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Soil-sebum partition coefficients for high molecular weight polycyclic aromatic hydrocarbons (HMW-PAH)

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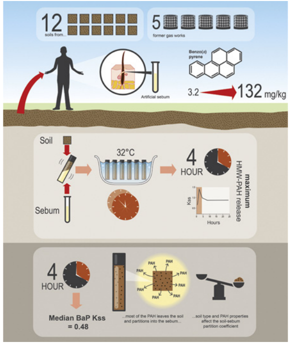
GRAPHICAL ABSTRACT



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ABSTRACT

In vitro high molecular weight polycyclic aromatic hydrocarbons (HMW-PAH) soil-sebum partition coefficients (K_{SS}) were measured for twelve soils collected from former UK gasworks. Concentrations of Σ16 USEPA PAH in the soils ranged from 51 to 1440 mg/kg. Time series extractions (0.5, 1, 2, 4, 8 and 24 h) at skin temperature (32 °C) of HMW-PAH from sebum to soil for two samples were conducted to determine the maximum release time-step. The maximum HMW-PAH release time-step was determined as 4 h, which was subsequently used as the extraction time for the remaining samples. The 4 h extraction for all samples showed HMW-PAH K_{SS} ranging from 0.06 to 1.4 (median = 0.59; mean = 0.59; standard deviation = 0.27; median absolute deviation = 0.29). Evaluation of K_{SS} data for the 4 h extractions showed that soil type and selected HMW-PAH properties (literature based molecular weight and octanol-carbon partition coefficients) affect the amount of HMW-PAH released from soil into sebum.

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1. Introduction

The skin is the largest human organ, comprising approximately 5% of total body mass, covering an area of 1.8 m^2 in a typical adult (Pannatier et al., 1978). The skin comprises three principal layers: 1) the epidermis; 2) the dermis; and 3) the hypodermis. The *stratum corneum* is the outermost layer of the epidermis and comprises solely non-viable cells. It forms a waterproof barrier and protects the underlying tissue from infection, dehydration, foreign chemicals and mechanical stress. Sweat and sebaceous glands are located in the dermis, producing sweat and sebum delivered to the *stratum corneum*. Sweat is a secretion that helps regulate body temperature and electrolytes. Sebum is a hydrophobic oily secretion that keeps the outer surface of the skin lubricated, preventing it from drying out and maintaining it as a waterproof barrier. Sebum comprises glycerides, free fatty acids, cholesterol, cholesterol esters, wax esters, and squalene (Stefaniak et al., 2010; Wertz, 2009). These lipids enhance the absorption of lipophilic chemicals through the skin (Michaels et al., 1975; Elias, 1983). Harvesting human or animal sebum for *in vitro* experiments is not feasible, meaning it needs to be formulated in the laboratory using commercially available reagents (Stefaniak et al., 2010; Wertz, 2009). Experiments designed to measure absorption of chemicals through skin are typically *in vivo* using live animals or *ex vivo* using cadaver skin (Beriro et al., 2016). There are important constraints to using living and cadaver tissue including ethical concerns, maintaining sample integrity and the reproducibility of absorption data. Laboratory simulated skin, either synthetic or biological, can overcome some of these issues and therefore presents a preferable substitute, reducing the need to use animals in dermal absorption research (Beriro et al., 2016). A recent systematic literature identified a gap in the literature for a standardised *in vitro* method to measure the dermal absorption of hazardous lipophilic chemicals contained in post-industrial soils (Beriro et al., 2016).

Polycyclic aromatic hydrocarbons (PAH) are a class of over one hundred hazardous organic chemicals, structurally characterised by two or more fused benzene rings (Agency for Toxic Substances and Disease Registry, 1995). Several PAH compounds have been shown to be genotoxic and carcinogenic in animals and humans (International Agency for Research on Cancer, 2010). PAH are formed by the incomplete combustion or pyrolysis of organic materials and occur in the environment as complex mixtures (Environment Agency, 2003; Thompson and Nathanail, 2003; Vane et al., 2014; Vane et al., 2007). The main environmental sources of PAH include the processing of coal, crude oil, the manufacture of aluminium, iron and steel; foundries; coal carbonisation including gasworks & coking works. Other sources include forest fires, the combustion of fossil fuels in power plants and for heating and cooking in domestic properties, the incineration of refuse, motor vehicle traffic exhaust fumes and tobacco smoke (World Health Organisation, 1998; Ramesh et al., 2012). Collectively these industrial, domestic and natural processes result in significant sources of atmospheric emissions and subsequent deposition. The principal factors responsible for anthropogenic PAH in soil are associated with waste, residue and/or surplus materials arising from post-industrial land uses (Environment Agency, 2003). The vast amount of coal tar pitch used in road manufacture has influenced urban environment, with an estimated 30 % of the total volumes produced used in road construction. For 1948, this equates to 750,000 tons, mixed 1:9 with aggregate it equates to 6.6 million tons. PAH occur at low levels (< 5 mg/ kg) in coal (Laumann et al., 2011) formed in the oxidation of resins (Stout et al., 2001). This is important because many of the PAH present at former gasworks sites originate from coal and/or coal tar, both of which are involved either as a raw material or by-product of industrialised coal carbonisation. Surveys of urban areas have shown that PAH are ubiquitous soil contaminants with concentrations varying considerably. In London, UK the Σ16 PAH concentrations recorded in a key study were between 4 and 67 mg/kg (n = 76) (Vane et al., 2014). High molecular weight PAH (HMW-PAH) contain ≥ 4 benzene rings while low molecular weight PAH (LMW-PAH) contain ≤ 3 benzene rings (CCME, 1999). For the purpose of this experiment, eight HMW-PAH were selected: pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Ch) benzo[*b*] fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1,2,3-cd*]pyrene (Ind), dibenz[*a,h*]anthracene (DBA). These compounds were chosen because they are most relevant to the dermal exposure pathway and considered to be some of the most toxic PAH of the United States Environmental Protection Agency (USEPA) 16 priority PAH pollutants (Beriro et al., 2016; Nisbet and Lagoy, 1992; Ruby et al., 2016; Cave et al., 2010; Abdel-Rahman et al., 2006).

Human health risk assessment (HHRA) is used to determine whether remediation of post-industrial land is required to protect human health from chronic exposure to soil contaminants. HHRA involves comparing representative concentrations of harmful chemicals in soil with assessment criteria indicative of minimal or negligible risk. The assessment criteria are a function of soil exposure and chemical toxicity. In England and Wales, guideline values are most commonly calculated using the Contaminated Land Exposure Assessment (CLEA) software developed by the Environment Agency (Environment Agency (2009a)). The BaP Generic Assessment Criteria (GAC) for a residential land use with plant uptake is 5 mg/kg (Nathanail et al., 2014; CL:AIRE, 2013). Concentrations above 5 mg/kg are considered for this study to be environmentally relevant due to the potential risk they pose to human health. The CLEA exposure scenario for BaP GAC reflects a UK conditions and is based on a female child receptor. It assumes that the ingestion exposure pathway accounts for 95 % of total intake, the dermal pathway for 5% and the inhalation pathway for a remaining 0.2 % (Nathanail et al., 2014). The proportion of BaP released from the soil entering systemic circulation, known as uptake, is referred to as the bioavailable fraction (Oomen et al., 2006). The default settings in CLEA for BaP assume bioavailability is 100 % for the ingestion pathway, 13 % for the dermal pathway and 100 % for the inhalation pathway (Nathanail et al., 2014). The bioavailable fraction of 13 % assumed for the dermal pathway is based on results from an *in vivo* study using rhesus monkeys and a single real-world soil spiked with radio-labelled BaP (Wester et al., 1990).

The current experiment is designed to measure the amount of HMW-PAH released from soil into sebum at skin temperature (32 °C) for selected gasworks soils. The experiment is progress toward the development of a physiologically-based *in vitro* dermal bioavailability test for HMW-PAH in soil. Set in the context of human health risk assessments for HMW-PAH in soil, the research responds to a gap in the literature for standardised *in vitro* dermal bioavailability measurements for soil contaminants (Beriro et al., 2016; Ruby et al., 2016). The study also builds on recent research using skin surface liquids (sebum and sweat) as a sink for consumer products (Geiss et al., 2018).. This advances science by deriving upper level estimates of HMW-PAH released from real-world contaminated soils to artificial sebum, the pre-cursor to dermal absorption. The experiment tests two null hypotheses: i) soil properties, in particular total organic carbon, have no effect on soil-sebum partitioning of HMW-PAH; and ii) soil-sebum partition coefficients do not vary between HMW-PAH compound. The study objectives are:

1. Calculate a soil-sebum partition coefficient (K_{SS}) (Equation 1) for HMW-PAH released from soil into artificial sebum at skin temperature (32 °C) for six time-steps (0.5, 1, 2, 4, 8 and 24 h) using a low (BaP = 5.5 mg/kg) and high concentration soil (BaP = 132.5 mg/kg);
2. Determine the optimum extraction time required to achieve the maximum release of benzo[*a*]pyrene from soil into sebum; and
3. Calculate a K_{SS} for HMW-PAH release from twelve soils using the maximum release time-step for benzo[*a*]pyrene; and
4. Evaluate the effect of soil type and HMW-PAH properties on their release into sebum.

$$K_{SS} = \frac{Sebum\ HMW\ PAH\ concentration\ (mg/kg)}{Soil\ HMW\ PAH\ concentration\ (mg/kg)}$$

Equation 1 Soil-sebum partition coefficient (K_{SS})

These hypotheses and objectives were chosen for the first study measuring real-world soil-sebum partition coefficients and to understand the potential effect of soil and chemical properties on the release of HMW PAH from the soil into sebum. It is important to understand the factors responsible as well as the proportion of HMW-PAH released into sebum because the mass available for dermal absorption compared to the total concentration present in the soil is proportionate to the risk to human health.

2. Methodology

The experiment was designed to reflect the first stage of dermal absorption of HMW-PAH into skin i.e. the partitioning of the chemicals from soil into sebum. Sebum-soil extractions were completed in triplicate after extraction for 0.5, 1, 2, 4, 8 and 24 h using two of twelve soil samples obtained from former gasworks located in England and Wales. The time-steps were selected because they are consistent with typical residential soil exposure durations (Environment Agency, 2009b) and they reflect the expected time required for the concentration of HMW-PAH to reach a steady-state in the artificial sebum. Where relevant, the approach is also consistent with guidance published by the Organisation for Economic Co-operation and Development (OECD) on conducting skin absorption studies (OECD, 2004).

All data processing, analyses and statistical evaluations were conducted using R (Version 3.5.1, 2018). The proprietary packages used include ggplot2 (Version 3.1.0), reshape2 (Version 1.4.3), dplyr (Version 0.8.3) and tibble (Version 2.0.1).

2.1. Collection and preparation of study soils

Twelve soil samples contaminated with HMW-PAH were collected from five former gasworks in England and Wales, UK. The former gasworks sites are owned by National Grid Property Holdings Ltd. The site names and locations are confidential, necessitating anonymised sample references for the purpose of this article. The soils selected were expected to contain environmentally relevant HMW-PAH concentrations, up to approximately one order of magnitude above published generic assessment criteria for BaP (Nathanail et al. (2014)).

Stones and other debris such as wood, metal and plastic were removed from the soils prior to comminution. The samples were freeze-dried and gently disaggregated using a pestle and mortar. They were then passed through a stainless steel mesh sieve (250 μm apertures). The sieved samples were placed in sealed amber glass jars and stored in cool and dry conditions away from sunlight. These comminution methods were selected as they have been shown to provide good data repeatability for contaminant exposure assessments over other techniques e.g. air drying and milling (Beriro et al., 2014). In the absence of formal guidance, the sieve size mesh size of 250 μm was selected as it is comparable with physiologically-based *in vitro* methods for measuring the oral bioaccessibility of chemical elements in soils (British Standard Institute, 2018). It is also this fraction that is considered to be the upper limit of particle size that is likely to adhere to children's hands, who are often the at-risk receptor for assessing contaminated sites (Cave et al., 2010).

2.2. Extraction and clean-up of HMW-PAH in soil

The soils were mixed with activated copper powder (0.5 g), to facilitate the removal of elemental sulphur, and clean granular anhydrous sodium sulphate to ensure thorough sample dispersal within each extraction cell. Each sample was extracted with dichloromethane/acetone (1:1v/v) using a Dionex ASE-200 accelerated solvent extraction (ASE) operated at 100 °C, 1500 psi. The extracts were reduced to $2-3$ mL using a TurboVap evaporation system (Caliper Life Sciences) and reduced further to 1.0 mL using a gentle stream of dry nitrogen gas (N_2).

Internal deuterated standards (1-methylnaphthalene-d10, fluorene-d10, fluoranthene-d10, benzo[*e*]pyrene-d12, perylene-d12, indeno [*1,2,3-cd*]pyrene-d12 dissolved in dichloromethane, methanol, acetone (50:40:10 v/v) were added to the extract at concentrations of between 19 000 and 63 000 ng/g dry/wt and diluted to an appropriate concentration using dichloromethane prior to gas chromatography triple quad mass spectrometry (GC–MS–MS) analysis.

2.3. Extractions of HMW-PAH from soil into sebum

The small quantities of artificial sebum required for the experiment were made by the British Geological Survey by mixing squalene (15 %), jojoba oil (25 %) (wax esters), triolein (30 %) (tri-glyceride), and oleic acid (30 %) (fatty acid). The recipe used is consistent with the relative proportions of the major components of human sebum (Stefaniak et al., 2010).

Soil (0.1 g) and sebum (1 g) were transferred into a glass vial (1.75 mL) fitted with PTFE line screw tops. The soil-sebum ratio selected was comparable to other published studies mimicking ‘wet skin conditions’ (Pawar et al., 2017; Ertl and Butte, 2012) and recommendation of a 1:10 ratio in the DIN 19738 standard (DIN, 2004).

The glass vial containing the soil and sebum was shaken using a vortex mixer for 30 s, loaded into a water bath set at 32 °C (skin temperature) and rotated end-over-end for the designated extraction time (0.5, 1, 2, 4, 8 and 24 h). At the end of each time-step, the sample was removed from the water bath and immediately centrifuged (3000 rpm, 3 min). The soil-sebum supernatant was removed using a glass Pasteur pipette and stored at 4 °C until sample clean-up by solid phase extraction (SPE).

2.4. Extraction and clean-up of HMW-PAH from sebum

The soil-sebum supernatant was subject SPE using a dual layer cartridge (Supelclean EZ-POP NP, 12 mL volume, 2.5 g bed weight, Supelco). The cartridge was conditioned using acetone (10 mL) and dried by drawing air through for 3 min using a gentle vacuum. The cartridge was weighed and the procedure repeated until a stable weight was attained. An aliquot of the supernatant was uniformly applied to the solid phase surface of the cartridge using a glass Pasteur pipette and re-weighed to obtain an exact mass of sebum (mean weight 0.44 g).

2.5. GC–MS–MS analysis of total and sebum-soil extracted soil PAH

GC–MS–MS was performed using a Varian 3800 gas chromatograph (GC) coupled to a Varian 1200 L triple quadrupole mass spectrometer operating in pseudo MS-MS mode. A volume of 1 μL of the sample was injected into the GC column using a split/splitless injector maintained at 280 °C, splitless from 0 to 0.7 min and a 1:20 split > 0.7 min. The GC was fitted with a fused silica Agilent PAH Select column (30 m length $\times$0.25 mm internal diameter $\times$0.15 μm film thickness). The GC oven-temperature programme was 60 °C (1 min. isothermal) to 320 °C (at 6 °C/min.) and held isothermally at 320 °C for 10 min. Helium was used as carrier gas (1 mL/min). The MS-MS settings are shown in Table 1.

2.6. Determination of total organic carbon

Total Organic Carbon (TOC %) was measured using Rock-Eval (6) pyrolysis (Newell et al., 2016). Approximately 60 mg dry wt. of freeze dried and sieved material was heated from 200 °C to 650 °C at 25 °C/min in an inert atmosphere of N_2 and the residual carbon was then oxidised from 300 °C to 850 °C at 20 °C/min (hold 5 min). The TOC was determined by summation of the pyrolysable and residual carbon parameters expressed as a weight %. The performance of the instrument

Table 1
MS-MS operating conditions.

Description	Parameter
Instrument	Varian 1200 L triple quadrupole mass spectrometer
Mode of operation	Electron impact (EI), selected reaction monitoring (SRM), pseudo MS-MS mode
Ionisation energy	70eV
Source temperature	250 °C
Scan rate	0.5 scans/second
Detector volatage	1500 V
Collision cell gas	Argon. analyser pressure with no argon = 2.9E-7 Torr, analyser pressure with argon = 1.2E-6 Torr, Q3 pressure with no argon = 0.962 mTorr, Q3 pressure with argon = 1.14 mTorr

was checked for every sample against the accepted values of the Institut Français du Pétrole (IFP) standard (IFP 160 000, S/N15-081840).

2.7. Quality control

The limit of detection (LoD) and limit of quantification (LoQ) for the GC–MS–MS analysis were determined initially from a calibration curve (5, 10, 20, 50, 100, 200 pg in triplicate) and then by repeated injections (n = 9) of the same standard at a mass of 20 pg, selected from the curve. The limit of quantification range for the eight HMW-PAH selected was 6–21 pg. Full results are shown in the Supporting Information (SI) (SI: Table 1).

Quality control of the soil analyses was achieved during a single run by the following procedure:

- Blank samples in duplicate (n = 2);
- Two certified reference material (CRM143, loamy soil) (CRM) samples in triplicate (n = 6);
- Six soil samples (n = 6);

Each sample was analysed for the USEPA 16 PAH and deuterated PAH (d-PAH) added prior to analysis. The CRM and surrogate d-PAH recovery rates are reported in the Supporting Information (SI: Table 2). Analysis of the procedural blanks showed that HMW-PAH concentrations therein contained concentrations ranging from not detected (< LoQ) to 0.13 mg/kg. The recovery of HMW-PAH for CRM143 ranged from 91 % to 115 % (mean 102 %, standard deviation 8%) with repeatability measured at ≤17 %. The bias when analytical data were compared to the certified values was high (0 to -52 %). The recovery of the deuterated PAH was ± 11 % (SI: Table 2).

Prior to GC–MS–MS analysis, internal deuterated standards were added to the extract at concentrations of between 19 000 and 63 000 ng/g dry/wt and diluted using dichloromethane. The standards added were 1-methylnaphthalene-d10, fluorene-d10, fluoranthene-d10, benzo[*e*]pyrene-d12, perylene-d12, indeno[*1,2,3-cd*]pyrene-d12dissolved in dichloromethane, methanol, acetone (50:40:10 v/v).

Quality control for the sebum-soil extractions was achieved by the following:

- All samples extracted in triplicate;
- Procedural blank in duplicate (n = 2); and
- 200 pg/mL QMX standard injected in triplicate at the start, middle and end of the run to determine a peak area response in comparison to the internal standards.

Surrogate d-PAH standards were not added to the soil-sebum extractions due to a concern that they might sorb to the soil matrix during extraction. It is reported that environmental samples including post-industrial soils contain rapidly and slowly desorbing PAH fractions (Ruby et al., 2016). The release of PAH at different rates means that sorption sites be vacant or competed for by both native HMW-PAH and the d-PAH recovery standards (Kjeller, 1998). This chemical behaviour is enhanced when PAH recovery from the sample matrix is especially low (Wolska et al., 2009), which also holds for sebum extracted HMW-PAH.

HMW-PAH in the procedural blanks for the soil-sebum extractions were below the limit of detection. The peak area response of the standards added at the start, middle and end of the GC–MS–MS analysis showed a relative standard deviation (%RSD) of ≤6% over all runs and standards (SI: Table 3). RSD of the sample triplicates was varied and was as much as 55 % with similarities noted between sample and extraction time-steps.

3. Results and discussion

3.1. Characterisation of study soils

Sample descriptions, HMW-PAH, Σ16 USEPA PAH and TOC are reported in Table 2. All HMW-PAH soil concentrations were above the GC–MS–MS limit of quantification. The concentrations of Σ16 USEPA PAH ranged between 51–1440 mg/kg. BaP concentrations ranged between 3.2–132 mg/kg. All but two of the samples (A1 and D4) were within the published human health GAC range of 5–77 mg/kg (Nathanail et al., 2014; CL:AIRE, 2013) (Fig. 1). TOC ranged between 1.6–14.2%. Sample A1 contained the highest content of TOC and HWM-PAH. Further analysis of the relationship between TOC and BaP shows a strong positive correlation (r = 0.84, Pearson's correlation coefficient) suggesting gasworks processes and products influence the organic content of the soil; which as a whole is comprised of both structural biopolymers and anthropogenic carbon (Cooper et al., 2019; Thomas et al., 2019). Recent studies on the composition of coal tar and other gasworks products show that their chemical composition is strongly influenced by the industrial process used to generate them (Boll et al., 2015; Gallacher et al., 2017), indicating the likelihood that each sample has a different physico-chemical properties. The PAH concentrations and range of organic carbon represent the differences in the sampling locations and processes associated with the individual gasworks (Table 2).

The concentrations of soil BaP in the study samples were broadly within range of published GAC (Nathanail et al., 2014) (Fig. 1) (~5 to 100 mg/kg). In line with other authors class these as 'environmentally relevant concentrations' (Ruby et al., 2016). Selecting real-world soils with such concentrations is important because it is at these levels where costly risk management decisions are made about whether or not to remediate soils. Dermal exposure experiments that use spiked or grossly contaminated soils do not easily meet this condition. Where possible studies should use real-world soils containing environmentally relevant concentrations of contaminants to increase the applicability of the science to real-world application (Beriro et al., 2016 and Ruby et al., 2016).

3.2. HMW-PAH soil-sebum partition coefficient

3.2.1. Time-series experiment

A high concentration (Sample A1) (BaP =132 mg/kg) and low concentration (Sample D2) (BaP = 6 mg/kg) soil (Table 2) were

Table 2
Sample descriptions, total organic carbon (%), concentrations (mg/kg) of HMW-PAH and Σtotal USEPA16 for the study soils.

Sample	Gasworks types	Soil description	Total organic carbon (%)	Concentration (mg/kg)								
				Pyrene	Benz[*a*] anthracene	Benzo[*b*] fluoranthene	Benzo[*k*] fluoranthene	Chrysene	Benzo[*a*] pyrene	Indeno [*1,2,3-cd*] pyrene	Dibenz[*a,h*] anthracene	Σ Total USEPA16 PAH
A1	Site of a former tar distillation plant within a Chemical works built to process the by-products of produced by a City gasworks. They are likely to be representative of a specific fraction of coal tar, so maybe enriched in certain PAH. This gasworks originally operated high temperature horizontal retorts (40 years) and then switched to Vertical retorts by 1920 (operated for about 40 – 50 years), and also operated a carburetted water gas (CWG) plant to make gas at time of peak demand. The source of the PAH tar is likely to be from the vertical retorts.	Gravelly made ground	14.28	239.68	108.43	115.65	56.00	106.54	132.46	16.31	66.36	1442.83
A2			9.25	116.19	56.62	48.75	24.63	53.21	63.61	7.16	30.42	731.48
B1	Site was a former town gasworks which operated between 1860 and 1915. It manufactured gas from coal using low temperature horizontal retorts.	Loamy soil	3.93	20.65	15.49	12.68	6.94	11.51	15.66	2.09	6.11	136.83
C1	Site was a small former town gasworks in Wales which operated between 1848 and 1938. It manufactured gas from coal using low temperature stop ended horizontal retorts.	Sandy gravelly made ground	1.65	7.56	4.32	5.67	2.71	3.97	4.54	0.79	2.93	51.30
D1	Site was a small former town gasworks which operated from between 1848 and 1936. It manufactured gas from coal using low temperature stop ended horizontal retorts.	Gravelly made ground	9.44	20.88	12.10	10.55	5.95	11.10	13.56	0.97	6.44	125.84
D2		Sandy made ground	7.38	10.42	5.12	4.66	2.37	4.59	5.57	0.48	2.73	59.26
D3			8.92	70.47	56.09	50.74	32.32	45.75	71.25	8.67	34.53	579.26
D4			11.72	85.78	93.31	93.45	61.28	77.99	127.25	21.04	72.82	921.70
D5		Gravelly made ground	2.10	17.02	8.71	8.88	4.81	8.07	11.56	1.29	5.24	105.62
E1	Site of a former gasholder station, adjacent to a former large town gasworks. The ground at the site appeared to have been constructed from waste materials from the gasworks when operational to raise ground levels. The adjacent gasworks were constructed in the late 19th century originally included high temperature producer fired horizontal retorts. The site switched to vertical retorts by the 1920s and operated a CWG plant.	Gravelly made ground	6.42	56.59	28.25	22.34	11.84	26.51	19.63	4.19	14.49	403.50
E2			4.69	64.33	31.65	20.36	9.60	26.71	19.86	2.59	11.69	304.20
E3		Sandy gravelly made ground	2.01	16.21	4.86	2.89	1.42	4.95	3.21	0.67	1.91	118.30

Table 3

K_{SS} descriptive statistics for 4 h time-step triplicate extractions for all twelve soil samples.

HMW-PAH	n	Minimum	Mean	Median	Maximum	Standard deviation	Median absolute deviation
Py	36	0.31	0.67	0.67	1.12	0.18	0.19
BaA	36	0.32	0.83	0.89	1.41	0.27	0.20
Ch	36	0.27	0.77	0.79	1.35	0.25	0.23
BbF	36	0.20	0.61	0.61	1.01	0.22	0.23
BkF	36	0.14	0.59	0.60	0.98	0.22	0.23
BaP	36	0.16	0.50	0.48	0.90	0.18	0.17
DBA	25	0.13	0.45	0.46	1.01	0.23	0.21
IdPy	36	0.06	0.30	0.28	0.93	0.17	0.15
All HMW-PAH	277	0.06	0.59	0.59	1.41	0.27	0.29

*11 extractions for DBA showed concentrations < LoQ, these values were removed because K_{SS} might be 0.

extracted at six individual time-steps (0.5, 1, 2, 4, 8, 24 h). HMW-PAH sebum concentrations were quantified and soil-sebum partition coefficients (K_{SS}) calculated for each PAH (Figs. 2 and 3). Full K_{SS} data is shown in the Supporting Information (SI: Table 4 and Table 5). K_{SS} timed extraction data shows that the maximum HMW-PAH release time-step is 2 h for Sample A1 and 4 h for Sample D2. Figs. 2 and 3 show rapid but variable kinetics for the release of HMW-PAH from soil in sebum up to ~4 h. Analytical precision was quantified from triplicate measurements and summarised using median absolute deviation (MAD) for each sample (SI: Table 4).

K_{SS} for Sample A1 (2 h time-step) is > 1.0 for 4-ring HMW-PAH (Py, BaA, Ch, BbF and BkF). It is clearly not possible to recover higher HMW-PAH concentrations in sebum than present in the soil. This may be explained by the following reasons: i) a sebum extraction efficiency greater than that of the solvent used for the total PAH quantification; and/or ii) uncertainty in the accuracy or precision of Sample A1 HMW-PAH content possibly caused by soil sample heterogeneity. K_{SS} for DBA in Sample D2 was not calculated because concentrations recovered from the supernatant were below the < LoQ.

MAD for the triplicate samples shows much higher precision at the 24 h time-step than the 2 h and 4 h time-step. The trend in the data suggests that the K_{SS} reaches equilibrium at ≥4 h, when K_{SS} decreases and appears to be at a steady stage (Figs. 2 and 3). This pattern is contrary to steady-state flux curves normally found in dermal absorption experiments, where concentration in a receptor solution usually increases steadily before stabilising (e.g. (Frasch et al., 2014)). The reason for the difference may be explained by an initial rapid but temporary release from the soil to sebum at 2 h and 4 h with a proportion of the HMW-PAH resorbed back onto the soil at later time-steps (Fig. 3). This is consistent with the suggestion that a proportion of the total HMW-PAH rapidly desorbs from the soil with the remainder being more tightly bound to the soil (Ruby et al., 2016). It also supports the decision not to use surrogate recovery standards to estimate the efficiency of the extraction given that their recovery was expected to be influenced by the availability of potential sorption sites in the source matrix (Kjeller, 1998; Wolska et al., 2009).

The results of the time-step experiment led to 4 h being selected as the most appropriate maximum release time-step. This value was selected using the results for Sample D2, influenced by the potential systematic error (K_{SS} > 1) shown in the 2 h time-step for Sample A1. It may be more appropriate to select a longer extraction time with lower MAD and greater precision (e.g. 24 h) but a 4 h extraction period provides a more conservative estimate of the potential amount of HMW-PAH that might released from soil to sebum in a real-world dermal exposure scenario. Using conservative parameter values in chronic exposure assessments is consistent with the principles of human health risk assessment in England and Wales, UK (Environment Agency, 2004). Further work on the solubility characteristics, saturation limits as well as physico-chemical properties of the soil, PAH and sebum would assist with identifying the cause of these preliminary observations made for the sorption kinetics of HMW-PAH in this experiment. Calculating PAH saturation limits for sebum would be a first step, ensuring that the soil-sebum ratio of 1:10 provides sufficient dissolved phase capacity for the concentrations of PAH present in the study soils. Further research on the effect of introducing sweat to the sebum mixture would also be of benefit, building on research by other authors who have focused on flame-retardants, plasticisers and metals (Pawar et al., 2017; Ertl and Butte, 2012; Marin Villegas et al., 2019).

3.2.2. Soil-sebum extractions at maximum time-step (4 h)

Concentrations of HMW-PAH in sebum at the 4 h time-step were quantified and K_{SS} calculated for eight compounds in each of the twelve soils (n = 288) (Fig. 4). Eleven ≤ LoQ data points for DBA were removed from the dataset prior to calculating summary statistics. K_{SS} for all eight HMW-PAH ranged from 0 to 1.4 (median = 0.59; mean = 0.57; standard deviation = 28.7; median absolute deviation = 28.9) (Table 3). K_{SS} for BaP ranged from 0.16 to 0.5 (median = 0.48; mean = 0.5; standard deviation of 0.18; median absolute deviation of 0.17) (Table 3). The K_{SS} ranges and median absolute deviation are high. This is due to the 4 h time-step being chosen as the preferred and most conservative extraction duration for the experiment, where Figs. 2 and 3 show earlier time-steps to be less stable with lower precision.

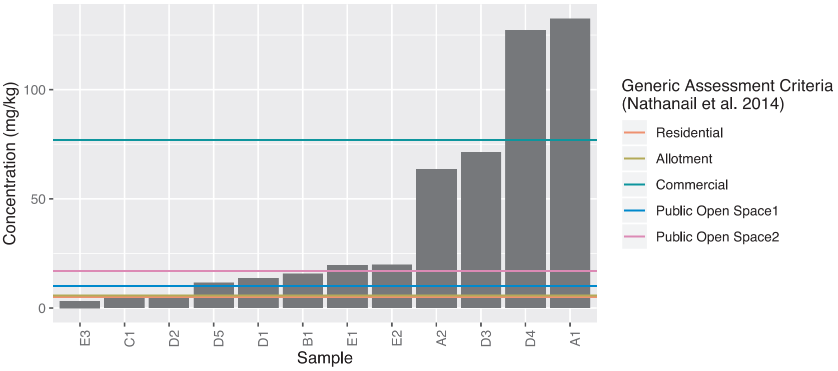


Fig. 1. Concentration of benzo[a]pyrene in study soils in the context of human health generic assessment criteria.

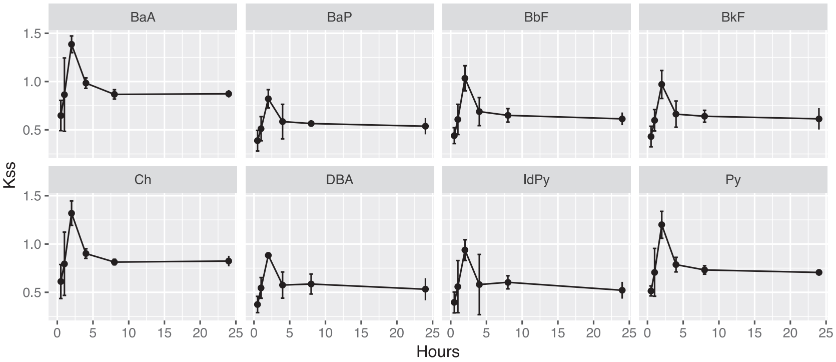


Fig. 2. Sample A1 time series median HMW−PAH K_{SS} with median absolute deviation error bars.

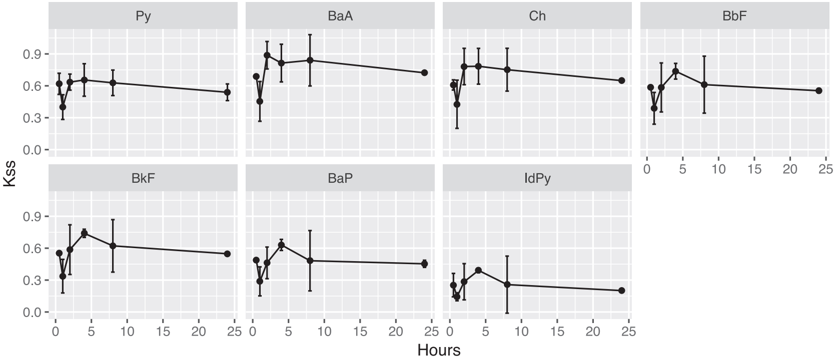


Fig. 3. Sample D2 time series median HMW−PAH K_{SS} with median absolute deviation error bars.

The precision of the experimental data is also measured using relative standard deviation (%RSD) for the triplicate extractions (SI: Table 4 and Table 5). %RSD was used in addition to median absolute deviation to help compare the data with other published studies. The mean relative standard deviation for all 4 h samples is 33 % and median is 24 % for each site. These values are broadly consistent with peer-reviewed soil PAH dermal absorption studies (Wester et al., 1990; Yang et al., 1989; Xia et al., 2016) although higher when compared to soil PAH bioaccessibility studies for the ingestion pathway which report values typically < 20 % (Cave et al., 2010; Tilston et al., 2011). Overall, the precision of this experiment is considered to be acceptable taking into account the decision to use the 4 h time-step rather than the more stable later time-steps (Figs. 2 and 3).

Comparing the results of this study with others is difficult because of the absence of similar work on soil and sebum. One study using a sebum and sweat mixture to evaluate the release of PAH from rubber consumer products showed very low release rates (0 % and 0.11 % after 1 h and between 0 % and 0.42 % after 4 h) (Geiss et al., 2018). The difference between the relatively high K_{SS} and the work by Geiss et al. is probably due to the sample matrix where PAH are more strongly bound to the rubber polymer than the post-industrial soils.

Median sample data for the 4 h extraction period are presented by molecular weight (MW) (four ring: Py < Ch < BaA < BbF < BkF; five/six ring: BaP < IdPy < DBA) and soil BaP concentration (Fig. 4) (non-detects based on < LoQ included). With the exception of Sample D5, K_{SS} for the lower molecular weight PAH (Py to BkF) is > 0.5 and < 0.5

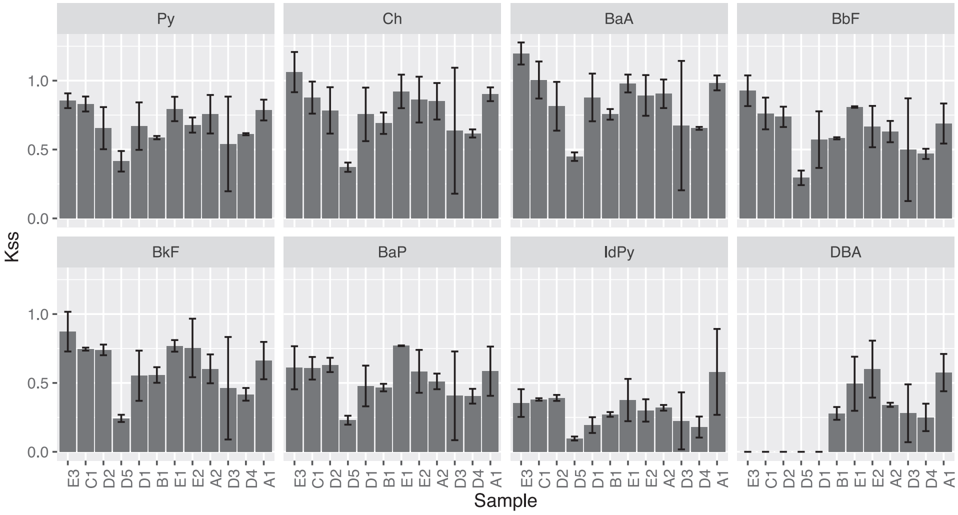
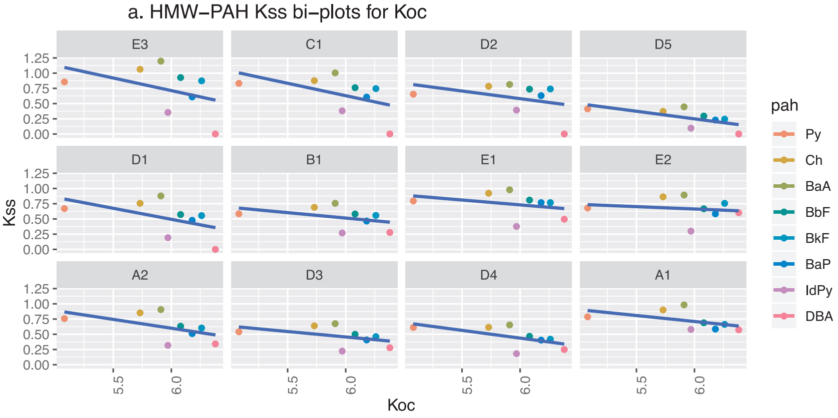


Fig. 4. Median HMW−PAH K_{SS} for 4 h extractions with median absolute deviation error bars.


a. HMW–PAH Kss bi–plots for Koc

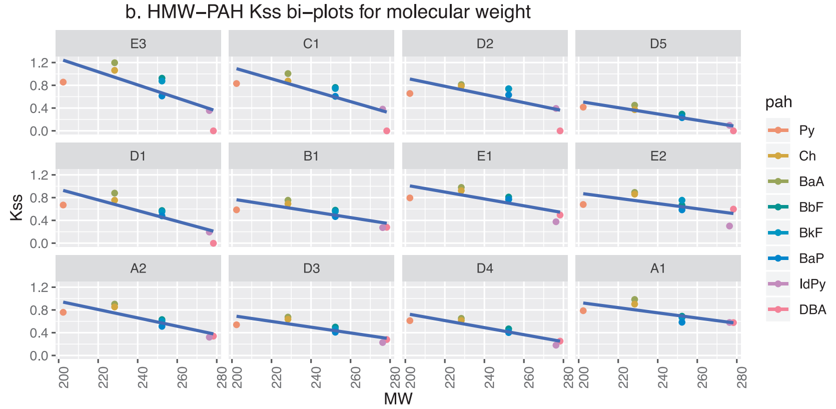

b. HMW–PAH Kss bi–plots for molecular weight

Fig. 5. a. HMW – PAH Kss bi – plots for Koc; b. HMW – PAH Kss bi – plots for molecular weight.

for the higher MW PAH (BaP to DBA) in most samples. K_{SS} is consistently lower for Sample D3, D4 and D5 than other samples (Fig. 4). The pattern for K_{SS} between samples shown in Fig. 4 indicates that sample type is an important factor in the release of HMW-PAH from soil to sebum.

Statistical evaluation of the relationship between soil PAH, K_{SS} and TOC was conducted. Linear regression models show the response of soil PAH concentrations to TOC is statistically significant where R^2 and *p*-values range for different PAH between 0.59, $p = 0.003$ (Py) and 0.71, $p = 0.0006$ (Ch), indicating that between 60 and 70 % of the variance found in TOC is due to soil PAH content. The cause of this relationship is likely to be that PAH is the principal source of organic carbon in the gasworks soils, where the higher the concentration, the higher the TOC. Furthermore, the soils used in the study were predominantly sandy gravelly/ gravelly made (artificial) ground (Table 2) which tend not to contain naturally high (> 5%) TOC. Conversely the linear regression models do not support a statistically significant K_{SS} response to TOC where R^2 and *p*-values range for between 0.196, $p = 0.1495$ (IdPy) and 4.377e-07, $p = 0.9984$ (BaA). Overall, these findings show there is a relationship between TOC and soil PAH but not TOC and K_{SS}. More research is required to understand which factors are responsible for the release of PAH from soil into sebum. The findings of the statistical analyses for TOC lead to the acceptance of the hypothesis that TOC has no effect on $K_{SS.}$ Conversely, Fig. 4 shows that sample type does influence K_{SS}, leading to the rejection of the null hypothesis that soil properties has no effect on K_{SS}. This is finding is supported by pubished research on the bioavailability and bioaccessibility of soil PAH which have shown that PAH release is at least partly dependent on soil properties. These properties include: particle size (clay and silt fraction) (De Jonge et al., 2008; Duan et al., 2014; Pu et al., 2004; Umeh et al., 2018), micro-pore structure (Duan et al., 2014; Dean and Ma, 2007), soil organic matter (De Jonge et al., 2008; Pu et al., 2004; Ukalska-Jaruga et al., 2019; Vane et al., 2007; Yu et al., 2018) and pH (De Jonge et al., 2008). Recent literature reviews (Beriro et al., 2016; Ruby et al., 2016) concluded a need to further study of the factors controlling the release of PAH from soil. The current authors suggest that a systematic literature review on the release of PAH from soil into environmental and biological matrices would usefully inform the direction of further research in this area.

The relationship between PAH properties molecular weight (MW) and octanol carbon partition coefficient (K_{OC}) with K_{SS} was evaluated using published values (Environment Agency, 2008). The results show MW and K_{OC} are both negatively correlated with K_{SS} (Fig. 5a and b). Linear regression models show response of K_{SS} to MW is statistically significant where R^2 and *p*-values range for the different samples between 0.4, $p = 0.09$ (Sample E2) and 0.84, $p = 0.001$ (Sample D4), indicating that between 40 % and 84 % of the variance found in K_{SS} can be explained by MW. Conversely, the response of K_{SS} to K_{OC} was mainly shown not to be statistically significant where R^2 and *p*-values range between 0.03, $p = 0.7$ (Sample E2) and 0.43, $p = 0.8$ (Sample D5), indicating that between 3% and 43 % of the variance found in K_{SS} can be explained by K_{OC}, notwithstanding the high *p*-values. These findings indicate there is a relationship between the release of HMW-PAH from soil into sebum and selected physico-chemical properties, MW and to a lesser extent K_{OC}. This leads to the rejection of the null hypothesis that soil-sebum partition coefficients do not vary with PAH compound. A wider study should be conducted to expand on the properties examined and the potential causes of any relationships.

4. Conclusions

This novel study reports HMW-PAH soil-sebum partition coefficients (K_{SS}) for twelve former gasworks soils contaminated with environmentally relevant concentrations of PAH (BaP = 3–133 mg/kg). Time series soil-sebum extractions at 32 °C over 48 h were completed for two soils and single time-step extractions at 4 h were completed for all soils. The 4 h time-step was chosen because it was the duration that resulted in the highest HMW-PAH release from soil into sebum . It is noted that the precision of the 4 h extraction period was less stable than later time-steps, which is put down to the nature of the matrix and the PAH kinetics in soil and sebum. K_{SS} for BaP ranged between 0.16 and 0.9 with a median of 0.48 and a median absolute deviation of 0.17 ($n = 36$). The relationship between soil TOC and soil HMW-PAH was shown to be statistically significant but there was no such relationship when TOC was compared with K_{SS}. Notwithstanding, K_{SS} data showed that HMW-PAH release is influenced by sample type. . It was also shown that selected PAH properties (MW and to a lesser extent K_{OC}) are negatively related with K_{SS}, indicating that both affect the release of HMW-PAH into sebum. These findings are preliminary observations made from the experiment data. Further work is required to establish the extent and role of PAH and soil properties, starting with a systematic review of the effect of soil properties and the release of PAH from environmental and biological matrices. Enhancements to future experimental designs would aid comparison of the data with full dermal absorption studies e.g. the inclusion of sweat with sebum and dermal absorption flux calculations. The quantification of K_{SS} in this study represents an important first step towards the development of standarsised dermal absorption studies for human health risk assessment for the chronic exposure of contaminated soils.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2020.122633.

References

Abdel-Rahman, M.S., Skowronski, G.A., Turkall, R.M., 2006. Impact of aging time on the dermal penetration of phenol in soil. Soil Sediment Contam. 15, 47–60.

Agency for Toxic Substances and Disease Registry, 1995. Public Health Statement: Polycyclic Aromatic Hydrocarbons (PAHs). ATSR, Atlanta, US.

Beriro, D.J., Vane, C.H., Cave, M.R., Nathanail, C.P., 2014. 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. Chemosphere 111, 396–404.

Beriro, D.J., Cave, M.R., Wragg, J., Thomas, R., Wills, G., Evans, F., 2016. A review of the current state of the art of physiologically-based tests for measuring human dermal in vitro bioavailability of polycyclic aromatic hydrocarbons (PAH) in soil. J. Hazard. Mater. 305, 240–259.

Boll, E.S., Nejrup, J., Jensen, J.K., Christensen, J.H., 2015. Chemical fingerprinting of hydrocarbon-contamination in soil. Environ. Sci. Process. Impacts 17, 606–618.

British Standard Institute, 2018. BS ISO 17924:2018. Soil Quality. Assessment of Human Exposure From Ingestion of Soil and Soil Material. Procedure for the Estimation of the Human bioaccessibility/bioavailability of Metals in Soil. Britsh Standards Institute, London, UK.

Cave, M.R., Wragg, J., Harrison, I., Vane, C.H., Van de Wiele, T., de Groeve, E., Nathanail, C.P., Ashmore, M., Thomas, R., Robinson, J., Daly, P., 2010. Comparison of ratch mode and dynamic physiologically rased rioaccessibility tests for pahs in soil samples. Environ. Sci. Technol. 44, 2654–2660.

CCME, 1999. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Polycyclic Aromatic Hydrocarbons (PAHs). Canadian Council of Ministers of the Environment, Canada.

CL:AIRE, 2013. Contaminated Land: Applications in Real Environments. SP1010 – Development of Category 4 Screening Levels for Assessment of Land Affected by Contamination. Department for Environment Food and Rural Affairs, London, UK.

Cooper, H.V., Vane, C.H., Evers, S., Aplin, P., Girkin, N.T., Sjögersten, S., 2019. From peat swamp forest to oil palm plantations: the stability of tropical peatland carbon. Geoderma 342, 109–117.

De Jonge, L.W., Moldrup, P., De Jonge, H., Celis, R., 2008. Sorption and leaching of short-term-aged PAHs in eight European soils: link to physicochemical properties and leaching of dissolved organic carbon. Soil Sci. 173, 13–24.

Dean, J.R., Ma, R., 2007. Approaches to assess the oral bioaccessibility of persistent organic pollutants: a critical review. Chemosphere 68, 1399–1407.

DIN, 2004. DIN 19738. Soil Quality - Bioaccessibility of Organic and Inorganic Pollutants From Contaminated Soil Material. German Institute for Standardisation (Deutsches Institut für Normung), Germany.

Duan, L., Palanisami, T., Liu, Y., Dong, Z., Mallavarapu, M., Kuchel, T., Semple, K.T., Naidu, R., 2014. Effects of ageing and soil properties on the oral bioavailability of benzo[a]pyrene using a swine model. Environ. Int. 70, 192–202.

Elias, P.M., 1983. Epidermal lipids, barrier function, and desquamation. J. Invest. Dermatol. 80, 44s–49s.

Environment Agency, 2003. Review of the Fate and Transport of Selected Contaminants in the Soil Environment: Draft Technical Report P5-079/TR1. Environment Agency, Bristol, England.

Environment Agency, 2004. Model Procedures for the Management of Land Contamination, CLR 11. Environment Agency, Bristol, England.

Environment Agency, 2008. Compilation of Data for Priority Organic Pollutants for Derivation of Soil Guideline Values. Science Report: SC050021/SR7. Environment Agency, Bristol, England.

Environment Agency, 2009a. CLEA Software (Version 1.06) Handbook. Science Report - Final SC050021/SR4. Environment Agency, Bristol, England.

Environment Agency, 2009b. Updated Technical Background to the CLEA Model. Science Report: SC050021/SR3. Environment Agency, Bristol, England.

Ertl, H., Butte, W., 2012. Bioaccessibility of pesticides and polychlorinated biphenyls from house dust: In-vitro methods and human exposure assessment. J. Expo. Sci. Environ. Epidemiol. 22, 574–583.

Frasch, H.F., Dotson, G.S., Bunge, A.L., Chen, C.P., Cherrie, J.W., Kasting, G.B., Kissel, J.C., Sahmel, J., Semple, S., Wilkinson, S., 2014. Analysis of finite dose dermal absorption data: implications for dermal exposure assessment. J. Expo. Sci. Environ. Epidemiol. 24, 65–73.

Gallacher, C., Thomas, R., Lord, R., Kalin, R.M., Taylor, C., 2017. Comprehensive database of Manufactured Gas Plant tars. Part A. Database. Rapid Commun. Mass Spectrom. 31, 1231–1238.

Geiss, O., Bianchi, I., Senaldi, C., Lucena, A., Tirendi, S., Barrero-Moreno, J., 2018. Skin surface film liquid as new migration medium for the determination of PAHs released from rubber containing consumer goods. Polycycl. Aromat. 1–10.

International Agency for Research on Cancer, 2010. Some Non-heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures (Volume 92). World Health Organisation, Lyon, France.

Kjeller, L.O., 1998. Addition of internal standards to participate sample matrices for routine trace analyses of semivolatile organic compounds: a source of systematical and random errors. Fresenius J. Anal. Chem. 361, 791–796.

Laumann, S., Micić, V., Kruge, M.A., Achten, C., Sachsenhofer, R.F., Schwarzbauer, J., Hofmann, T., 2011. Variations in concentrations and compositions of polycyclic aromatic hydrocarbons (PAHs) in coals related to the coal rank and origin. Environ. Pollut. 159, 2690–2697.

Marin Villegas, C.A., Guney, M., Zagury, G.J., 2019. Comparison of five artificial skin surface film liquids for assessing dermal bioaccessibility of metals in certified reference soils. Sci. Total Environ. 692, 595–601.

Michaels, A.S., Chandrasekaran, S.K., Shaw, J.E., 1975. Drug permeation through human skin: theory and in vitro experimental measurement. Aiche J. 21, 985–996.

Nathanail, C.P., McCaffrey, C., Gillet, A., Ogden, R., Nathanail, J., 2014. LQM/CIEH S4ULs for Human Health Risk Assessment. LQM Press, Nottingham, UK.

Newell, A.J., Vane, C.H., Sorensen, J.P.R., Moss-Hayes, V., Gooddy, D.C., 2016. Long-term Holocene groundwater fluctuations in a chalk catchment: evidence from Rock-

Eval pyrolysis of riparian peats. Hydrol. Process. 30, 4556–4567.

Nisbet, I.C.T., Lagoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

OECD, 2004. Organisation for Economic Co-operation and Development. Guideline for the Testing of Chemicals. Skin Absorption: in Vitro Method. OECD, Paris, France.

Oomen, A.G., Brandon, E.F.A., Swartjes, F.A., Sips, A.J.A.M., 2006. How Can Information on Oral Bioavailability Improve Human Health Risk Assessment for Leadcontaminated Soils? RIVM Report 711701042/2006. National Institute for Public Health and the Environment, Bilthoven, The Netherlands.

Pannatier, A., Jenner, P., Testa, B., Etter, J.C., 1978. The skin as a drug-metabolizing organ. Drug Metab. Rev. 8, 319–343.

Pawar, G., Abdallah, M.A.E., De Sáa, E.V., Harrad, S., 2017. Dermal bioaccessibility of flame retardants from indoor dust and the influence of topically applied cosmetics. J. Expo. Sci. Environ. Epidemiol. 27, 100–105.

Pu, X., Lee, L.S., Galinsky, R.E., Carlson, G.P., 2004. Evaluation of a rat model versus a physiologically based extraction test for assessing phenanthrene bioavailability from soils. Toxicol. Sci. 79, 10–17.

Ramesh, A., Archibong, Hood, D., Guo, Z., Loganathan, B., 2012. Global environmental distribution and human health effects of polycyclic aromatic hydrocarbons. In: Bommanna, G., Loganathan, P., Kwan-Sing, L. (Eds.), Global Contamination Trends of Persistent Organic Chemicals. Taylor & Frances Group, London, UK.

Ruby, M.V., Lowney, Y.W., Bunge, A.L., Roberts, S.M., Gomez-Eyles, J.L., Ghosh, U., Kissel, J.C., Tomlinson, P., Menzie, C., 2016. Oral bioavailability, bioaccessibility, and dermal absorption of PAHs from soil - state of the science. Environ. Sci. Technol. 50, 2151–2164.

Stefaniak, A.B., Harvey, C.J., Wertz, P.W., 2010. Formulation and stability of a novel artificial sebum under conditions of storage and use. Int. J. Cosmet. Sci. 32, 347–355.

Stout, S.A., Magar, V.S., Uhler, R.M., Ickes, J., Abbott, J., Brenner, R., 2001. Characterization of naturally-occurring and anthropogenic PAHs in urban sediments—Wycoff/Eagle harbor superfund site. Environ. Forensics 2, 287–300.

Thomas, M.J., Collinge, E., Witt, M., Palacio Lozano, D.C., Vane, C.H., Moss-Hayes, V., Barrow, M.P., 2019. Petroleomic depth profiling of Staten Island salt marsh soil: 2ω detection FTICR MS offers a new solution for the analysis of environmental contaminants. Sci. Total Environ. 662, 852–862.

Thompson, C.K., Nathanail, C.P., 2003. In: Thompson, C.K., Nathanail, C.P. (Eds.), Chemical Analysis of Contaminated Land. Blackwell Publishing, Oxford, UK.

Tilston, E.L., Gibson, G.R., Collins, C.D., 2011. Colon extended physiologically based extraction test (CE-PBET) increases bioaccessibility of soil-bound PAH. Environ. Sci. Technol. 45, 5301–5308.

Ukalska-Jaruga, A., Smreczak, B., Klimkowicz-Pawlas, A., 2019. Soil organic matter composition as a factor affecting the accumulation of polycyclic aromatic hydrocarbons. J. Soils Sediments 19, 1890–1900.

Umeh, A.C., Duan, L., Naidu, R., Semple, K.T., 2018. Time-dependent remobilization of Nonextractable Benzo[a]pyrene residues in contrasting soils: effects of aging, spiked concentration, and soil properties. Environ. Sci. Technol. 52, 12295–12305.

Vane, C.H., Harrison, I., Kim, A.W., 2007. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, U.K. Sci. Total Environ. 374, 112–126.

Vane, C.H., Kim, A.W., Beriro, D.J., Cave, M.R., Knights, K., Moss-Hayes, V., Nathanail, P.C., 2014. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. Appl. Geochem. 51, 303–314.

Wertz, P.W., 2009. Human synthetic sebum formulation and stability under conditions of use and storage. Int. J. Cosmet. Sci. 31, 21–25.

Wester, R.C., Maibach, H.I., Bucks, D.A.W., Sedik, L., Melendres, J., Liao, C., Dizio, S., 1990. Percutaneous absorption of [C]DDT and [C]Benzo[a]pyrene from soil. Toxicol. Sci. 15, 510–516.

Wolska, L., Gdaniec-Pietryka, M., Konieczka, P., Namieśnik, J., 2009. Problems of PAH quantification by GC-MS method using isotope-labelled standards. Talanta 78, 730–735.

World Health Organisation, 1998. In: Safety, I.P.O.C. (Ed.), Environmental Health Criteria Document No. 202 - Selected Non-Heterocyclic Aromatic Hydrocarbons. World Health Organisation, Geneva, Switzerland.

Xia, H., Gomez-Eyles, J.L., Ghosh, U., 2016. Effect of polycyclic aromatic hydrocarbon source materials and soil components on partitioning and dermal uptake. Environ. Sci. Technol. 50, 3444–3452.

Yang, J.J., Roy, T.A., Krueger, A.J., Neil, W., Mackerer, C.R., 1989. In vitro and in vivo percutaneous absorption of benzo[a]pyrene from petroleum crude-fortified soil in the rat. Bull. Environ. Contam. Toxicol. 43, 207–214.

Yu, L., Duan, L., Naidu, R., Semple, K.T., 2018. Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: putting together a bigger picture. Sci. Total Environ. 613–614, 1140–1153.