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Effects of drying and comminution type on the quantification of Polycyclic Aromatic Hydrocarbons (PAH) in a homogenised gasworks soil and the implications for human health risk assessment

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HIGHLIGHTS

- Drying and comminution treatment has a significant effect on PAH concentrations.
- LMW PAH concentrations are higher for air and freeze drying then oven drying.
- Milling improves analytical precision in comparison to sieving.
- Pre-treatment combination can affect the outcome of a human health risk assessment.

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ABSTRACT

This research investigates the effect of nine physical treatment types comprising a serial combination of three drying (air, freeze and oven) and two comminution (milling and sieving) methods on the quantification of PAH in a soil sample from a former gasworks. Results show that treatment type has a significant effect on PAH concentration ($p \leqslant 0.05$). Naphthalene, 1-methylnaphthalene and 2-methylnaphthalene concentrations were significantly higher for air drying and freeze drying treatments than for oven drying. It is suggested that naphthalene and similarly volatile PAH losses were greater for oven drying due to the application of fanned warm air which is thought to cause volatilisation. Analytical precision was significantly improved for milled samples compared with sieved samples. The reason milling results in greater precision is assigned to the improved solvent extraction efficiency when natural grain size is altered due to crushing. The analytical data were compared to residential generic assessment criteria (GAC) used for risk-based land management. It was shown that the naphthalene GAC was lower than all freeze drying and air drying concentrations but was within the oven drying concentration range, illustrating that a false negative could be concluded during risk evaluation is oven dried data were used. Overall, it is recommended that air drying or freeze drying is a better choice than oven drying if the quantification of low molecular weight PAH forms an important objective of sample characterisation for risk-based land management, otherwise freeze drying and milling is recommended.

1. Introduction

1.1. Background

Polycyclic Aromatic Hydrocarbons (PAH) are a class of semi-volatile organic compound that are structurally characterised by two or more fused benzene rings. PAH are common in soils and sediments, which gives cause for concern because of their toxic, mutagenic and/or carcinogenic activity (Menzie et al., 1992; Nathanail et al., 2009). Reliable PAH quantification is important for good science as well as the potential impact poor quality data might have on human health. Concentrations of PAH that exceed regulatory guidance values often require intervention measures to reduce the risk to a more acceptable level (Jennings, 2012). In England and Wales, the justification for intervention often involves modelling the fate, transport and exposure pathways of contaminants to derive generic assessment criteria (GAC) or site specific assessment criteria (SSAC) (Environment Agency, 2004, 2008; Defra, 2011). GAC are scientific risk-based conservative estimates of the chemical concentration in soil that might be harmful to a

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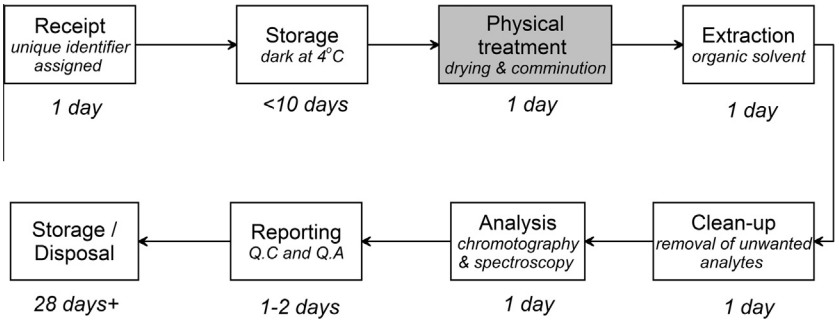

Fig. 1. Typical lifecycle of a soil or sediment sample once received by a laboratory for analysis of PAH.

person if they are chronically exposed to it given generic land use and exposure scenarios (Environment Agency, 2009). SSAC are similar to GAC but are derived using site specific land use and exposure scenarios. PAH concentrations must be quantified by laboratory analysis before GAC can be used; Fig. 1 illustrates the typical lifecycle of a sample once it arrives at the laboratory. Various studies have shown that the accuracy and precision of PAH quantification can be affected by the physical sample preparation technique used prior to extraction and analysis (Berset et al., 1999; Shu and Lai, 2001; Thompson and Nathanail, 2003; Belkessam et al., 2005; Khan et al., 2005; Narizzano et al., 2013) but to date none have provided a comprehensive statistical evaluation of their effect. This work demonstrates that the selection of drying and comminution type has a statistically significant effect that can influence the outcome of the risk evaluation stage of human health risk assessment (HHRA) for risk-based land management.

Effective sample preparation prior to extraction involves removing as much moisture as possible from the sample followed by comminution (Fig. 1). PAH losses may occur as an unintended consequence of drying due to their volatility, meaning the selection of the drying method is important. Non-chemical drying methods involve removing moisture by evaporation or sublimation. Berset et al. (1999) reported that air drying was liable to lower losses of naphthalene, one of the low molecular weight (<202.25 g mol^{-1}) PAH with relatively high volatility, than freeze drying. Belkessam et al. (2005) examined the effect of different drying techniques and recommended that light drying is preferable to more drastic techniques such as freeze drying or cryogenic crushing. More recently Narizzano (2013) reported that low molecular weight PAH are more susceptible to losses caused by oven drying temperature (40–50 °C) and air drying than heavy molecular weight compounds. In each case, studies lacked a comprehensive statistical analysis of the effect of drying type and comminution that is provided by this study. After drying, samples are typically disaggregated prior to comminution. Sample comminution is the physical reduction in particle size of a sample and is typically achieved by milling or sieving (Fig. 1). The influence of sample particle size on PAH concentration has been examined in the context of oral bioaccessibility by Siciliano et al. (2010) and Ruby and Lowney (2012). Ruby and Lowney (2012) show that PAH concentrations in soils are higher for smaller particle sizes (e.g. 250 μm) than larger ones (e.g. 2000 μm), although they also report that particle size and enrichment may not always be a function of one and other i.e. larger particles may contain greater sorbed contaminant mass than smaller ones. Notwithstanding, enrichment of PAH generally occurs in the fine (<45 μm) fraction of soils (Siciliano et al., 2010). The purpose of comminution is principally to remove physical contaminants, leaving only particles of the desired size and state. Sieving leaves only particles that are small enough to pass through the diagonal of the sieve mesh aperture (e.g. 2 mm), ensuring that particle integrity is preserved. Milling effectively crushes the sample to a fine powder, usually <250 μm (Environment Agency, 2006).

In the UK, laboratories producing analytical data for soils for regulatory purposes must be accredited to the Monitoring Certification Scheme (MCERTS) (Environment Agency, 2012) and have their methods accredited to the British, European and international standard ISO/IEC 17025 (British Standards Institute, 2005). Non-accredited laboratories that are conducting research or are not producing data that will be used for regulatory purposes will usually have similar management systems. Data quality is managed differently in the U.S, laboratories are required to follow prescribed methods for their regulatory analyses e.g. Methods 3540C and 3550C require a chemical drying step prior to extraction and analysis (United States Environmental Protection Agency, 2013). The Environment Agency for England and Wales recognise that low molecular weight PAH are 'borderline determinants' i.e. neither volatile nor non-volatile, placing the onus on the analyst to select physical treatment methods that are fit for purpose and do not lead to significant loses of analytes (Environment Agency, 2006). In reality PAH are determined as one analytical suite using a single method. Other guidelines e.g. ISO 14507 (British Standards Institute, 2003) recommend chemical drying of samples prior to PAH quantification. ISO 13877, however, recommends air drying a sample at room temperature, mortar crushing and sieving to <2 mm prior to analysis by high performance liquid chromatography (HPLC) (International Organisation of Standardization, 1998). BS EN 16179: 2012 suggests that pre-treatment of samples prior to organic analysis should be either freeze drying or chemical drying only (British Standards Institute, 2012). Experience suggests that oven drying and sieving to <2 mm is common practice although techniques vary between laboratories. The wide variety of in-house or prescribed methods that have been devised by analysts, standards committees and government bodies results in the potential for wide divergence in PAH quantification. There is currently unified method supported by published data for the physical treatment of soil or sediment samples prior to PAH quantification. A necessary preliminary step guiding the development of a standardised physical treatment combination is a robust statistical evaluation of the effect that drying and comminution techniques have on the reliability and repeatability of PAH concentration data.

2. Methods

2.1. Sample preparation

Soil was sampled from a former gasworks in West Yorkshire. A bulk sample was taken from an excavated stockpile that was created as part of a remediation programme and was known to be contaminated with gasworks wastes. Upon return to the laboratory

the soil sample was assigned a unique identifier prior to being coned and quartered to form a homogenised stock sample. This approach was selected in preference to using a range to soils in order to compound the effect of variables such as co-contaminants or physico-chemical properties. A matrix of experiments was undertaken in which a serial combination of physical treatments were tested on the homogenised sample, namely:

- Examination of five drying methods, *i.e.* air drying at ~20 °C, freeze drying using a BOC Edwards Heto 6000 freeze dryer, and fan-assisted oven drying for 24 h at 20 °C, 30 °C and 40 °C.
- Examination of two comminution types, *i.e.* each dried sample was sieved to <2 mm, a sub-set was either analysed at this stage or agate ball milled under repeatable milling conditions and then analysed.

PAH concentrations in 'as received' samples were not investigated because it is believed that in practice some form of physical treatment is applied prior to the determination of PAH. The methods selected for this study were designed to align with current practice and led to the evaluation of nine treatment combinations, a summary of these and their assigned nomenclature are shown in Fig. 2. The testing regime was designed principally to test for differences between freeze and oven drying. Air drying followed by motor crushing and sieving 2 mm was used as a control treatment (as per ISO 13877) (International Organisation of Standardization, 1998).

2.2. High performance liquid chromatography analyses

The PAH analysed by HPLC/Fluorescene were: 1-methylnaphthalene (1MN), 2-methylnaphthalene (2MN), naphthalene (Nap), acenaphthene (Ace), fluorene (Fluor), phenanthrene (Phen), anthracene (Anth), fluoranthene (Fanth), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chrys), benzo[b]fluoranthene (BbF), perylene (Per), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DBA), benzo[g,h,i]perylene (BghiP), indeno[1,2,3-c,d]pyrene (IP) and Σ18 PAH. The list includes fifteen of the sixteen PAH defined by USEPA as priority pollutants (USEPA, 1987). Acenaphthylene was omitted because it cannot be detected using HPLC/Fluorescene. Additional PAH include 1-MN, 2-MN and Per.

Each sample was analysed five times, with the exception of the air dried soil which was analysed ten times. All analyses were by means of HPLC/Fluorescence. For the PAH extraction of each sample, approximately 5 g was weighed into a pre-cleaned 30 mL amber bottle. To this was added 25 mL of a 1:1 v/v mix of acetonitrile and tetrahydrofuran, both of HPLC grade. The bottle was sealed with a screw-cap closure containing a PTFE-faced silicone rubber septum. After sealing the bottle was shaken to suspend the contents, which, were then sonicated in a heated ultrasonic bath (Camlab, 300W) for 45 min at 70 °C. During this period the bottle was occasionally inverted and shaken to continually re-suspend the sample. The bottle was then stored in the dark for about 2 h, to permit some clarification of the supernatant, before taking a 2 mL aliquot in a gas-tight glass syringe, attaching a 0.2 μm in-line syringe filter (25 mm dia. – Nylon 66), and filtering the extract into an amber 4 mL vial (with PTFE-faced screw cap closure) having first discarded the first few drops of filtrate. The clarified extracts were stored in a refrigerator cooled to ~3 °C to await analysis which took place as soon as possible after extraction.

Quality control (QC) was achieved using certified reference material (CRM), blanks and duplicate samples. The CRM was a well-characterised, low-level PAH proficiency-testing marine sediment, i.e. QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) QPH048MS to the above procedure (except that a weighed 2.5 g was used) and analysing it by the same method as for the samples. A procedural blank prepared from 15 g white quartz sand (Sigma Aldrich, UK) – a material devoid of PAH – was treated in a similar fashion. A total of six CRM samples, three procedural blanks and nine duplicate sample determinations were conducted at intervals throughout the analysis of the samples. Limits of quantification (LoQs) for each PAH were determined from the analysis of the procedural blanks. The areas of peaks in the blanks with the same retention times as a given PAH were averaged and three times the standard deviation was added to that average to give the LoQ of that PAH.

Filtered sample extracts (including those of the QC and the procedural blank) were injected into the HPLC system (Waters 400E) via a 5 μl sample loop (Rheodyne). The eluent flow-rate through the separation column (Hypersil Green PAH, 250 × 4.0 mm i.d.) and a guard column (Hypersil Green PAH Guard, 10 × 4.0 mm i.d.) was 0.7 mL min^{-1} with a back pressure of ~1000 psi. Separation of 18 PAH was achieved within 40 min by gradient programming the eluent. The column temperature was maintained at 25 °C using a Grace-Vydac 7995R Column Heater/Cooler. Far-UV HPLC grade acetonitrile (Rathburn Ltd.) and HPLC grade water (Milli-Q) were pumped as a 65%:35% mix, respectively, at the start

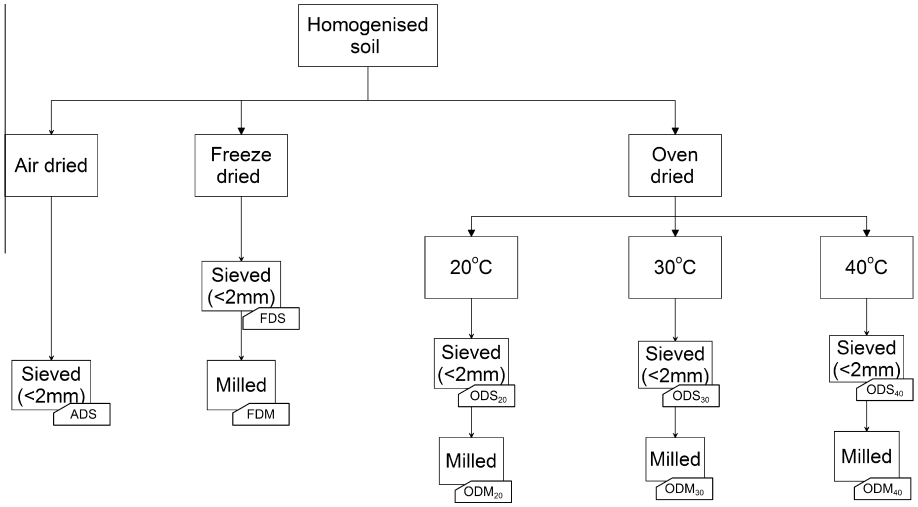

Fig. 2. Serial physical soil treatments and associated nomenclature.

of each chromatographic run. This condition was maintained for 5 min into the run. Thereafter, up to 27 min, the proportion of acetonitrile was continuously increased from 65% to 100% using a concave gradient (Waters curve 9). From 14 min until the end of the run (40 min) elution with 100% acetonitrile was maintained. PAH detection was accomplished employing a scanning fluorescence detector (Waters 474), using the following excitation and emission wavelengths (nm) Nap-Fluor 275/325; Phen 252/373; Anth-Pyr 240/425; BaA-Chrys 254/395; BbF-BaP 350/440; DBA-IP 300/470.

2.3. Data evaluation

Data evaluation comprised descriptive and inferential statistical summaries of the data for treatment type and PAH concentration. All data were compared with published residential land use Land Quality Management/Chartered Institute of Environmental Health (LQM/CIEH) GAC for PAH to check for any exceedances (Nathanail et al., 2009). PAH data with concentrations above the relevant GAC were evaluated further to determine whether the outcome of any risk-based decision-making for land contamination management might be affected by treatment type.

Homogeneity of variance between treatments was tested separately for each PAH using Levene's test and Bartlett's test using <0.05 as the critical p-value. The null hypothesis for both tests is that the data are homoscedastic (of equal variance):

$$H_0: \ \delta^2 1 = \delta^2 2 = \delta^2 3 = \cdots = \delta^2 9$$

where δ^2 is the variance for each of the respective nine physical treatments.

One way analysis of variance (ANOVA) was used to test differences between the mean values of each treatment type for individual PAH exhibiting homoscedastic data. The Kruskal Wallace rank sum test was used to compare the mean values between treatments for all remaining PAH, using <0.05 as the critical p-value. In each case the null hypothesis is that there is no difference between the treatments:

$$H_0: \ \mu 1 = \mu 2 = \mu 3 = \cdots = \mu 9$$

where μ is the mean for each of the respective nine physical treatments.

Tukey's Honest Significant Differences (HSD) test was used to test for differences between treatments for selected PAH with homoscedastic data and significantly different means. The null hypothesis for the HSD was the same as the ANOVA test.

3. Results

3.1. Data evaluation

Concentrations of Σ18 PAH ranged from 320 to 420 mg kg^{-1} with a mean of 375 mg kg^{-1}, these data are broadly consistent with soils moderately contaminated with coal tar products (García et al., 2012; Lorenzi et al., 2012). Boxplots and summary statistics for individual PAH concentrations across all treatments are shown in Fig. 3 and Table 1 respectively. The statistical distribution shows a positive skew for Nap, 1MN, 2MN, Anth, BaA, Per and Ind (Table 1) with outliers identified for Fluor, BaA and BghiP (Fig. 3); these features are quite typical for geochemical data (Reimann and Filzmoser, 2000). Boxplots for individual PAH and treatments are shown in Fig. 4. Results show that air and freeze dried concentrations are generally higher than oven dried data for low molecular weight PAH e.g. Nap, 1MN and 2MN and show that the concentration range derived for sieved treatments tends to be greater than for milled treatments e.g. BbF and BkF; there are also extreme values identified for specific treatments and PAH and in a number of plots data is skewed.

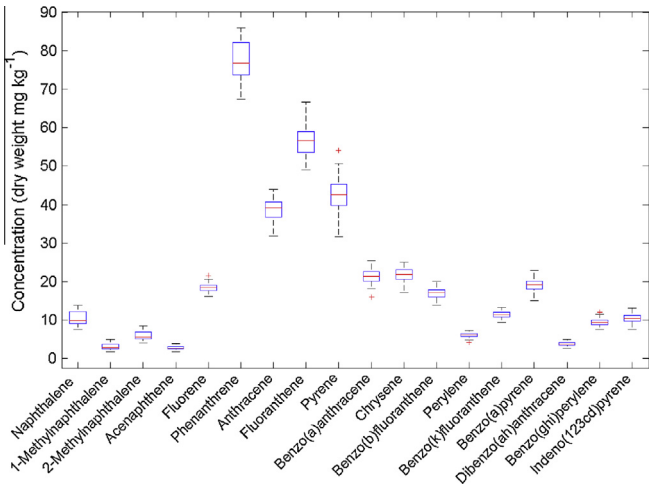

Fig. 3. Combined PAH concentrations for all physical treatment types.

Table 1
Summary statistics for PAH concentrations over all treatment types.

	Minimum (mg kg^{-1})	Mean (mg kg^{-1})	Maximum (mg kg^{-1})	Standard deviation (mg kg^{-1})	Variance	Skewness	Kurtosis
Naphthalene	7.55	10.37	13.80	1.78	3.18	0.38	2.03
1-Methylnaphthalene	1.67	3.03	4.91	0.83	0.69	0.43	2.13
2-Methylnaphthalene	3.93	6.01	8.49	1.27	1.61	0.41	2.04
Acenaphthene	1.75	2.76	3.89	0.50	0.25	0.19	2.55
Fluorene	16.14	18.39	21.46	1.13	1.27	0.27	2.89
Phenanthrene	67.36	77.15	86.01	5.04	25.37	-0.17	1.95
Anthracene	31.73	38.71	43.87	2.95	8.70	-0.32	2.52
Fluoranthene	48.97	56.31	66.67	3.95	15.63	0.23	2.59
Pyrene	31.61	42.55	54.06	4.65	21.63	-0.03	2.87
Benzo[a]anthracene	15.98	21.29	25.32	1.90	3.61	-0.31	2.86
Chrysene	17.07	21.81	24.98	1.79	3.19	-0.28	2.68
Benzo[b]fluoranthene	13.84	16.86	20.05	1.32	1.75	-0.15	2.80
Perylene	4.09	6.06	7.28	0.64	0.41	-0.63	3.51
Benzo[k]fluoranthene	9.39	11.31	13.27	0.87	0.76	-0.22	2.57
Benzo[a]pyrene	15.02	18.98	22.81	1.66	2.76	-0.07	2.85
Dibenzo[a,h]anthracene	2.57	3.67	4.92	0.53	0.28	0.19	2.51
Benzo[g,h,i]perylene	7.45	9.34	11.93	0.99	0.99	0.20	2.84
Indeno[1,2,3–c,d]pyrene	7.57	10.33	13.05	1.07	1.15	-0.30	3.09
Total PAHs	320.37	374.92	429.99	26.59	706.83	-0.02	2.18

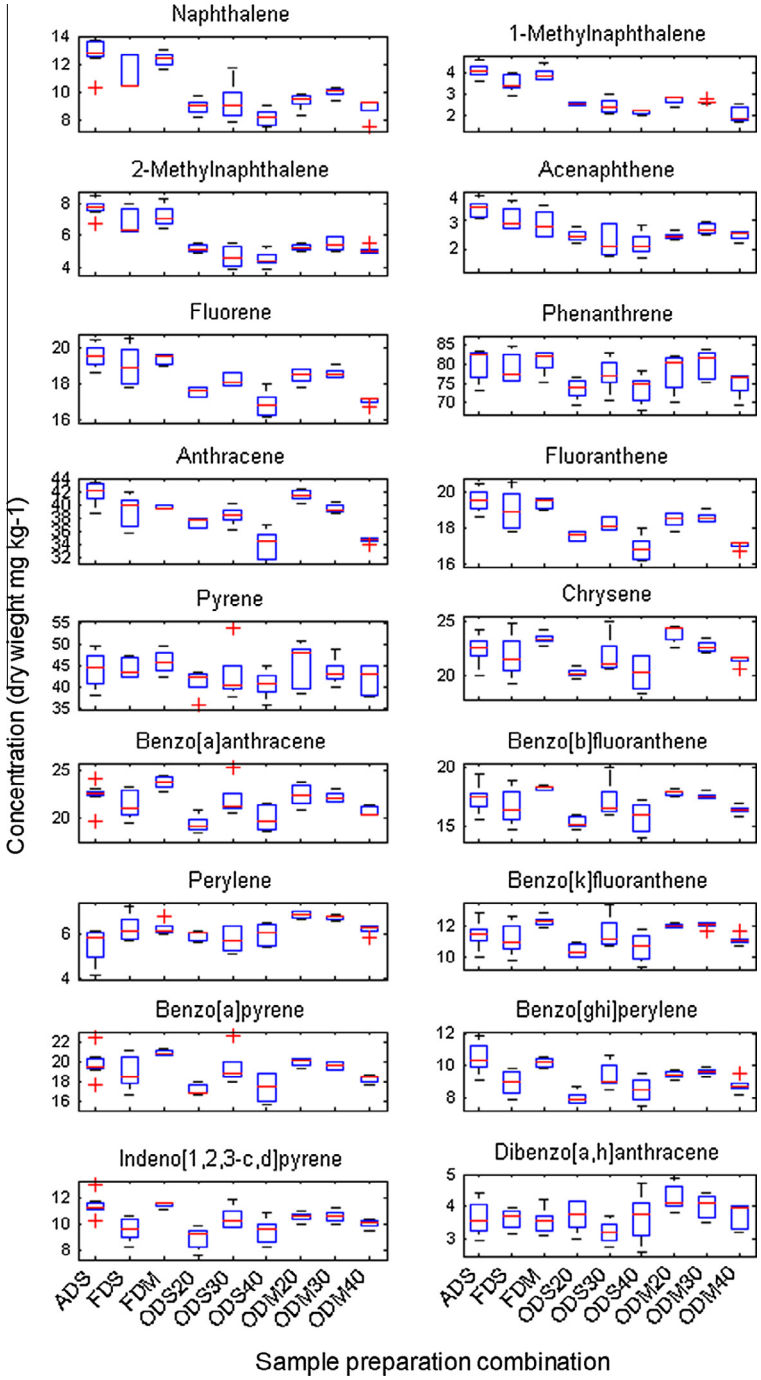

Fig. 4. Boxplots for each PAH showing concentrations determined for each of the nine physical treatment types.

Individual PAH concentration data for each treatment were subjected to Levenne's and Barlett's tests for homogeneity of variance. A detailed summary of these test results is shown in Table 2. Nap, 2MN, Ace, Fluor, Phen, Pyr, BaA, Ind, DBA, Σ18 PAH and %RSD were shown by either one of the two tests to be homoscadastic so differences between means were subsequently compared using ANOVA. The Kruskal–Wallis ranked sum test was used to test for differences between means for remaining PAH. A detailed summary of the ANOVA and Kruskal–Wallis results is reported Table 3. Significant differences between treatments were identified for all individual PAH and %RSD with the exception of Pyr and DBA.

Tukey's Honest Significant Differences (HSD) test was applied to selected individual PAH (Nap, 2MN and Ind) and %RSD where data were shown to be homooscedastic (Table 2). These were chosen as representative of low and high molecular weight PAH. A detailed summary of the HSD results for selected PAH is shown in Tables 4–7 – light grey highlighted boxes indicate a significant difference between the relative treatment types. Results show that there are significant differences in the mean PAH concentrations between treatments for Nap and 1MN as well as significant differences in precision for sieving and milling Table 7. These results suggest that treatment type affects both reliability and repeatability.

3.2. Comparison with regulatory guidance values

Comparison between PAH data and published residential land-use LQM/CIEH GAC were made; only benzo(k)fluoranthene and

Table 2
Summary of test results for homogeneity of variance using Levene's and Bartlett's tests.

PAH	Levene's test			Bartlett's test	
	F-statistic	*p*-Value	Accept H_0	*p*-Value	Accept H_0
Naphthalene	1.524	0.181	✓	0.1547	✓
1-Methylnaphthalene	2.962	0.0109	✗	0.001892	✗
2-Methylnaphthalene	2.334	0.0374	✗	0.1186	✓
Acenaphthene	3.986	0.00157	✗	0.05367	✓
Fluorene	3.699	0.00267	✗	0.01251	✗
Phenanthrene	0.618	0.757	✓	0.9803	✓
Anthracene	4.173	0.00112	✗	0.0007186	✗
Fluoranthene	1.07	0.404	✓	0.1044	✓
Pyrene	1.159	0.348	✓	0.6098	✓
Chrysene	2.222	0.0467	✗	0.00872	✗
Benz[a]anthracene	1.362	0.243	✓	0.175	✓
Benzo[b]fluoranthene	2.222	0.0467	✗	0.008872	✗
Perylene	3.971	0.00162	✗	0.003056	✗
Benzo[k]fluoranthene	2.565	0.0237	✗	0.001635	✗
Benzo[a]pyrene	2.751	0.0158	✗	3.671e−14	✗
Benzo[g,h,i]perylene	2.432	0.0308	✗	0.03204	✗
Indeno[1,2,3-c,d]pyrene	1.437	0.212	✓	0.07156	✓
Dibenzo[a,h]anthracene	0.959	0.481	✓	0.007179	✗
Σ18 PAH	2.366	0.0351	✗	0.09714	✓
RSD	2.168	0.322	✓	0.02279	✓

Notes: ✓ Accept H_0, ✗ Reject H_0 at ⩽0.05 confidence level.

Table 3
Comparison of mean PAH concentration between treatments using ANOVA and Kruskal Wallace tests.

PAH	ANOVA			Kruskal Wallace	
	F-statistic	*p*-Value	Accept H_0	*p*-Value	Accept H_0
Naphthalene	19.62	1.87e−11	✗		
1-Methylnaphthalene				2.54e−06	✗
2-Methylnaphthalene	30.58	1.7e−14	✗		
Acenaphthene	8.12	2.18e−06	✗		
Fluorene				2.55e−06	✗
Phenanthrene	2.73	0.17	✗		
Anthracene				1.07e−05	✗
Fluoranthene	4.43	7.01-e04	✗		
Pyrene	0.96	0.48	✓		
Chrysene				1.06e−03	✗
Benz[a]anthracene	6.35	2.89e−05	✗		
Benzo[b]fluoranthene				8.13e−04	✗
Perylene				8.93e−04	✗
Benzo[k]fluoranthene				1.68e−03	✗
Benzo[a]pyrene				2.60e−04	✗
Benzo[g,h,i]perylene				8.03e−05	✗
Indeno[1,2,3-c,d]pyrene	8.07	2.34e−06	✗		
Dibenzo[a,h]anthracene	0.97	0.476	✓		
Σ18 PAH	6.58	2.04e−05	✗		
RSD	19.28	<2e−16	✗		

Notes: ✓ Accept H_0, ✗ reject *a* at ⩽0.05 confidence level.

Table 4
HSD comparison of mean naphthalene concentrations between treatments.

Treatment	ADS	FDS	FDM	ODS_{20}	ODS_{30}	ODS_{40}	ODM_{20}	ODM_{30}	ODM_{40}
ADS									
FDS									
FDM									
ODS_{20}									
ODS_{30}									
ODS_{40}									
ODM_{20}									
ODM_{30}									
ODM_{40}									

Reject H_0 when $p < 0.05$ (light grey); Accept H_0 (dark grey).

Table 5
HSD comparison of mean 2-methylnaphthalene concentrations between treatments.

Treatment	ADS	FDS	FDM	ODS_{20}	ODS_{30}	ODS_{40}	ODM_{20}	ODM_{30}	ODM_{40}
ADS									
FDS									
FDM									
ODS_{20}									
ODS_{30}									
ODS_{40}									
ODM_{20}									
ODM_{30}									
ODM_{40}									

Reject H_0 when $p < 0.05$ (light grey); Accept H_0 (dark grey).

Table 6
HSD comparison of mean Indeno[1,2,3-cd]pyrene concentrations between treatments.

Treatment	ADS	FDS	FDM	ODS_{20}	ODS_{30}	ODS_{40}	ODM_{20}	ODM_{30}	ODM_{40}
ADS									
FDS									
FDM									
ODS_{20}									
ODS_{30}									
ODS_{40}									
ODM_{20}									
ODM_{30}									
ODM_{40}									

Reject H_0 when $p < 0.05$ (light grey); Accept H_0 (dark grey).

Table 7
HSD comparison of %RSD between treatments.

Treatment	ADS	FDS	FDM	ODS_{20}	ODS_{30}	ODS_{40}	ODM_{20}	ODM_{30}	ODM_{40}
ADS									
FDS									
FDM									
ODS_{20}									
ODS_{30}									
ODS_{40}									
ODM_{20}									
ODM_{30}									
ODM_{40}									

Reject H_0 when $p < 0.05$ (light grey); Accept H_0 (dark grey).

naphthalene showed exceedances. Fig. 5 illustrates that the residential GAC (2.5% and 6% SOM) for BkF (Nathanail et al., 2009) is within the lower concentration range for air dried, freeze dried and sieved, oven dried and sieved at 20 and 40 °C treatment types. All other concentrations for remaining treatments are above the GAC. Fig. 6 shows that the residential GAC (6% SOM) for Nap (Nathanail et al., 2009) is within the oven dried treatment concentration range but well below the lowest air drying and freeze drying concentration. The diagrams illustrates that there is a potential for different conclusions to be drawn by risk assessors depending on treatment type selected prior to analysis i.e. a false negative or Type II error.

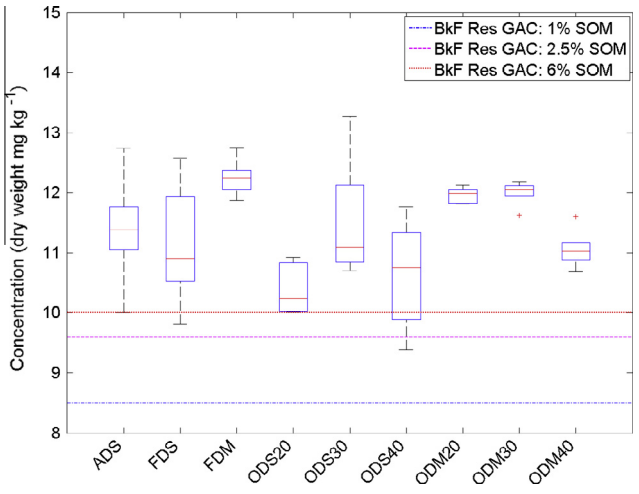

Fig. 5. Benzo(k)fluoranthene concentrations for nine physical treatment types annotated with generic assessment criteria for residential land-use at 1%, 2% and 6% soil organic matter.

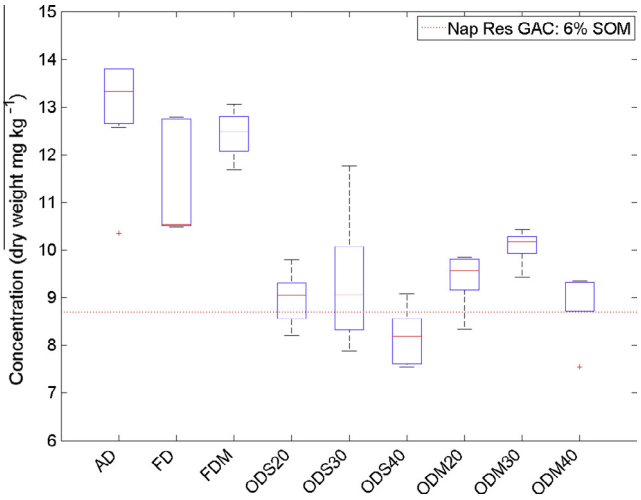

Fig. 6. Naphthalene concentrations for nine physical treatment types annotated with generic assessment criteria for residential land-use and 6% soil organic matter.

4. Discussion

4.1. Reliability and repeatability between treatment types

Boxplots of the PAH concentrations determined after physical treatment illustrate differences for many of the PAH analysed (Fig. 4). The results of the ANOVA and Kruskal–Wallace results show significant differences for 18 of the 20 tests. The following discussion firstly addresses PAH concentration differences related to drying type and then by those related to comminution type.

The choice of drying technique has a statistically significant effect on low molecular weight PAH concentration i.e. Nap, 1MN and 2MN (Table 3 and Fig. 4). Tukey's HSD testing shows that PAH concentrations derived after oven drying are significantly lower for Nap and 1MN than air drying and freeze drying (Tables 4 and 5). These PAH have comparatively high vapour pressures, which for Nap, 1MN and 2MN at 40 °C it is reported to be ~50 Pa (Environment Agency, 2008), and for high molecular weight PAH is mostly <1 Pa at the same temperature (Mackay et al., 2006). An additional factor that may cause losses of the more volatile PAH arising for the oven drying treatments is the movement of air over the sample controlled by the use of a fan powered air circulation. The temperature of the oven is not shown to have a significant effect on the concentrations. Berset et al. (1999) and Narizzano et al. (2013) suggest, however, that a temperature effect can be measured at >40 °C and >30 °C respectively. The wide range of physico-chemical properties for PAH (Environment Agency, 2008) makes it hard to select a one-size-fits-all treatment type and leads to the conclusion that in practice the selection of drying method comes down to a balance between potential vaporisation loss and the use of low cost of more expedient techniques such as oven drying. This reflects the recommendation by the Environment Agency for England and Wales that for borderline determinants i.e. semi-volatile compounds, potential significant loses should be accounted for during method selection (Environment Agency, 2006). In practice, the same method, often oven drying, is used for all PAH quantification. Thus, it is particularly important to note that this study shows that using oven drying for low molecular PAH could mean reporting significantly lower concentrations in a soil/sediment sample than if air or freeze drying were used (Tables 4 and 5). These findings may also be relevant to other semi-volatile compounds (e.g. petroleum hydrocarbons). Overall, it is recommended that air drying or freeze drying is a better choice than oven drying if the quantification of low molecular weight PAH forms an important objective of sample characterisation or human/environmental risk assessment.

Milling tends to result in a much lower concentration ranges, i.e. greater precision than sieving (Table 7). For Nap, 2-MN, BaP, Ind, this is supported by statistically significant differences in the mean %RSD between treatments (Table 7) – it is expected that these results are influenced by DBA and Phen, which both show no difference between mean concentrations, meaning if they were excluded from the HSD analysis, the differences between %RSD are likely to be even more pronounced. Notwithstanding, the physical effect of sieving on the particle size distribution of a soil/sediment is one of separation only. Solvent extraction requires the sample to be fully penetrated in order for the PAH to be released into solution meaning there is a possibility that the solvent will not completely remove all PAH from the sieved soil/sediment particles due to particle micro-structure and associated sorption. Milling on the other hand is a destructive technique than reduces particles to <250 μm (Environment Agency, 2006). In doing so, the physical structure of the soil/sediment is altered, which consequently alters its sorption characteristics. A milled sample displays greater homogeneity and improved access by the solvent to PAH sorption sites than sieved samples. The inferred effect is that extraction is more consistent, resulting in better precision (Table 7). Milling treatments do not tend to result in significantly higher concentrations than sieving (Tables 4–6). It is recommended that milling be preferred over sieving, unless sample integrity is important, in which case sieving should be used instead e.g. for oral bioaccessibility studies (Ruby and Lowney, 2012). Again a balance must be struck between the reliability and repeatability of the analytical results and the analytical objectives assigned to the soil/sediment sample.

4.2. Implications for human health risk assessment

Where a site in England is affected by contamination and a change of land-use is proposed under the National Planning Policy Framework the responsibility for securing a safe development rests with the developer and/or landowner (CLG, 2012). This places an onus on these stakeholders and their advisors to ensure that data is able to meet the objectives of the site investigation and risk assessment. To illustrate the potential effect treatment type may have on land contamination management, the study data were compared with published residential LQM/CIEH GAC (Nathanail et al., 2009). Exceedances of GAC by the study data exist for benzo(k)fluoranthene and naphthalene only. Further evaluation of the data showed that exceedances were only present for certain

treatment types (Figs. 5 and 6). The remainder of this discussion will therefore focus on the Nap, but is equally relevant to BkF. If oven drying was used as the preferred treatment type prior to sample analysis of soil from a potentially contaminated site and the reported concentrations compared with the 6% SOM GAC for a residential land-use (which is common practice in industry), it is possible that the sampled soils would be considered suitable for this use. This situation might result in a false negative or Type 2 Error being committed during the risk evaluation stage of a risk assessment, since if the same soil was sampled and freeze dried instead of oven dried then the reported concentration would be above the 6% SOM GAC thereby triggering further investigation and detailed quantitative risk assessment. This is especially important because the differences in Nap concentrations between oven drying (all temperatures) and freeze drying (except ODM_{30}) as well as air drying are statistically significant ($p \leqslant 0.05$) (Table 4).

5. Conclusions

Nine physical treatment combinations were evaluated to determine their effect on the quantification of PAH in a homogenized soil sample sourced from a former gasworks in the UK. The analytical data for the nine treatment combinations demonstrates that treatment type has a statistically significant effect on selected low molecular weight PAH concentration. ANOVA and Kruskal–Wallace tests showed significant differences between concentrations and treatment type for all PAH except Pyr and DBA. Tukey's HSD test showed Freeze drying and air drying concentrations of Nap, 1-MN and 2-MN were statistically different to oven drying concentrations and that milling generally improves data precision compared with sieving. Differences between treatment types were considered in the context of human health risk assessment for Nap, showing that there is a distinct possibility of a false negative (Type II error being committed based on treatment type, the cause of which being that for Nap oven drying concentrations are significantly lower than air or freeze drying concentrations. Overall, it is recognised that freeze drying and milling will result in greater precision and reduce the likelihood of underestimating concentrations, especially for naphthalene compounds. The reason for the differences in concentration range is believed to relate to the volatility of these analytes and the effect of fanned warm air introduced by oven drying. For milled samples, the significant increase in precision is assigned to the destructive effect that milling has on the soil structure and the associated improvement to sample homogenisation and solvent extraction efficiency prior to analysis. It is acknowledged that freeze drying and milling will not always match the available laboratory resources. It is recommended that the selection of physical treatment type should be a balanced one that carefully considers the objectives of PAH quantification and the application of the resultant data. Interesting extensions to this work might include examination of the effect of sample pre-treatment on organic compounds similar to PAH and the effect of co-contaminants such as hydrocarbons on the PAH losses and soils or sediments with different physico-chemical properties.

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