

# Behavior of Sewage Sludge-Derived PAHs on Pasture

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A field experiment was set up to investigate the retention of PAHs by pasture grass following sludge application. In addition to information on compound-specific loss rates, the influence of meteorological variables and sludge–pasture contact time on the weathering process were investigated. The rates of loss were compound specific with half-lives ranging from <1 to 10 d. The lighter PAHs were rapidly lost from the grass surface primarily by volatilization. For the intermediate and heavier PAHs, loss was slower with rain playing an important role in the weathering process. Growth dilution was also important in reducing the contaminant levels in the grass. The effect of sludge–pasture contact time prior to weathering by rain on the residual levels remains unclear. In terms of risk of exposure, there is the potential for persistent organic contaminants to be introduced into the grazing animal food chain if sewage sludge is applied to pasture land.

## Introduction

The concentrations of organic contaminants in vegetation are influenced by several processes, summarized in Figure 1. Several inputs can potentially contribute to the burden of chemical associated with the plant. Most notably these include atmospheric deposition and transfers from the soil. Several factors can dilute or remove compounds from the plant, including growth dilution, particle wash-off, volatilization, photodegradation, and plant metabolism. The concentration of chemical remaining on the vegetation over time potentially supplies terrestrial food chains, such as the pasture grass → grazing livestock → human pathway. Hence, several studies have sought to provide understanding of the processes that influence plant concentrations, focusing on the air–plant (1–6) and soil–plant (1, 7–10) transfer routes of persistent, semivolatile, and bioaccumulative compounds. These have generally shown that air–plant transfer via dry gaseous, particulate, and wet deposition dominates the supply of semivolatile organic contaminants (SOCs) (such as PCBs, PCDD/Fs, and PAHs) to the above-ground portions of plants. Root uptake from soil and translocation of such hydrophobic compounds are usually inefficient processes (1, 8–10).

In certain circumstances there can be additional inputs to the above-ground portions of plants, such as from the spraying of pesticides or the application of sewage sludge to agricultural land. These activities can also introduce poten-

tially toxic chemicals into the human food chain. Sewage sludge amendment of agricultural land is an important and economic disposal route, which also brings associated benefits through the recycling of nitrogen, phosphorus, and organic carbon to soils and hence improved crop yields. Most industrialized countries therefore deliberately apply sewage sludge to agricultural soils, typically to arable land but also sometimes to pasture grassland.

Sewage sludge contains other substances, notably heavy metals and trace organic contaminants, that partition onto the sludge solids during the wastewater treatment process. Hence, sludge amendment of soil can potentially introduce trace contaminants directly into agricultural food chains. Regulatory measures have therefore been put into place in Europe, North America, and elsewhere by the appropriate authorities to limit the amounts of sludge and the chemical contaminants entering agricultural soils. These limits have primarily been set for heavy metals, with very few countries setting limits for organic contaminants to date. This is because (i) there is still a lack of detailed data on the levels, fate, and behavior of organic contaminants in sewage sludges and sludge-amended soils that has hindered the risk assessment process; (ii) the regulation of organic contaminant limits would be extremely costly; and (iii) there is a lack of consensus on whether limits are necessary/beneficial (11–14).

Quantitative pathways analyses show that if sludge is applied to arable land, there is very little likelihood that persistent organic contaminants will enter the food chain via crop uptake (8–11). A more important pathway is if sludge is applied to pasture land (15–19). In this situation, some organic compounds may potentially transfer and bioaccumulate in grazing animals, either because some sludge may remain adhered to the vegetation itself or because animals can accidentally ingest surface soil as they feed (19–22). This pathway is also important for the transfer of some heavy metals and a potential concern for pathogen transfer. Some countries, such as the United States, have decided not to allow the addition of sludge to pasture land, while others impose a “no grazing” period to allow time for the sludge to be washed off/removed from the vegetation surface and incorporated into the soil. In the U.K., this no-grazing ban is 3 weeks, and concerns have been expressed that this period may be too short to allow complete removal of the sludge-borne contaminants from the pasture under the range of environmental conditions that may be experienced in the field.

Potential compound loss pathways from the sludge-treated surface include the following: volatilization from the plant surface, windblow and/or wash-off of the sludge cake, photolysis, cuticular shedding, biodegradation by leaf microflora, etc. Retention of sludge particulates and the associated organic contaminants will presumably be influenced by the pasture type, the lifecycle stage of the plants, and the timing of application. Plants growing close to the soil surface, those with growth forms that are effective at intercepting particles, or those contaminated by the trampling activities of grazing animals will presumably have the highest concentrations of soil/sludge particles and, therefore, the greatest potential to be contaminated. An additional uncertainty centers on the fate of sludge-borne SOC on the leaf surface: do they remain associated with the sludge particles, or can they partition off the sludge and into the plant cuticular waxes?

To address the general gap in the literature on the fate of SOC in sludge-amended pasture and hence inform the regulatory decision-making process, we conducted a field

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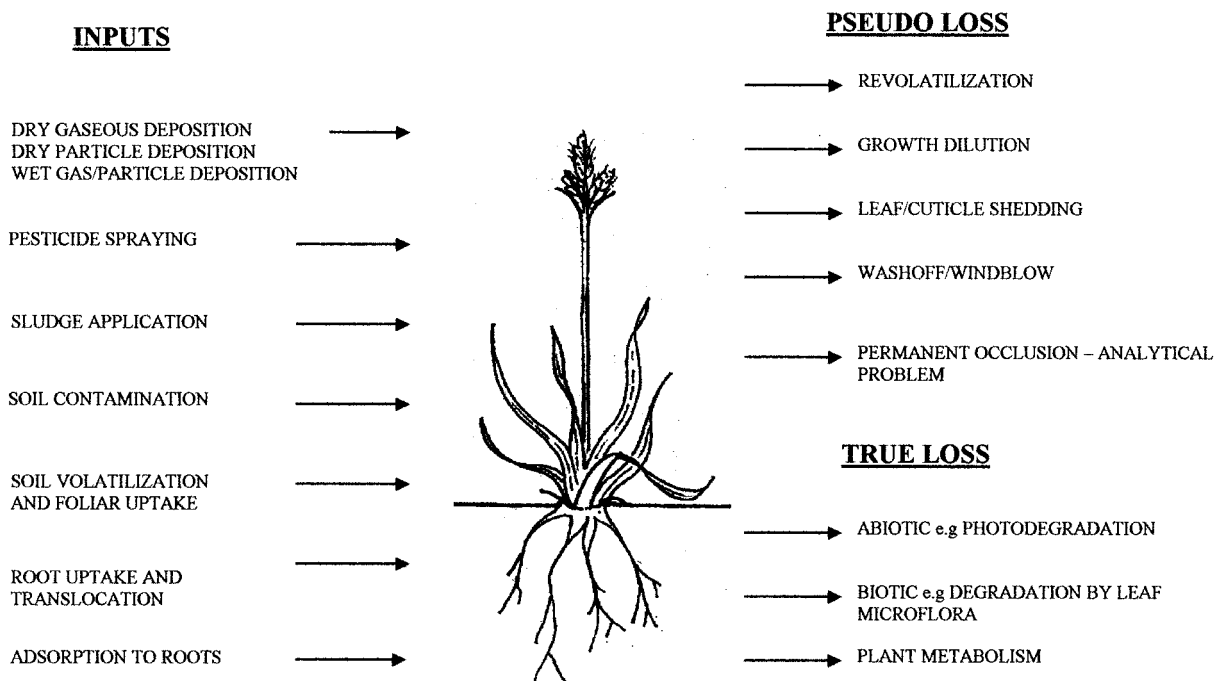


FIGURE 1. Uptake and loss pathways of SOC by vegetation.

study simulating standard U.K. agricultural practices. We monitored the loss of PAHs from the pasture surface following sewage sludge application. PAHs were chosen because they are ubiquitous in sludge and have a wide range of physicochemical properties (23) and a validated method was in place for their analysis in vegetation in our laboratory (24). In addition to monitoring loss and making inferences about the loss processes, we also investigated (i) the influence of meteorological variables that may affect removal rates in the field and (ii) the effect of sludge–pasture contact time on PAH loss rates. Potential confounding factors that needed to be addressed in the study were the supply of PAHs via atmospheric deposition and the stimulation of pasture growth arising from sludge addition.

## Materials and Methods

**Field Plot.** The field plot was set up on an established sward of unimproved upland pasture at a semirural field station site owned by Lancaster University in northwest England. The species mix of the sward was *Lolium perenne* (~30%), *Holcus lanatus* (~30%), *Agrostis capillaris* (~10%), *Poa pratensis* (~10%), *Cynosurus cristatus* (~10%), and a range of other grasses and forbs. An area of pasture 10 m × 10 m was fenced off, and the sward was cut down to ground level. This area was divided into 0.6 m × 0.6 m plots, each individual plot corresponding to one treatment/replicate. The experiment was set up using a randomized design, and three replicate samples, each from a different plot selected at random, were taken for each time/treatment point.

Five treatments were prepared: (i) control, where no sewage sludge was added; (ii) exposed, where the sward had sewage sludge added but was left uncovered and exposed to the prevailing environmental conditions; (iii) sheltered, where the sward had sewage sludge added but was immediately protected from the rain using shelters; (iv) sheltered for 1 week and then exposed; (v) sheltered for 2 weeks and then exposed. The latter two treatments were designed to investigate the effect of contact time between the PAHs in the sludge and the grass surface prior to any rain/wash-off. The treatments are hereafter referred to as control, exposed, shelter, 1 week, and 2 week, respectively. The shelters used to protect the sward from the rain consisted of a wire netting

frame with a polyethylene covering situated at 25 cm above the sward surface. They were open on all sides, allowing air to circulate freely underneath, thereby minimizing wind and temperature artifacts.

The native sward was cut back in May 1997 prior to the experiment and left for 3 d. Digested sludge (4% dry wt, DW) from a semi-urban wastewater treatment plant was collected directly from the tanker truck supplying the sludge to the land and immediately applied to the appropriate plots on day 0 at a loading of 0.04 kg m<sup>-2</sup> using a watering can fitted with a rosette to ensure even application of the sludge. This is similar to the average loading rate of sludge to grassland in the U.K. of 0.29 kg m<sup>-2</sup>. During subsequent sampling on days 1, 3, 4, 5, 7, 11, 14, 16, 19, 22, 28, and 34, the pasture was cut using hand-held shears to 2 cm above the base of the sward to avoid soil contamination. Immediately after harvest the yield (g/m<sup>2</sup>) was recorded, a subsample was taken for dry weight determination (see below), and the grass was stored in polyethylene bags in a freezer at -25 °C until analysis as described below. It was stored unwashed to represent its condition in the field. Background air samples were collected to coincide with the grass samples using a conventional high-volume sampler, separating the PAH gas and particle phases. Several papers have been published on the measurement of PAHs at this site using high-volume air samplers (25, 26). Rainfall and temperature data were obtained throughout the experiment from a meteorological station operating at the site. The experiment was run over 34 d.

**Materials Used.** All solvents used were of HPLC or glass distilled grade. Silica gel (Merck, Silica gel 60, 0.063–0.200 mm) for the fractionation of the air samples was activated at 350 °C overnight. Silica gel (Aldrich, grade 923, 100–200 mesh) for the vegetation cleanup precolumn was activated at 700 °C for 18 h. Alumina (Sigma, type F-20, 80–200 mesh) was activated by storing for a minimum of 24 h at 120 °C prior to use. Anhydrous granular sodium sulfate (BDH, Analar) was baked at 450 °C overnight. All sorbents were stored in sealed containers at 120 °C until just prior to use. Bio-Beads SEC column packing (Bio-Rad Laboratories, S-X3 beads, 200–400 mesh) were swollen in 1:1 hexane:DCM overnight before use.

The pre-extraction grinding of the sludge-amended pasture was carried out using a Waring stainless steel commercial blender. For Soxhlet extraction, the samples were loaded into Whatman cellulose extraction thimbles that had been pre-extracted in DCM for 6 h. An all-glass Quickfit Soxhlet system was used in conjunction with an electro-thermal heating mantle. Samples were concentrated on a Büchi rotary evaporator equipped with a Haake–Fisons cooler and water bath held at 32 °C. All laboratory glassware was baked at 450 °C and/or solvent rinsed prior to use.

PAH target compounds were purchased as a mixture in toluene (Standard Reference Material 2260) from the National Institute of Standards and Technology (NIST). Deuterated surrogate and internal standards were obtained as crystalline standards from CDN Isotopes, Canada. 1,3,5-Triphenylbenzene was obtained as a crystalline standard from Sigma–Aldrich, U.K.

**Extraction and Cleanup.** *Grass.* A total of ~25 g of sludge-amended grass was frozen using liquid nitrogen and ground up with ~50 g of sodium sulfate. A 50-ng sample of each individual deuterated surrogate PAH was added, and the grass was Soxhlet extracted in DCM for 4 h. Cleanup was by a silica–alumina precolumn, followed by size exclusion chromatography (SEC). After final concentration of the sample, deuterated PAH internal standards were added prior to analysis by GC–MS. For each replicate, a subsample was taken for DW analysis. The sample was dried in an oven at 120 °C until a constant weight was recorded. The analytical method has been described in detail elsewhere (24).

*Sludge.* A total of ~2.5 g of centrifuged sludge solids (14% DW) was ground up with ~40 g of sodium sulfate using a pestle and mortar. A 100-ng sample of each individual deuterated surrogate PAH and copper turnings was added, and the sludge was Soxhlet extracted in DCM for 4 h. Cleanup and analysis were as described above for grass.

*Air.* The glass fiber filters and PUF plugs were spiked with 100 ng of each individual deuterated surrogate PAH prior to being Soxhlet extracted for 12 h in hexane. Fractionation and cleanup was by a 3-g silica column. After final concentration of the sample, deuterated PAH internal standards were added prior to analysis by GC–MS.

**Instrumental and Data Analysis.** The GC–MS analyses were performed using a HP 5890 Series II GC equipped with a 30-m HP5MS column (0.25 mm i.d. and 0.25 µm film thickness) and 2 m deactivated HP retention gap (0.53 mm i.d.). This was connected to a HP 5972 MSD operating in selected ion monitoring mode (SIM), with the electron energy at 70 eV, the EI source held at 176 °C and the interface temperature at 300 °C. Cool on-column injection of a 1-µL sample was performed using an automatic HP 7673 injector. The injector program was 60 °C for 0.05 min, 25 °C min<sup>-1</sup> to 300 °C, which was held for 7.5 min. The oven temperature program was 60 °C for 1 min, 20 °C min<sup>-1</sup> to 130 °C, and 6 °C min<sup>-1</sup> to 310 °C, which was held for 15 min. The injector pressure was 11 psi for 1 min, 0.5 psi min<sup>-1</sup> to 27.5 psi, and 20 psi min<sup>-1</sup> up to a final pressure of 35 psi held until the end of the run. Helium was used as the carrier gas.

The compounds analyzed and the abbreviations used in the text are now listed. Those compounds marked in *italics* were used as the internal standards, the compounds in **bold** as the surrogate standards: *naphthalene-d8*, *Nap-d8*; naphthalene, Nap; 2-methylnaphthalene, 2mNap; **1-methylnaphthalene-d8**, **1mNap-d8**; 1-methylnaphthalene, 1mNap; biphenyl, Biph; 2,6-dimethylnaphthalene, 2,6dmNap; acenaphthylene, Acy; *acenaphthene-d10*, *Ace-d10*; acenaphthene, Ace; 2,3,6-trimethylnaphthalene, 2,3,6tmNap; **fluorene-d10**, **Fl-d10**; fluorene, Fl; *phenanthrene-d10*, *Phen-d10*; phenanthrene, Phen; **anthracene-d10**, **Anth-d10**; anthracene, Anth; 1-methylphenanthrene, 1mPhen; *fluoranthene-d10*, *Fluo-d10*; fluoranthene, Fluo; **pyrene-d10**, **Py-d10**; pyrene,

Py; **p-terphenyl-d14**, **pTerph-d14**; *benzo[a]anthracene-d10*, *BaA-d10*; benz[a]anthracene, BaA; chrysene, Chry; benzo[b]fluoranthene, BbF; benzo[k]fluoranthene: BkF; benzo[e]pyrene, BeP; **benzo[a]pyrene-d12**, **BaP-d12**; benzo[a]pyrene, BaP; *perylene-d12*, *Per-d12*; perylene, Per; 1,3,5-triphenylbenzene, 135TPB; indeno[123-cd]pyrene, IP; dibenz[ah]anthracene, DahA; **benzo[ghi]perylene-d12**, **BghiP-d12**; and benzo[ghi]perylene, BghiP. A detailed list of the ions monitored for the PAH analysis has been given in Smith et al. (24).

**Quantification.** Each ring class of PAHs had its own individual surrogate standard and internal standard. The surrogate standard solution was applied to the sample immediately prior to extraction to produce recovery data for QA purposes. The internal standard solution was added to the cleaned-up sample extract prior to transfer to the GC vial, to correct for sample volume and instrument variation. The parent and surrogate analytes were quantified against the appropriate internal standard.

An internal standard quantification procedure was used using HP Environmental Data Analysis software. A total of 11 standards was available to provide a concentration range of ca. 1–2500 pg/µL. Because of the nonlinearity in the MS response with concentrations ranging over 3 orders of magnitude (in particular for the heavier MW PAHs), the calibration was split up into two linear ranges: 1–100 and 100–2500 pg/µL. All samples were quantified on each of the two calibrations, and the final result was selected at the appropriate cutoff point between the above two calibration graphs using a logic function in the data spreadsheet. At the overlap of the two calibration graphs, the results obtained by the high and low quantification methods were the same.

Average recoveries for the grass analysis were 1mNap-d8, 90% (RSD 15%); Fl-d10, 98% (RSD 6%); Anth-d10, 106% (RSD 17%); Py-d10, 106% (RSD 7%); pTerph-d14, 109% (RSD 6%); BaP-d12, 129% (RSD 15%); BghiP-d12, 111% (RSD 20%). Average recoveries for the sludge analysis were 1mNap-d8, 99% (RSD 2%); Fl-d10, 102% (RSD 3%); Anth-d10, 118% (RSD 3%); Py-d10, 108% (RSD 1%); pTerph-d14, 102% (RSD 1%); BaP-d12, 104% (RSD 1%); BghiP-d12, 117% (RSD 2%). The high recoveries (yet good reproducibility) seen for the analysis of the heavier compounds in the grass, in particular BaP, are a matrix specific analytical phenomenon; the reasons for this have been discussed elsewhere (24).

The data below are **not** recovery corrected. In each batch of six samples, one was a blank. The data are all blank corrected using the appropriate batch blank value. Method detection limits have been defined in detail in Smith et al. (24).

All grass data are expressed on a dry weight basis. Expressing results on a lipid weight basis is fraught with problems because of the difficulties in relating the amount of extractable material (usually operationally defined by extraction of the vegetation using organic solvents, e.g., refs 27 and 28) to a meaningful physical entity such as the plant SOC sorption compartment. Expression of the results on a lipid basis is also only valid when the contaminant concentration varies in direct proportion to the lipid content; otherwise erroneous conclusions may be reached (29, 30). In particular, this is an issue for those particle-bound compounds, for which plant uptake is not directly affected by the quantitative and qualitative nature of the cuticular lipids.

## Results and Discussion

**Composition of the Sewage Sludge.** The concentrations of the individual PAHs in the digested sewage sludge applied to the grass sward are shown in Figure 2a. The total PAH (24 compounds) concentration was 45 mg/kg DW (RSD = 9%, *n* = 5). The digested sludge had a DW content of 3.9% (RSD



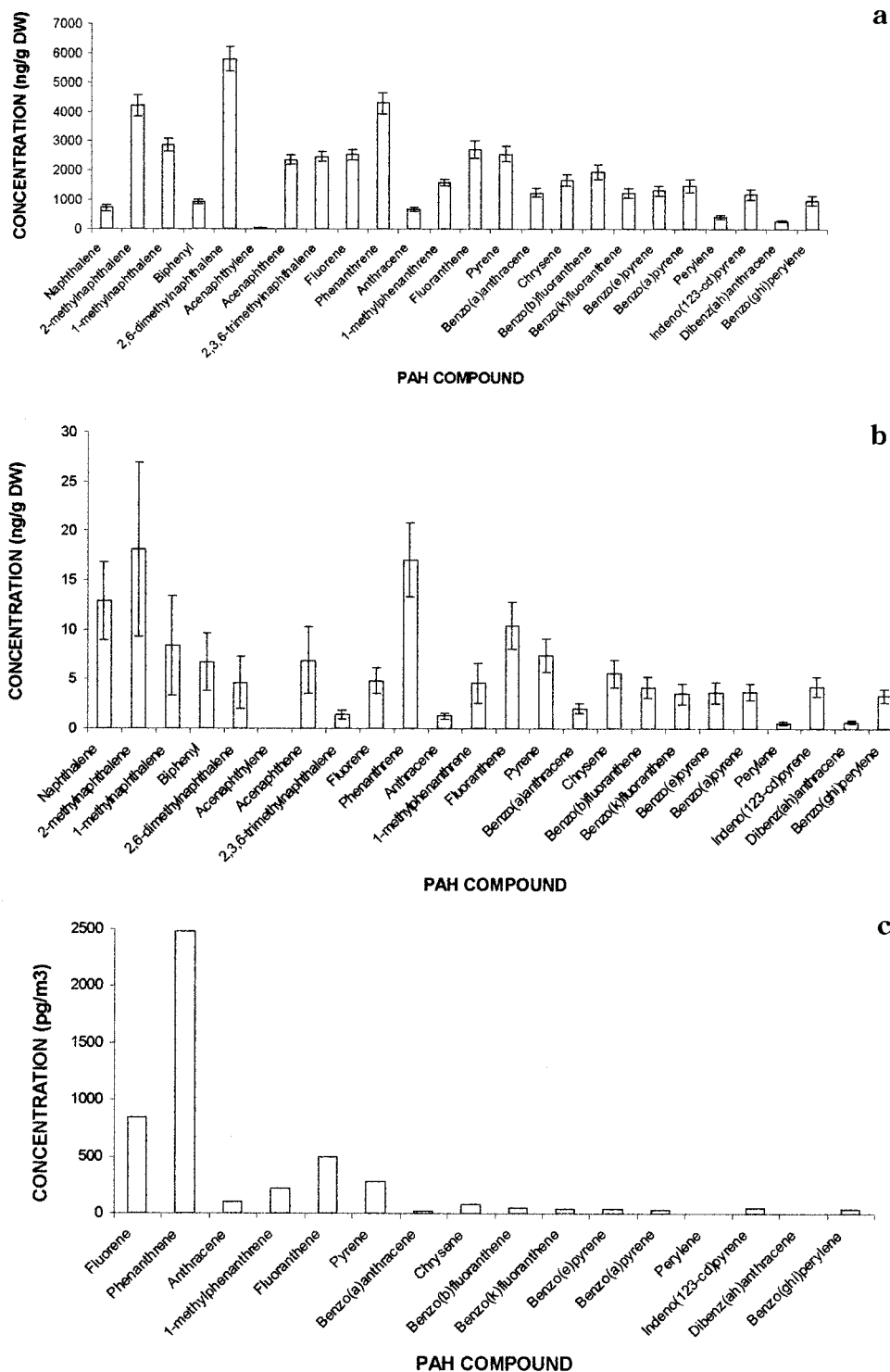


FIGURE 2. (a) PAH profile for the sewage sludge. Error bars represent 1 standard deviation. (b) Average PAH profile over the experimental period for the control grass. Error bars represent 1 standard deviation. (c) Average PAH profile over the experimental period for the air (vapor and particle). Note air data from fluorene onward only.

= 0.1%,  $n = 5$ ). These values are typical of those for digested sewage sludge arising from a semi-urban catchment (31).

**Grass Yields.** Figure 3 shows the changes in grass yield for three treatments (control, exposed, shelter) over the course of the experiment. The apparent yields of the sludge-amended grass treatments were elevated above that of the control at  $t = 0$ , as a result of the sludge amendment (~40 g/m<sup>2</sup> solids added). Over the experimental period, the increased yield relative to the control, as a result of this initial retention of sludge solids, is maintained. Therefore, it appears that some

of the sludge solids remain attached to the grass surface for prolonged periods after application. However, the actual rates of growth were similar in the sludged and control plots. This needs to be borne in mind in the subsequent discussion.

**Control Plot PAH Concentrations.** The average total PAH concentration of the pasture from the control plot was 136 ng/g (DW), typical for a semirural location (3–5). The control plot PAH concentrations showed some variation over time, but this was only within a factor of 2. These changes will reflect interactions between the vegetation and air, primarily

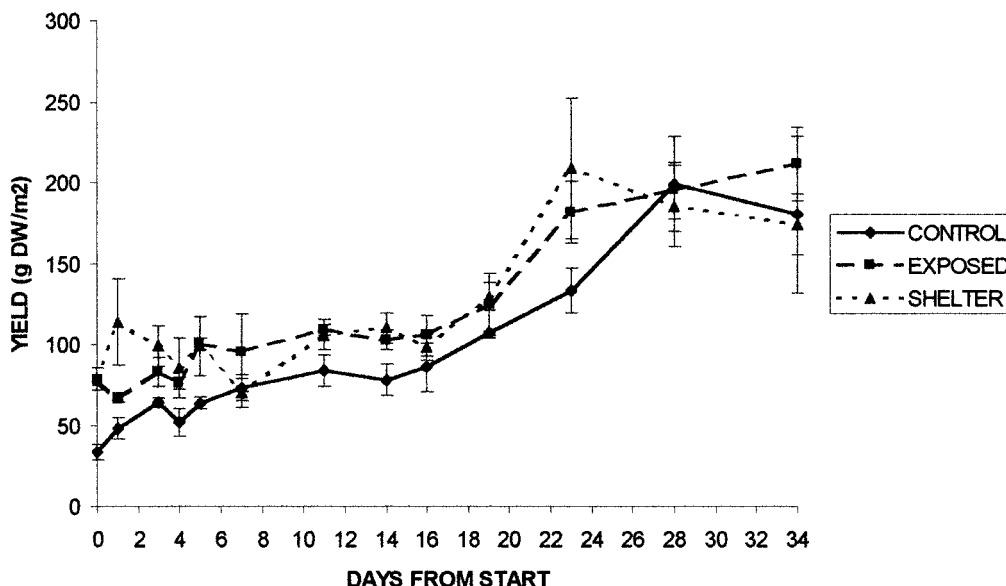


FIGURE 3. Grass yields for the control, exposed, and shelter treatments. Error bars represent 1 standard deviation.

via deposition/volatilization (2) but also because of the influence of some of the other processes highlighted in Figure 1. As expected, the PAH composition of the control plot grass (Figure 2b) broadly reflects the mixture of compounds present in the air (Figure 2c). Acy occurred at levels below the method detection limits in the control grass. The fractionation method used for the cleanup of the air samples resulted in the five lightest PAHs (Nap, 2mNap, 1mNap, Biph, and 2,6dmNap) being lost in the first fraction. Therefore, the air PAH profile does not include these compounds. The grass profile is dominated by the lighter compounds (i.e., Nap, 2mNap, and Phen), which are predominantly in the gas phase in air. It is possible that air–pasture interactions may have been different for the various treatments. For example, the use of shelters may affect the deposition of particle-bound PAHs to the grass surface, and the presence of sludge-derived PAHs on the grass surface may influence the equilibration process with the atmosphere.

**Composition of Grass Immediately prior/after Sludge Amendment.** The total PAH concentration of the grass was increased by a factor of ca. 30, to 3700 ng/g DW, immediately after sludge addition to the treated plots. All the compounds increased in concentration, although the size of the increase varied from a factor of 3 (Nap) to >140 (2,6dmNap), reflecting the abundance of compounds in the sludge (Figures 2a and 4a). Despite the addition of sludge, the control and sludge-treated plots had a broadly similar mixture of PAHs at  $t = 0$ , although there were some differences between the profiles primarily for the lighter two-ring PAHs. This would indicate a similar source of PAHs to these different matrixes for the intermediate and heavier PAHs. Atmospheric deposition would be the obvious contender, directly supplying the grass sward and the wastewater treatment plant catchment.

Because the sludge application rate and PAH concentrations were known, it was possible to calculate the mass of each compound applied per square meter to the treated plots and to compare this to the mass actually found on pasture at the beginning of the experiment. The difference gives the amount that was not retained by the pasture, moving directly to the soil. This calculation showed that only a small proportion was retained by the pasture, varying between 8 and 26% for individual compounds. The greatest retention was for the high molecular weight compounds.

**Comments on the Field Conditions through the Experiment.** Figure 5 shows the temperature, rain, and cumulative

rain over the course of the experimental period. In particular, it is instructive to note that there was no rain over the initial 2 weeks of the experiment. This will of course have profound implications on the weathering processes between the treatments, which were designed to differentiate the effects of rain from other loss mechanisms. This is discussed further below. Temperature conditions were typical of those in late spring/early summer in the U.K., when sludge application to land most commonly takes place.

#### PAHs on Amended Pasture at End of the Experiment.

To give an initial impression of the trends on sludge-treated plots over time, Figure 4b shows the absolute concentrations on the control, exposed, and shelter plots at  $t = 28$  d. It is immediately apparent that there was a substantial reduction in PAH concentrations on both treated plots over time (compare to Figure 4a, for example). Total PAH concentrations on the exposed and sheltered plots had declined to only 2 and 4 times those on the control pasture, respectively, at the end of the experiment. This reduction varied between individual compounds and treatments. Generally, lighter PAHs declined rapidly to background levels during the study, while the intermediate and heavier PAHs declined more slowly, so that they remained elevated above background after 28 d. There were differences in the rates of removal of intermediate and heavier compounds between the two treatments; as expected, rain increased removal rates (see Figure 4b). The minor yield (growth dilution) differences noted earlier were insufficient to explain the treatment differences. This is discussed further below. It is therefore clear that some SOC residue can persist on pasture beyond the 3-week no-grazing ban imposed in the U.K., under prevailing environmental conditions.

Changes in the contribution of different PAH to the total over time on the different plots were apparent from a comparison of the profiles for  $t = 0$  and 28 d in Figure 4a,b.

**Trends over Time for Selected Compounds and Different Treatments.** It is instructive to compare the trends over time for different compounds. Five individual compounds have been selected for this purpose (namely, Fl, Phen, BaA, BeP, and BghiP). These are 2-, 3-, 4-, 5- and 6-ringed PAHs, respectively; were present at high concentrations in the sludge and treated pasture; and were accurately and reproducibly quantified in all the samples.

Figure 6a,b compares the time course of these compounds on the exposed and sheltered plots. The percentage of the

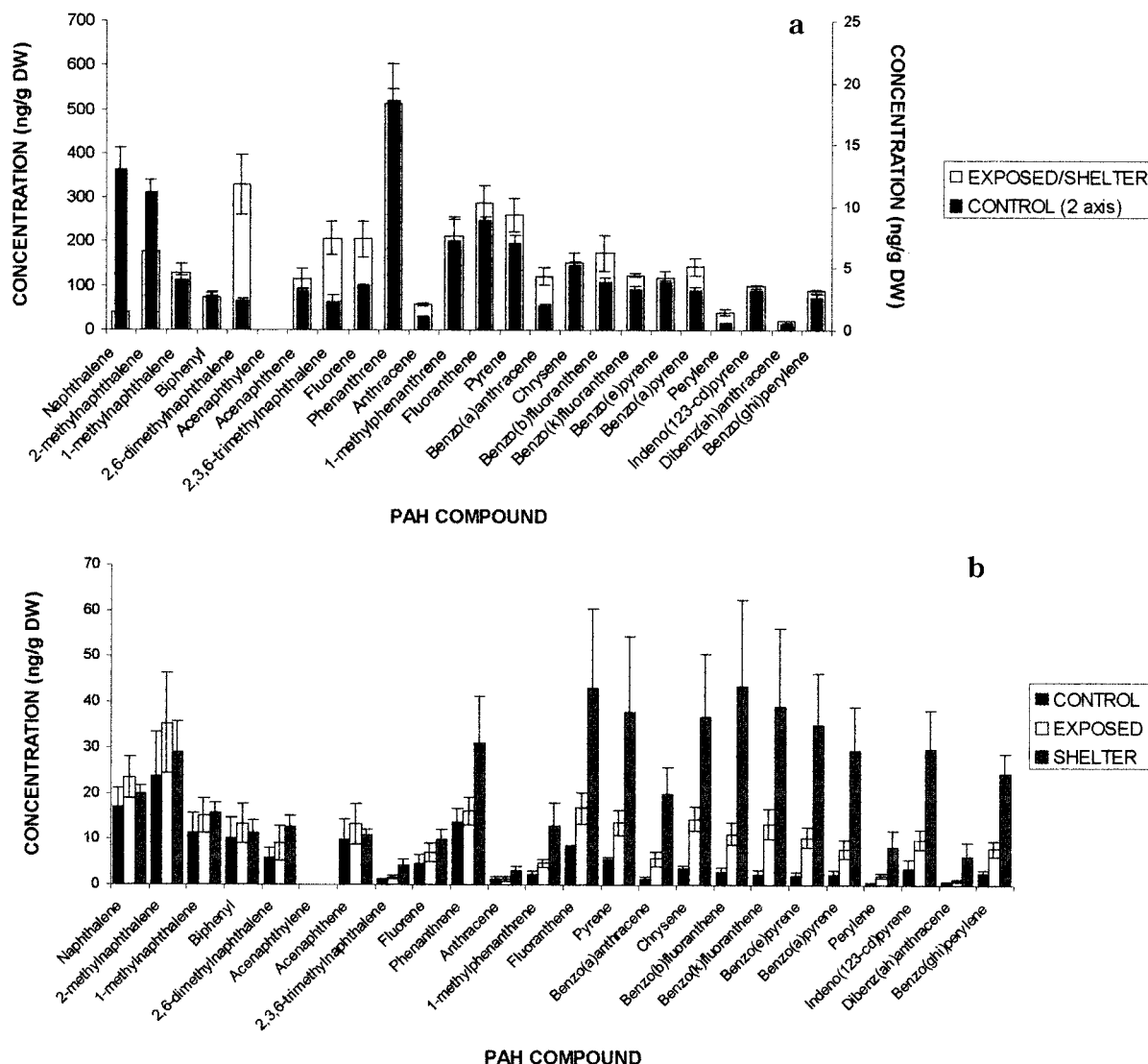


FIGURE 4. (a) PAH grass profile for the control, exposed, and shelter treatments at 0 d. Error bars represent 1 standard deviation. (b) PAH grass profile for the control, exposed, and shelter treatments at 28 d. Error bars represent 1 standard deviation.

$t = 0$  mass loading per unit area that remained at  $t = 1, 3, 4, 5, 7, 11, 14, 16, 19, 22, 28,$  and  $34$  d, after taking account of the background burden on the control plot, are shown in Figure 6. These data show that (i) the lower MW compounds were lost from the pasture surface more rapidly than the heavier MW compounds, Fl and Phen essentially reached background levels in about 2 weeks; and (ii) heavier MW compounds were more persistent on the sheltered plot than the exposed plot, an indication that a portion of the initial mass loading can remain associated with the pasture for a considerable period of time.

**Calculation of Half-Lives.** A useful way to compare treatments more fully is to calculate half-lives for the compounds on the pasture. The decrease in contaminant concentrations (i.e., mass compound/mass vegetation) over time provides an estimate of the "total" loss rate. This can be used to calculate an apparent half-life, although the effect of growth dilution is implicit in the calculations. Nonetheless, the apparent half-life could be used in dose assessment models because livestock graze a given mass of vegetation. An alternative approach is to plot the observed decrease on an inventory basis, i.e., the amount of PAH per unit area of ground. This effectively removes the effect of growth dilution and the half-lives obtained just reflect the various physical and chemical processes removing PAHs from the pasture.

Analysis of the data by forming differences between treatment and control plots would have resulted in correlated data, as the same controls are used for all treatments. This would have invalidated the results from standard statistical analysis, in particular, standard errors would be incorrect. The alternative approach was to model treatment and control data together incorporating a separate parameter for each day of the control data to allow an unstructured model of day-to-day variation. Each treatment had an additional trend over time, which took the form of an exponential decline to a lower bound. The focus of interest was in the parameter measuring the rate of the exponential decline and whether this was different for different treatments. This model is not linearizable by a simple transformation, so the nonlinear model fitting procedures of the statistical software package SPSS Version 10 were required. Preliminary investigation of the data indicated that a log-normal distribution was appropriate, so that analysis was conducted on the assumption of normality of the log-transformed data.

Table 1 shows the half-lives with their associated 95% confidence intervals for the full range of PAHs analyzed (apart from acenaphthylene, which occurred at levels below the method detection limits in the control grass), calculated on both a concentration and an inventory basis. These have also been plotted against  $\log K_{ow}$  in Figure 7a,b for those

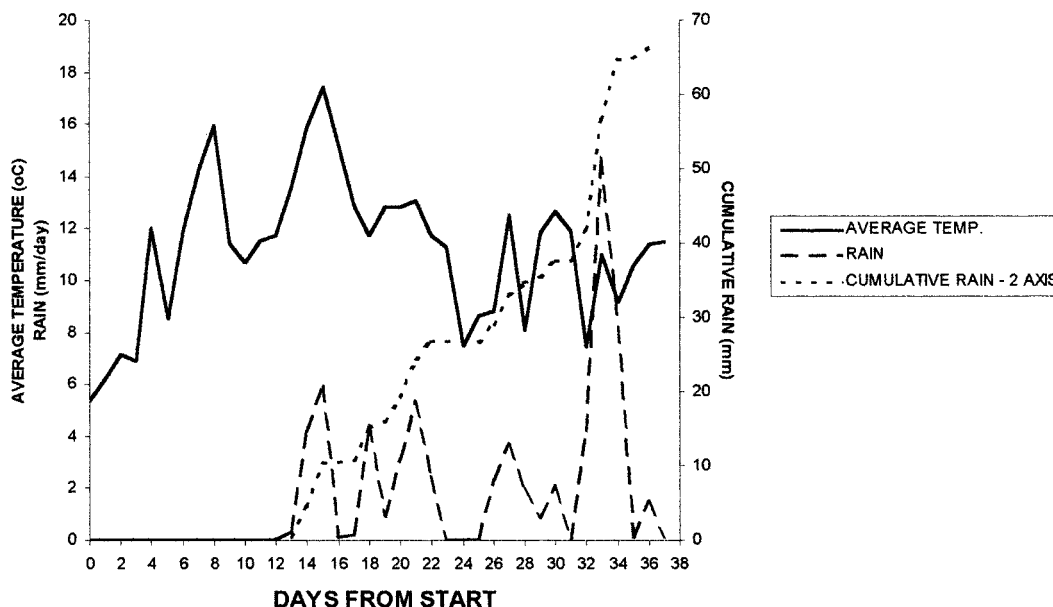


FIGURE 5. Meteorological conditions over the experimental period.

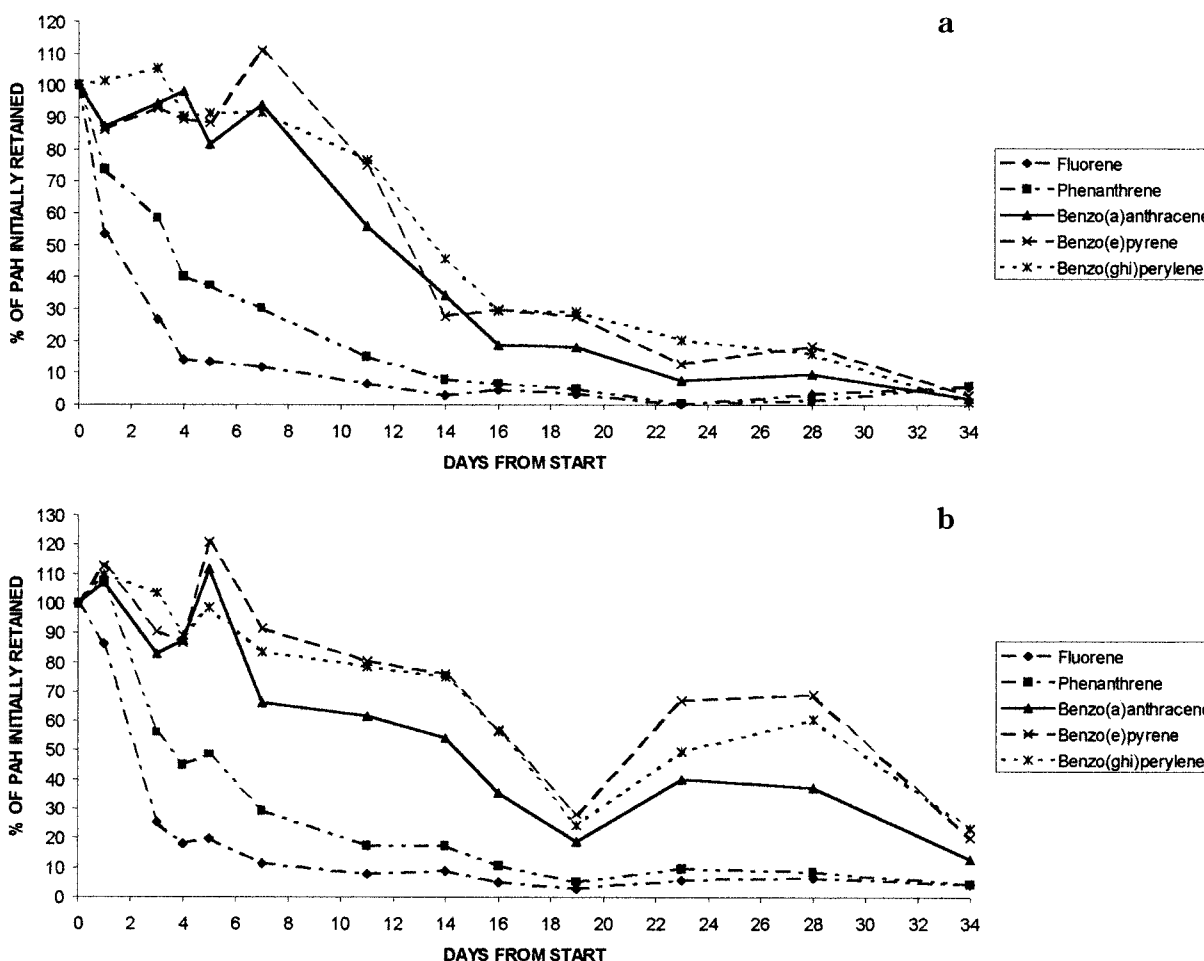


FIGURE 6. (a) Plots of the percentage mass of selected PAHs remaining over time for the exposed treatment. (b) Plots of the percentage mass of selected PAHs remaining over time for the shelter treatment.

compounds for which good  $K_{ow}$  data were available (23).

**Compound Half-Lives.** Comparison of the half-lives for the range of PAHs within a particular treatment shows a trend of increasing half-life with increasing MW (Table 1, Figure 7a,b). This is indicative of either different loss mechanisms or a shift in their importance relative to one

another, as one moves through the compound class. The importance of a particular loss mechanism will of course be influenced by the compound's physicochemical properties. For example, losses by volatilization or leaching from the sludge particles associated with the vegetation will be more important for the lighter MW PAHs.

TABLE 1. Calculated Half-Lives in Days (with Their 95% Confidence Intervals) for Sludge-Derived PAHs on Pasture Grass

	concentration basis						inventory basis					
	exposed			shelter			exposed			shelter		
	half-life	95% min	95% max	half-life	95% min	95% max	half-life	95% min	95% max	half-life	95% min	95% max
naphthalene	0.8	0.5	4.4	0.5	0.3	7.0	1.4	0.9	2.7	2.3	1.5	4.5
2-methylnaphthalene	1.6	1.2	2.2	2.1	1.6	3.0	1.9	1.5	2.7	2.7	2.1	4.0
1-methylnaphthalene	3.1	2.4	4.3	4.1	3.2	5.8	4.3	3.4	6.1	5.7	4.3	8.3
biphenyl	1.4	1.1	1.9	1.7	1.3	2.3	1.7	1.3	2.2	2.2	1.7	3.0
2,6-dimethylnaphthalene	1.6	1.2	2.2	2.1	1.6	3.0	3.7	3.0	4.9	4.89	3.8	6.5
acenaphthylene												
acenaphthene	1.8	1.4	2.4	2.2	1.7	3.1	2.4	1.9	3.5	3.3	2.5	4.8
2,3,6-trimethylnaphthalene	2.7	2.3	3.3	3.7	3.2	4.5	3.2	2.7	3.9	4.4	3.7	5.5
fluorene	2.5	2.1	3.1	3.2	2.8	3.9	3.3	2.8	4.1	4.2	3.6	5.3
phenanthrene	3.6	3.3	3.9	4.6	4.2	5.1	4.3	3.9	4.8	5.7	5.1	3.8
anthracene	3.5	3.2	4.0	4.9	4.4	5.4	4.2	3.7	4.7	6.0	5.3	6.8
1-methylphenanthrene	4.1	3.8	4.5	5.2	4.9	5.7	5.0	4.6	5.5	6.6	6.0	7.3
fluoranthene	5.1	4.7	5.6	7.2	6.5	8.0	6.5	5.9	7.3	10.0	8.9	11.5
pyrene	5.1	4.7	5.6	7.1	6.5	7.9	6.5	5.8	7.3	9.9	8.7	11.4
benz[a]anthracene	5.3	4.9	5.8	7.6	6.9	8.6	6.9	6.0	7.7	11.0	9.6	13.0
chrysene	6.3	5.7	6.9	8.8	7.9	10.0	8.5	7.5	9.8	13.5	11.5	16.4
benzo[b]fluoranthene	6.0	5.4	6.6	9.4	8.3	10.8	7.9	7.0	9.1	14.9	12.3	18.7
benzo[k]fluoranthene	6.6	6.0	7.4	10.1	8.9	11.8	9.2	8.1	10.7	17.0	13.8	22.0
benzo[e]pyrene	6.2	5.7	6.9	10.0	8.8	11.6	8.5	7.5	9.7	16.6	13.6	21.2
benzo[a]pyrene	5.4	4.9	6.0	8.3	7.4	9.4	7.0	6.2	8.1	12.3	10.4	15.0
perylene	5.5	5.1	6.1	8.6	7.7	9.7	7.3	6.5	8.2	13.1	11.1	15.9
indeno[123-cd]pyrene	6.5	5.7	7.4	10.0	8.7	11.9	8.8	7.6	10.5	16.4	13.2	21.6
dibenz[ah]anthracene	5.8	5.1	6.6	9.3	8.0	11.1	7.6	6.6	9.0	14.7	11.9	19.5
benzo[ghi]perylene	6.4	5.8	7.2	9.6	8.5	11.2	8.7	7.7	10.2	15.5	12.8	19.6

For both the exposed and shelter treatments the half-lives of the heavier compounds (i.e., from about BaA onward,  $\log K_{ow}$  of approximately 6) start to level off. This may be an indication that these compounds are all bound to a particular size range and/or type of sludge particle; therefore, the environmental behaviors of these compounds are no longer directly dependent on their physicochemical properties but rather reflect the particle-mediated behavior. For lower MW compounds, other property-dependent loss mechanisms operate, notably volatilization. For these compounds, we believe that wash-off is not important in explaining these data because there was no rain until 2 weeks into the experiment.

**Treatment Half-Lives.** Comparison of the half-lives between the treatments shows an increased half-life for the shelter plots when compared to the exposed plots. For both the concentration and the inventory half-lives, this difference was significant only from 2,3,6tmNap onward. For very light PAHs, volatilization is believed to be the dominant loss mechanism. However, for the remaining PAHs rain has an important influence on the weathering process. The rapid decline seen in the shelter plots indicates that other loss mechanisms apart from rain (see Figure 1) are also significant.

The half-lives of the 2- and 3-ringed PAHs are very rapid, being of the order of 1–3 d. We believe this primarily reflects volatilization losses and suggests that compound uptake/clearance (i.e., partitioning between the plant surface and the air gas phase) could be measurable over periods of several hours for some compounds.

**Growth Dilution.** The effect of growth dilution in reducing the PAH contaminant is evident when comparing the half-lives calculated on a concentration and an inventory basis (see Figure 7a,b). Dilution by growth has an important influence in reducing the half-lives, as can be seen from the increased half-lives when they are calculated on an inventory basis. The dilution effect is similar for both the exposed and shelter treatments, as would be expected given the similar yields shown in Figure 3.

**1 and 2 Week Contact Time.** The influence of contact time between the sludge and the grass prior to weathering

remains unclear. Unfortunately, for the initial 2 weeks of the experimental period there was no rain (see Figure 5); therefore, the loss history for these two treatments and that of the exposed plots were the same, with the result that similar final concentrations were reached. The absence of rain will of course result in reduced removal for the intermediate and heavier PAHs as discussed above. However, given the significant decrease in concentrations even in the absence of rain, it is anticipated that the effect of sludge–pasture contact time on PAH removal will be rather minor.

#### Comments on Removal Rates and Their Implications.

The empirical calculation of the half-lives does not allow for the significance of loss mechanisms other than rain to be quantified. Therefore, inferences can only be made as regards to the physical mechanisms operating, based upon the likely behavior according to known compound properties.

It is clear from this study that some contaminant residues remain associated with the pasture after the 3-week no-grazing period used in the U.K. While the lightest compounds had reached background levels in the prescribed period, about 5% of the  $t = 0$  concentrations of the heaviest PAHs remained in the exposed plots. Under the scenario of “no rain”, ~25% remained. There is therefore the potential for persistent SOCs to be introduced into the grazing animal food chain. However, in terms of the risk assessment for the introduction of SOCs into the food chain, it is necessary to quantify the relative importance between the direct intake of grass contaminated by sludge and the incidental ingestion of soil while feeding.

The initial sward density and the sludge thickness/application rate will have an influence on the retention of sludge solids and their associated contaminant burden (15–17). An increase in any of these parameters will result in higher initial retention. The species composition of the sward will also have a potential influence on the initial retention of the sludge (16).

In this experiment, a relatively thin digested sludge was used (4% DW), and the grass was cut down 3 d prior to application. In addition, the application rate of sludge to the



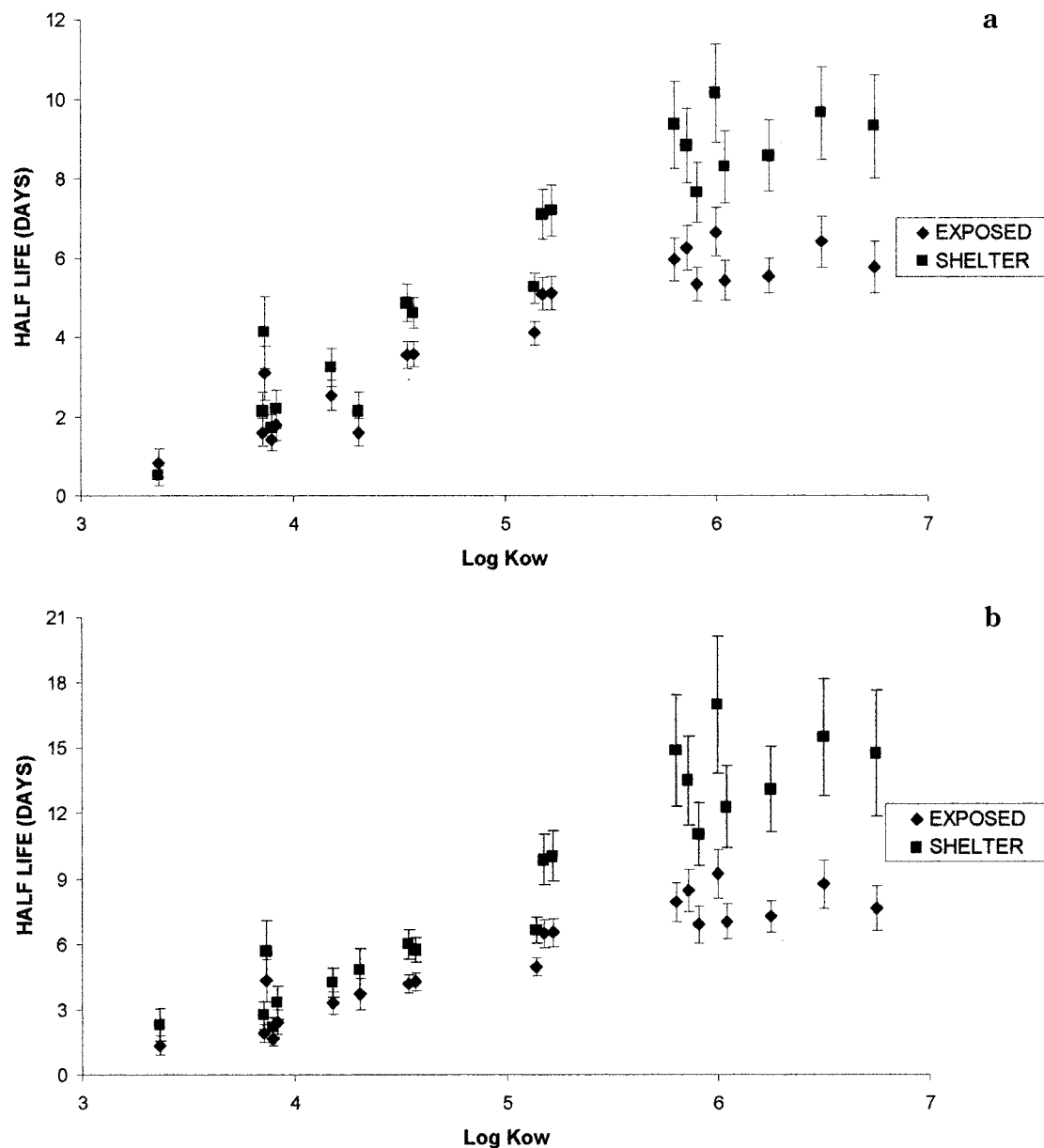


FIGURE 7. (a) Half-lives of sludge derived PAHs on pasture grass for the exposed and shelter treatments—calculated on a concentration basis. Error bars represent 95% confidence intervals. (b) Half-lives of the sludge-derived PAHs on the pasture grass for the exposed and shelter treatments—calculated on an inventory basis. Error bars represent 95% confidence intervals.

grass sward was in the lower range of those loadings typically employed in the U.K. The PAH concentrations in the sludge were representative of a semi-urban catchment. The experimental conditions used here are therefore clearly not a “worst case” scenario.

Although the physicochemical properties of the PAHs investigated here may be used to estimate the potential for other compound classes to be introduced into the food chain via this route, this should be done with care because loss processes (e.g., photodegradation) can vary between compound classes. Given the apparent importance of the particle-mediated behavior of the heavier MW PAHs, it is essential to gain a more thorough understanding of the nature of the association of these compounds with the particulate and colloidal matter in the sludge. For example, there will be an influence of particle size on the extent of wash-off or windblow from the plant surface (32). In addition, a knowledge of the nature of PAH–sludge–pasture binding/dissociation is important in helping to understand the crucial

issue of the bioavailability of these organic contaminants to livestock.

### Acknowledgments

We are grateful to the U.K. Ministry of Agriculture, Fisheries and Food, Food Contaminants Division, for funding this research.

### Literature Cited

- (1) Simonich, S. L.; Hites, R. A. *Environ. Sci. Technol.* **1995**, *29*, 2905–2914.
- (2) McLachlan, M. S. *Environ. Sci. Technol.* **1999**, *33*, 1799–1804.
- (3) Jones, K. C.; Grimmer, G.; Jacob, J.; Johnston, A. E. *Sci. Total Environ.* **1989**, *78*, 117–130.
- (4) Jones, K. C.; Sanders, G.; Wild, S. R.; Burnett, V.; Johnston, A. E. *Nature* **1992**, *356* (5), 137–140.
- (5) Wild, S. R.; Jones, K. C.; Johnston, A. E. *Atmos. Environ.* **1992**, *26A*, 1299–1307.
- (6) Wild, S. R.; Berrow, M. L.; McGrath, S. P.; Jones, K. C. *Environ. Pollut.* **1992**, *76*, 25–32.

- (7) Ryan, J. A.; Bell, R. M.; Davidson, J. M.; O'Connor, G. A. *Chemosphere* **1988**, *17*, 2299–2323.
- (8) Wild, S. R.; Jones, K. C. *J. Environ. Qual.* **1992**, *21*, 217–225.
- (9) Wegman, M. A.; Daniel, R. CH.; Hani, H.; Iannone, A. *Toxicol. Environ. Chem.* **1987**, *14*, 287–296.
- (10) O'Connor, G. A.; Lujan, J. R.; Jin, Y. *J. Environ. Qual.* **1990**, *19*, 587–593.
- (11) O'Connor, G. A. *Sci. Total Environ.* **1996**, *185*, 71–81.
- (12) Duarte-Davidson, R.; Jones, K. C. *Sci. Total Environ.* **1996**, *185*, 59–70.
- (13) Beck, A. J.; Johnson, D. L.; Jones, K. C. *Sci. Total Environ.* **1996**, *185*, 125–149.
- (14) Wild, S. R.; Jones, K. C. *Sci. Total Environ.* **1992**, *119*, 85–119.
- (15) Chaney, R. L.; Lloyd, C. A. *J. Environ. Qual.* **1979**, *8*, 407–411.
- (16) Jones, S. G.; Brown, K. W.; Deuel, L. E.; Donnelly, K. C. *J. Environ. Qual.* **1979**, *8*, 69–72.
- (17) Buttigieg, D. A.; Klessa, D. A.; Hall, D. A. *The contamination of herbage following the application of sewage sludge to pasture*; WRC Report 0078; WRC: 1990.
- (18) Wilson, S. C.; Alcock, R. E.; Stewart, A. E.; Jones, K. C. *J. Environ. Qual.* **1997**, *26*, 1467–1477.
- (19) Fries, G. F. *J. Environ. Qual.* **1982**, *11*, 14–20.
- (20) Fries, G. F. *Sci. Total Environ.* **1996**, *185*, 93–108.
- (21) Fleming, G. A. Soil ingestion by grazing animals; a factor in sludge treated grassland. In *Factors influencing sludge utilisation practices in Europe*; Davis, R. D., Haeni, H., L'Hermite, P., Eds.; Elsevier Applied Science Publishers: London and New York, 1986; pp 43–50.
- (22) Stark, B. A.; Hall, J. E. Implications of sewage sludge application to pasture on the intake of contaminants by grazing animals. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals*; Hall, J. E., Sauerbeck, D. R., L'Hermite, P. L., Eds.; Commission of the European Communities: Brussels, 1992; pp 134–157.
- (23) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Vol. II, Polynuclear aromatic hydrocarbons, polychlorinated dioxins, and dibenzofurans*; Lewis Publishers: Chelsea, MI, 1991.
- (24) Smith, K. E. C.; Northcott, G. L.; Jones, K. C. Development and validation of a method for the trace analysis of polycyclic aromatic hydrocarbons (PAHs) in pasture grass. Submitted for publication in *Chemosphere*.
- (25) Lee, R. G. M.; Hung, H.; Mackay, D.; Jones, K. C. *Environ. Sci. Technol.* **1998**, *32*, 2172–2179.
- (26) Lee, R. G. M.; Jones, K. C. *Environ. Sci. Technol.* **1999**, *33*, 705–712.
- (27) Simonich, S. L.; Hites, R. A. *Environ. Sci. Technol.* **1994**, *28*, 939–943.
- (28) Bohme, F.; Welsch-Pausch, K.; McLachlan, M. S. *Environ. Sci. Technol.* **1999**, *33*, 1805–1813.
- (29) Hebert, C. E.; Keenleyside, K. A. *Environ. Toxicol. Chem.* **1995**, *14*, 801–807.
- (30) Doctor, P.; Gilbert, R. O.; Pinder, J. E., III. *J. Environ. Qual.* **1980**, *9*, 539–546.
- (31) Wild, S. R.; McGrath, S. P.; Jones, K. C. *Chemosphere* **1990**, *20*, 703–716.
- (32) Smith, K. E. C.; Jones, K. C. *Sci. Total Environ.* **2000**, *246*, 207–236.

*Received for review August 7, 2000. Revised manuscript received February 12, 2001. Accepted February 19, 2001.*

ES000178L