Presence of Priority Polycyclic Aromatic Hydrocarbons, Chromium, Copper and Lead in Two selected Brownfield Sites in United Kingdom

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ABSTRACT: In recent years, concerns about adverse effects of increasing land contamination paralleled with the increasing demand for land has emphasized need for sustainable remediation strategies. Soil samples were collected from two brownfield sites, in Saltley, Birmingham and Swansea, South Wales, United Kingdom and analysed to establish the extent of contamination by priority polycyclic aromatic hydrocarbon (PAH) compounds. Saltley site had a total PAH concentration of 41.0 mg kg^{-1} with high concentrations of phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene and benzo[a]pyrene, total benzo[a]pyrene equivalent value of 6.0 mg kg^{-1} and total carcinogenic PAH of 19.0 mg kg^{-1}. At the Swansea site, total PAH concentration ranged from 5.0 – 85.0 mg kg^{-1} with pyrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[a]pyrene as the predominant PAHs, total benzo[a]pyrene equivalent value of 0.9 – 2.0 mg kg^{-1} and total carcinogenic PAH concentration of 2.6 – 11.0 mg kg^{-1}. Heavy metal concentrations were above the ambient background concentrations for urban/industrial area. Both brownfield sites had a mixture of PAH and heavy metal contamination in varying concentrations with implication for the selection of efficient remedial strategies to enable their redevelopment.

Technological advancement and industrialization has led to the inadvertent release of various contaminants into the environments (Patel *et al*., 2020). Most contaminated sites contain a mixture of organic such as polycyclic aromatic hydrocarbons (PAHs), and/or inorganic compounds such as heavy metals of anthropogenic origin (Glick, 2010; Antonio *et al*., 2011). Although PAHs are naturally occurring compounds, prolonged use of fuels, industrial emissions, car exhausts, incineration and atmospheric deposition has made PAHs ubiquitous environmental contaminants (USEPA, 2008, Nam *et al*., 2009). Although geogenic processes naturally result in the presence of metals at background concentrations in soils, anthropogenic activities such as mining, fuel processing and traffic emissions are important sources of metals (Nadal, *et al.*, 2009). High PAH concentrations are found in urban soils, roadside soils and even higher concentrations in contaminated sites such as old gas works worldwide including in the United Kingdom (Marusenko *et al*., 2011). Densely populated areas in the United Kingdom such as the South, Midlands and some parts of Northern England have greater inputs of PAH emission compared to less densely populated areas (Bradley *et al*., 1994; Nam *et al*., 2008). The increasing number of contaminated sites is paralleled by an increase in land demands for purposes such as agriculture, housing, recreation and infrastructure (Luo *et al.,* 2009). To tackle adverse effects of contamination while meeting land demands, many countries including the United Kingdom promote remediation of derelict sites known as brownfields for redevelopment instead of using greenfields; agricultural land (Environment Agency, 2006; USEPA, 2008; Luo *et al.,* 2009). However, there are few studies on PAHs and metals co-contamination in brownfields despite their adverse effects on different organisms and remediation approaches including bioremediation. Studies have reported the effects of heavy metals on different enzymes involved in PAH degradation (Gran-Scheuch *et al*., 2020). Consequently, site assessment is important for the selection of appropriate remedial strategies. Annually, soil contamination information generated from site investigations for regulatory purposes are rarely published in peer reviewed

journals (Vane *et al*., 2014). This study was undertaken to determine the extent of PAH and heavy metal contamination in typical brownfield sites in the United Kingdom.

MATERIALS AND METHODS

Brownfield site details: Two contaminated sites proposed for redevelopment projects were surveyed. The first site was an old derelict gas work station located in Saltley, Birmingham undergoing preliminary investigations at the time of visit while the other site, was a former oil refinery premises located at Swansea, South Wales under remediation by biopiling and monitored natural attenuation. At the Swansea site, wood chips were added to the biopiles and mixed periodically by to facilitate aeration for microbial degradation. There were three biopiles at the Swansea site; top soil biopile, NSR biopile and Rhead biopile with top soil biopile said to be the least contaminated.   Also present at the Swansea site were wastes from pipeline and sludge being treated using an equipment for oil recovery. For reasons of confidentiality, the exact locations and full site details cannot be mentioned.

Soil sample collection: Soil samples were randomly collected in triplicate from a trial pit at Saltley site, and from the three biopiles and wastes (pipeline and sludge) at the Swansea site. Grab samples were collected from a depth of 0 to 1 m and 1-2 m from soils dug out from sampling pit while surface samples were randomly collected from biopiles and sludge. All samples were collected in 60 mL glass jars with Teflon lined caps using a decontaminated hand trowel (Pies *et al*., 2007). The samples were transported in a cold box (4°C) to the Wolfson Laboratory, School of Geography, Earth and Environmental Sciences, University of Birmingham and stored in a freezer at 4°C. Soil samples were homogenized by sieving with a 2 mm sieve (Vane *et al*., 2014).

PAH analysis: Sodium sulfate (7 g) was added to soil samples (5 g) to remove any moisture and followed by addition of 15 mL of 2:1 hexane: acetone mixture, 5 mL of 1:4 triethylamine: acetone mixture, and p-terphenyl-d14 in a microwave extraction tube (Chigbo *et al*., 2013). The content of the tube was mixed using a vortex mixer (VWR, UK) and shaken by inversion to dislodge soil material from the base. Extraction was carried out with a microwave extraction unit (CEM MARS) with the following conditions: temperature ramp to 100 °C at 800 W for 12 min, hold at 100 °C at 800 W for 10 min then cool for 5 min in accordance with the USEPA method 3546 (USEPA 2007). Following the extraction, the clear extracts were transferred into glass tubes (20 mL). For the solid

phase extraction, SPE HF Mega BE-SI 2 g 12 mL cartridges (Agilent, UK) were conditioned with 5 mL of hexane then, 1 mL of sample extract was added and eluted with 10 mL of 1:1 hexane: dichloromethane mixture. The eluant was collected in a clean 20 mL glass tube and concentrated to a final volume of 1 mL under a gentle stream of nitrogen gas. Samples were prepared in 2 mL vials (Agilent, UK) by adding a semi-volatile internal standard mix to the concentrated sample extracts from soil samples for GC-MS analysis. GC-MS analysis for the 16 priority PAHs was performed with an Agilent gas chromatograph-mass selective detector (Agilent Technologies 6890N Network GC System) as described by Afegbua and Batty (2018).

Heavy metal analysis: Three gram of ground oven-dried soil was weighed and placed in a 15 mL digestion tube. 23 mL of concentrated hydrochloric acid and 7 mL of concentrated nitric acid were added to the soil, agitated and allowed to stand overnight. A condenser was placed over each tube and refluxed for 2 hours on a DigiPREP MS (SCP SCIENCE) heating block at 80°C. The tubes were allowed to cool and the resulting digest was filtered through a Whatman number 1 filter paper into a 100 mL volumetric flask. 1 mL of 10% Potassium chloride was added as an ionisation suppressant to the digest and made up to 100 mL with repeated washings of the digestion tube and filter paper. The resulting solution was stored at 4 °C until analysis by FAAS for chromium, copper and lead. Acid digests were analysed on AAnalyst 300 atomic absorption spectrophotometer (PerkinElmer Instrument) following calibration with standard solutions (Fluka, UK) of individual metals (Cr, Cu and Pb) to be analysed (Chigbo *et al*., 2013). Percentage recovery of Cr, Cu and Pb following acid digestion and analysis of certified soil reference material SS-2 (*Enviro*MAT SCP Science, UK) were 99.88%, 99.45% and 102.10% respectively. All samples were analysed in triplicates.

Data analysis: Results from PAH and heavy metal analysis were expressed in mean and standard error. For the PAHs, other calculations were computed; (i) total PAH (tPAH or ΣPAHs) equivalent to the sum of the 16 priority PAHs analysed, (ii) total carcinogenic PAH (cPAH or Σcarc. PAHs) is the sum of all the carcinogenic PAHs; benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenzo[*a,h*]anthracene and indeno[*1,2,3-cd*]pyrene (iii) the percentage of the carcinogenic PAHs to the total PAHs is given as Σcarc. PAHs/ΣPAHs*100. (iv) the total benzo[*a*]pyrene equivalent value was calculated as total equivalent concentration as

benzo[a]pyrene, using the toxicity equivalent (TE) for each PAH (Tsai *et al.*, 2004), and the formula; Total benzo[a]pyrene equivalent value (B[*a*]P-TE) = $\Sigma_i C_i$ X TE_i where: C_i – concentration of the respective PAHs µg kg^{-1} and TE_i – the toxicity equivalent of the corresponding PAHs. The toxic equivalent factors (TEF) for the 16 priority PAHs is 0.001 (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Fluoranthene and Pyrene), 0.01 (Anthracene, Chrysene and Benzo[*g,h,i*]perylene), 0.1 (Benzo[*a*]anthracene, Benzo[*b*]fluoranthene, Benzo[*k*]fluoranthene, Indo[*1,2,3*]pyrene) and 1 (Benzo[*a*]pyrene, Dibenzo[*a,h*]anthracene) (Tsai *et al.*, 2004).

RESULTS AND DISCUSSION
PAH concentration: Saltley site had a tPAH of 41.6 mg kg^{-1}, B[*a*]P-TE of 5.79 mg kg^{-1}, and cPAH of 19.43 mg kg^{-1}. The predominant compounds include phenanthrene (3.12 mg kg^{-1}, anthracene (3.64 mg kg^{-1}, fluoranthrene, (6.75 mg kg^{-1}), pyrene (5.56 mg kg^{-1}), benzo[*a*]anthracene (3.67 mg kg^{-1}), benzo[*b*]fluoranthene (2.57 mg kg^{-1}), benzo[*a*]pyrene (4.02 mg kg^{-1}), indeno[*1,2,3-c,d*]pyrene (2.47 mg kg^{-1}

$^{-1}$), and benzo [*g,h,i*] perylene (2.52 mg kg^{-1}) as shown in Table 1. For the Swansea site, sludge displayed a cPAH of 10.8 mg kg^{-1} (12.7% of tPAH) and a high concentration of all analytes (>1 mg kg^{-1}) with the exception of indeno[*1,2,3-c,d*]pyrene, benzo[*g,h,i*]perylene and dibenzo[*a,h*]anthracene which were 0.95, 0.90 and <detection limit respectively. Swansea site biopiles and wastes had a tPAH ranging from 5.47 – 10.5 mg kg^{-1}, B[*a*]P-TE of 0.94- 1.86 mg kg^{-1} and cPAH of 2.63 – 6.55 mg kg^{-1} (Table 1). Rhead biopile displayed a cPAH of 6.55 mg kg^{-1} (62.3% of tPAH). Interestingly, the B[*a*]P-TE value of Swansea sludge (2.10 mg kg^{-1}) and Rhead biopile (1.86 mg kg^{-1}) were comparable despite the difference in tPAH concentration of 84.9 and 10.5 mg kg^{-1} respectively. NSR biopile and pipeline waste had a cPAH of 6.04 mg kg^{-1} (70.4% of tPAH) and 3.85 mg kg^{-1} (39.6% of tPAH) with a corresponding B[*a*]P-TE value of 1.2 and 1.1 respectively. Top soil biopile had the lowest cPAH concentration (2.63 mg kg^{-1}) and a corresponding B[*a*]P-TE of 0.940 mg kg^{-1} (Table 1). *Table 2*: Mean concentrations of 16 priority PAH compounds, total carcinogenic PAH, total PAH and benzo[*a*]pyrene equivalent value. (Average ± SE, n=3). ND - Not detected/below detection limit.

Table 1: PAH concentration: in the study area

PAH (mg.kg^{-1})	Saltley site	South Wales Site				
		Top soil biopile	NSR biopile	Rhead biopile	Pipeline Waste	Sludge
Naphthalene	0.21±0.140	ND	ND	ND	0.167±0.0998	2.65±0.116
Acenaphthylene	0.27±0.134	ND	ND	0.255±0.129	ND	4.10±0.0302
Acenaphthene	ND	ND	ND	ND	ND	4.98±0.0504
Fluorene	ND	ND	ND	ND	0.301±0.0134	14.90±0.300
Phenanthrene	3.12±1.09	ND	ND	ND	1.12±0.0679	37.3±0.0598
Anthracene	3.64±1.11	0.418±0.0157	0.391±0.0488	0.213±0.107	1.65±0.0709	2.26±0.0436
Fluoranthene	6.75±2.31	0.814±0.359	0.408±0.131	0.513±0.364	1.49±0.0725	2.00±0.0932
Pyrene	5.56±1.83	0.952±0.519	1.34±0.286	2.06±0.149	1.14±0.0543	6.01±0.0937
Benzo[*a*] anthracene	3.67±1.14	0.628±0.00212	1.631±0.152	1.48±0.0476	1.30±0.070	1.75±0.0563
Chrysene	3.74±1.10	0.149±0.137	1.19±0.211	1.27±0.402	0.600±0.0183	4.23±0.125
Benzo [*b*] fluoranthene	2.57±0.684	0.166±0.166	0.641±0.144	0.642±0.229	0.411±0.0840	1.23±0.196
Benzo[*k*] fluoranthene	2.41±0.575	0.259±0.259	0.803±0.155	0.766±0.192	0.597±0.0701	1.23±0.101
Benzo[*a*]pyrene	4.02±1.18	0.748±0.0182	0.972±0.112	1.23±0.412	0.935±0.0194	1.44±0.283
Indeno[*1,2,3*]c,d pyrene	2.47±0.744	0.675±0.00401	0.803±0.153	0.945±0.285	ND	0.952±0.260
Dibenzo[*a,h*] anthracene	0.55±0.273	ND	ND	ND	ND	ND
Benzo[*g,h,i*] perylene	2.52±0.754	0.663±0.00189	0.763±0.239	0.887±0.315	ND	0.900±0.238
cPAH	**19.4**	**2.63**	**6.04**	**6.55**	**3.85**	**10.82**
B[*a*]P-TE	**5.79**	**0.940**	**1.38**	**1.86**	**1.19**	**2.10**
tPAH	**41.6**	**5.47**	**8.93**	**10.5**	**9.72**	**84.9**

Heavy metal concentration: The chromium, copper and lead mean concentrations for Saltey and Swansea brownfield sites are presented in Table 2. For the Swansea site, Rhead biopile had the highest concentration of chromium with 37.6 mg kg^{-1} while pipeline waste had the lowest with 11.3 mg kg^{-1}. The concentration of copper was highest in the sludge with 392 mg kg^{-1} while pipeline had the lowest with 38.5 mg kg^{-1}. The highest lead concentration was present in Rhead biopile with 239 mg kg^{-1} and lowest in

pipeline waste with 23.4 mg kg^{-1}. Pipeline waste was found to contain the lowest concentrations of Cu, Cr and Pb compared to the other biopiles and sludge. tPAHs concentrations in Saltley and Swansea sites particularly, Saltley soil (41.6 mg kg^{-1}) and Swansea sludge (84.9 mg kg^{-1}) were above the expected mean ambient background PAH concentrations at urban/industrial sites in the UK (11.2 mg kg^{-1}) (Environment Agency, 2007). This could be attributed to the various anthropogenic activities resulting in

contamination with coal and crude oil in the Saltley and Swansea sites respectively on based on the site information and history provided. Between the early 19th century and early – mid 20th century, there were intense industrial activities in the United Kingdom based on coal burning while wood burning for domestic heating was quite common (Nam *et al*., 2008). A variety of other land uses caused contamination in the United Kingdom such as railway land, engineering works, gas and coke works, chemical works, power stations and refineries (Environment Agency, 2002). The most common contaminants identified on contaminated land sites in the UK were metals, metalloids and organic compounds. Apart from industrial emission, other sources of contamination may include car exhausts, incineration and atmospheric deposition (Wild *et al*., 1990). In England the energy and waste industries were identified as the greatest source of pollution of contaminated land while for that of Wales is attributed to the deposit of ash (Environment Agency, 2009). Consequently, it is very likely that some PAHs contaminations in both sites may have been caused during the industrial era although fresh contaminations due to combustion, traffic emission, atmospheric deposition and oil spillage (in the case of the Swansea site) may have occurred in the recent years (Nam *et al*., 2008).

Table 2: Mean concentrations (mg kg^{-1}) of Cr, Cu and Pb following AAS analysis (Average ± SE, n=3).The mean ambient background soil concentrations of Cr, Cu and Pb at urban/industrial sites in the United Kingdom are 51.6-86.0, 30.9-51.5 and 78.8-131 mg kg^{-1} respectively (Environment Agency, 2007).

Brownfield Sites	**Chromium** (mg kg^{-1})	**Copper** (mg kg^{-1})	**Lead** (mg kg^{-1})
Saltley, Birmingham	72.5±3.89	186±17.5	132±25.0
Swansea, South Wales			
Top soil	28.5±3.00	142±12.3	200±26.0
NSR biopile	26.2±0.530	206±3.88	103±10.5
Rhead biopile	37.6±4.52	123±15.7	300±68.2
Pipeline	11.3±0.250	38.5±0.660	23.4±7.53
Sludge	35.0±1.99	392±8.40	122.2±27.1

The highest tPAH concentration (84.9 mg kg^{-1}) displayed by samples from Swansea sludge in comparison to the other samples may be explained by the fact that high concentration of organic contaminants as well as toxic metals are usually expected in sludge with the highest PAH concentration in waste products of refinery process (Kuriakose and Manjooran, 1994). Also our finding of the lowest tPAH concentration in the top soil biopile agreed with the site manager's assessment of the PAH levels. With respect to the PAH profiles, the predominance of fluoranthene, pyrene, chrysene, benzo[*a*]pyrene, benzo[*b*]fluoranthene and benzo[*g,h.i*]perylene (Table 1) in both sites agree with source apportionment studies of PAH profiles in UK soils dominated by fluoranthene, pyrene, phenanthrene, chrysene, benzo[*b*]fluoranthrene, benzo[*k*]fluoranthrene, and benzo[*a*]pyrene irrespective of the area whether rural, urban or industrial (Wild and Jones, 1995; Environment Agency, 2007). Also there is an expected presence of medium molecular weight PAHs such as fluoranthene and pyrene at very high concentrations in anthropogenic sites (Nadal *et al*., 2011). The PAH profile and high fluoranthene concentration in Saltley agrees with the finding of a study by Cousins *et al*. (1997) where contemporary surface soil samples collected from 46 locations widely distributed over the United Kingdom were analysed for 12 PAH compounds (anthracene, acenaphthene, fluorene, fluoranthene, phenanthrene, chrysene, benzo[*a*]anthracene, benzo[*b*]fluoranthrene, benzo[*k*]fluoranthrene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene and benzo [*g,h,i*]perylene). This is also supported by the findings of Vane *et al*. (2014) who reported the predominance of 4–6 ring PAH in soil samples collected in London, United Kingdom. This indicates PAH from mainly fossil fuel combustion however, other processes such as leaching, volatilisation and biodegradation may affect the PAH distribution (Vane *et al*., 2014). Furthermore, the low PAH concentration of low molecular weight PAH (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene) confirms greater susceptibility to microbial degradation than higher molecular weight PAHs which exhibit greater environmental persistence (Vane *et al*., 2014). This is as a result of the decrease in solubility and increase in hydrophobicity as molecular weight increases (Bojes and Pope, 2007, Vane *et al*., 2014). Hence, microbial degradation and volatilization may account for the low concentrations of some lower molecular weight PAHs compared to higher molecular weight PAHs (Table 1) with the exception of the Saltley site and Swansea sludge samples where contaminant toxicity and bioavailability may affect microbial degradation (Tian *et al*., 2008). Other limiting factors of microbial degradation such as aeration, nutrient levels (especially nitrogen and phosphorus) may have had an impact on the PAH concentration and profile (Patel *et al*., 2020).

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Heavy metal concentration at Saltley and Swansea sites: Heavy metal concentrations of both sites were above the mean ambient background soil concentration of 51.6-86.0 mg kg^{-1} (Cr), 30.9-51.5 mg kg^{-1} (Cu) and 78.8-131 mg kg^{-1} (Pb), may be attributed to site location and activities at different stages in extraction, refining and manufacturing processes (Environment Agency, 2007). As previously mentioned, the industrial revolution in the United Kingdom also led to an increase in metal concentrations in soils (Environment Agency, 2007). Most metals are strongly retained in soils with minimal losses by erosion and leaching as such any soil metal concentration is the result of cumulative additions and those derived by geogenic processes on parent rocks (Environment Agency, 2007). It is important to note that although the use of biopiling as a remedial strategy at the Swansea site may be efficient for PAH contaminated soils, an alternative strategy would be required for the heavy metal remediation as reflected by high copper and lead concentration in the top soil biopile (Table 2) (Scullion, 2006). On the whole, remediation strategies are still required on both sites to achieve concentrations below mean ambient background concentrations (Environment Agency, 2007).

Risk to human health: Saltley with B[*a*]P-TE value of 5.79 mg kg^{-1} and South Wales (top soil, NSR biopile, Rhead biopile, pipeline and sludge with B[*a*]P-TE values 0.94, 1.38, 1.86, 1.19 and 2.10 mg kg^{-1} respectively) both exceeded the soil clean up target levels (SCTL) for industrial direct exposure of 0.6 mg kg^{-1} (CCME, 2010) and median value of 0.7 mg kg^{-1} for B[*a*]P-TE (FDEP, 2005 and Jennings, 2012). However, concentrations of the non-carcinogenic PAHs in both sites were below SCTL values for industrial/commercial direct exposure. Background concentration of PAHs in both sites must be compared with SCTL for remediation but soil PAH concentration between 1-3 mg kg^{-1} are considered to be in the upper range (WHO, 2000). Consequently, based on the tPAH, cPAH and B[*a*]P-TE values there is an indication of the risk of both sites to human health depending on the proposed land use. Although the sites generally had Cr, Cu and Pb concentrations above the given ambient background concentrations it would also be important to use bioavailable concentrations of the heavy metals in assessing health risks and monitoring remediation success. The risk assessment and the proposed redevelopment projects may determine and the need for remediation.

Conclusion: The presence of the PAHs and heavy metals at Saltley and Swansea sites may be attributed to activities during the industrial era in the United Kingdom as well as recent anthropogenic activities. However, the hydrophobic nature of PAHs which facilitates adsorption to soil organic matter content may have affected their bioavailability and fate over the years. Soil microbes may have been involved in natural attenuation and biopiling, however effective remediation may be affected by a number of factors such as concentration of contaminants present and bioavailability.

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