benzo[k]fluoranthene(5)	73	68	80	77	72	71
Benzo[a]pyrene(5)	71	69	88 ^a	75	69	76
Dibenzo[a,h]anthracene(5)	69	66	86 ^a	77	72	76
Benzo[g,h,i]perylene(6)	79	73	92	79	72	86
Indeno[1,2,3-c,d]pyrene(6)	75	76	75	88	80	76

All PAHs were significantly reduced ($p < 0.05$) compared to the initial level in both planted and the unplanted soils.

^a Indicates a significant difference ($p < 0.05$) between planted and unplanted treatments

Table 5
PAH percentage recoveries after 12 weeks plant growth in coking works soil.

PAH (rings)	Unplanted	<i>Festuca arundinacea</i>	<i>Festuca rubra</i>	<i>Lolium perenne</i>	<i>Trifolium pratense</i>	<i>Trifolium repens</i>
Phenanthrene(3)	83	89	82	89	89	89
Anthracene(3)	76	85	85	67	45 ^a	88
Fluoranthene(4)	81	86	80	84	90	79
Pyrene(4)	87	87	86	87	95	84
Benzo[a]anthracene(4)	79	82	76	78	78	74
Chrysene(4)	87	88	79	86	94	79
Benzo[b]fluoranthene(5)	89	90	85	88	96	86
Benzo[k]fluoranthene(5)	85	84	79	83	84	76
Benzo[a]pyrene(5)	85	86	82	84	89	89
Dibenzo[a,h]anthracene(5)	76	76	63	75	80	63
Benzo[g,h,i]perylene(6)	93	91	84 ^a	87	95	82 ^a
Indeno[1,2,3-c,d]pyrene(6)	79	83	76 ^a	78	84	75 ^a

^a Indicates a significant difference ($p < 0.05$) between planted and unplanted treatments.

4. Discussion

In our study the addition of a 7 PAH mixture resulted in a rapid and similar degree of reduction in the levels of all 7 PAHs (Table 3). Despite the stabilisation period after soil treatment and prior to setting up the greenhouse experiment it is possible that volatilization could remain a mechanism for naphthalene loss but is less likely for the other, less volatile, PAHs. The decline in PAH levels is attributed primarily to microbial breakdown though it is possible that there may have been some irreversible adsorption onto the soil or other abiotic loss mechanism. Sun et al. [20] showed large abiotic losses of phenanthrene and pyrene from a freshly spiked sterile soil to which they were unable to attribute a mechanism. There was no effect of plants when compared with the unplanted treatment, however, this may have been due to the very rapid loss of PAHs.

Addition of the PAHs in a complex coal tar mixture (Table 4) resulted in distinct differences in the behaviour of the component PAHs. Because of the larger number of PAHs tested it is possible to make comparisons between PAHs. The 2 and 3 ringed PAHs declined more rapidly than the 4, 5 and 6 ringed compounds and at a rate comparable with the previous experiment. Reduction is attributed primarily to microbial breakdown and adsorption onto soil with the lower molecular weight PAHs being more easily degraded. Fluoranthene and pyrene declined more slowly in the coal tar mixture than in the pure PAH mixture. Other components present in the coal tar mixture such as BTEX and phenols, its greater complexity or its physical form might influence microbial degradation compared to the 7 PAH mixture. Several examples

have been reported of competitive inhibition between PAHs in mixtures [21]. Clear phytoremediation effects were observed mainly for phenanthrene and the 4 ringed PAHs where dissipation in the unplanted treatment was much slower than for the lower molecular weight PAHs allowing the effect of planting to be seen. No effect of plants was observed for the 5 and 6 ringed PAHs where microbial degradation is very slow, however, Soleimani et al. [22] reported a small increase in the rate of loss of the high molecular weight 5 and 6 ringed PAHs in the presence of plants in comparison to an unplanted control treatment in their greenhouse study. They suggested that the high molecular weight PAHs do not serve as an energy source for microorganisms but are broken down by co-metabolism in which case plant stimulation of the microbial population would be expected to have a beneficial effect.

Much of the literature has focussed on spiking good quality agricultural soils with individual or mixtures of a small number of pure PAHs and comparing their disappearance in vegetated and non-vegetated treatments. A wide range of plant species has been tested in such pot experiments but this approach has met with mixed success. Many studies have found rapid microbial breakdown and clear phytoremediation effects in pot experiments using soils freshly spiked with PAHs, including the more recalcitrant 5 and 6 ringed PAHs [8,11,23–25]. There is, however, the criticism that freshly applied PAHs may not behave in the same way as aged residues in historically contaminated soils. Soils from contaminated sites have been used in some greenhouse pot experiments and in situ bioremediation techniques including phytoremediation have been examined in a small number of large field trials. Successful phytoremediation of a range of low and high molecular

weight PAHs in soils from contaminated sites such as gas and coke works has been demonstrated in greenhouse experiments using tree species [26,27] and grasses and legumes [28] and in field experiments [5,14]. The high variability and poor physical properties of soils from contaminated sites mean that usually soil aggregates are broken down and the soil homogenized to reduce variability and improve physical conditions in preparation for laboratory and greenhouse studies. Joner et al. [29] pointed out this produces very different conditions and often results in a flush of PAH degradation. They found that in a soil historically contaminated with creosote the 3, 4 and 5 ringed and to a lesser extent 6 ringed PAHs were highly bioavailable as a result of soil disturbance. This was attributed to the breakdown of aggregates, improved aeration and the loss of inhibitory volatiles. These effects could influence or mask the effects of plants grown in the soil and therefore not reflect what occurs in field conditions. Consequently, the present study used a stabilization period of 4 weeks following the soil preparation to reduce the effects of soil disturbance.

The results for the unplanted control soil are shown in Table 5. The loss of the 3 ringed PAHs (phenanthrene and anthracene) plus fluoranthene and pyrene was similar in magnitude to that of the higher molecular weight PAHs but due to the greater variability was not statistically significant. The low molecular weight PAHs such as naphthalene were not present so losses due to volatilization are not considered significant. The main loss mechanism is likely to be microbial degradation which would be controlled by the size of the PAH degrading microbial population, the activity of the population and the bioavailability of the PAHs. The stabilisation period was used to minimise any flush of degradation resulting from increased bioavailability due to soil disturbance and desorption of PAHs in soil preparation which could create an artificially high degradation rate. PAHs in contaminated soil such as gasworks are very recalcitrant under field conditions even though there are often large numbers of PAH decomposing microorganisms present. Alexander [30] details the effects of ageing on bioavailability as organic molecules such as PAHs within soils and sediments are sequestered in tiny pores and sorbed to hydrophobic molecules in the organic matter. Therefore they are inaccessible either to microorganisms or even to their extracellular enzymes. It follows then that diffusion from these sites would be very slow. In addition Hong et al. [31] showed that PAHs adsorb more strongly to the anthropogenic carbon forms that may be present in contaminated soil as a result of oil and gas manufacturing processes than to natural soil organic matter therefore reducing their water solubility and consequently bioavailability.

There was no clear evidence for phytoremediation in the coking works soil (Table 5). For phytoremediation to be effective plant roots must increase the bioavailability of PAHs by facilitating contact between microorganisms and contaminants and not just increase microbial activity. As a phytoremediation effect was observed with the coal tar treatment but not with the coking works soil this suggests that the presence of plant roots did not increase the bioavailability of the PAHs in the coking works soil.

5. Conclusions

This study demonstrates clearly that in soils spiked with pure PAHs or coal tar the rate of loss of PAHs is much greater than in historically contaminated soils. Thus studies on freshly spiked soils do not inform us with realistic time frames for the degradation of historically contaminated land. In pure PAH spiked soil we saw no evidence of phytoremediation. In the coal tar spiked soil the 3 and 4 ringed compounds from fluorene to chrysene demonstrated strong evidence of phytoremediation. However, in the historically contaminated soil there was very little evidence of phytoremediation.

There were clear differences in the losses of the PAHs depending on ring size amongst the 16 PAHs tested.

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