Northumbria Research Link

Citation: Sánchez-Piñero, Joel, Bowerbank, Samantha, Moreda-Piñeiro, Jorge, López-Mahía, Purificación and Dean, John (2020) The occurrence and distribution of polycyclic aromatic hydrocarbons, bisphenol A and organophosphate flame retardants in indoor dust and soils from public open spaces: Implications for human exposure. Environmental Pollution, 266 (Part 1). p. 115372. ISSN 0269-7491

Published by: Elsevier

URL: https://doi.org/10.1016/j.envpol.2020.115372 <https://doi.org/10.1016/j.envpol.2020.115372>

This version was downloaded from Northumbria Research Link: http://nrl.northumbria.ac.uk/id/eprint/44406/

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: http://nrl.northumbria.ac.uk/policies.html

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)

Northumbria University NEWCASTLE

University Library

The Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons, Bisphenol A and Organophosphate Flame Retardants in Indoor Dust and Soils from Public Open Spaces: Implications for Human Exposure

Joel Sánchez-Piñero[1], Samantha L. Bowerbank[2], Jorge Moreda-Piñeiro[1], Purificación López-Mahía[1] and John R. Dean[2*]

[1] Grupo de Química Analítica Aplicada (QANAP), University Institute of Research in Environmental Studies (IUMA), Centro de Investigacións Científicas Avanzadas (CICA), Department of Chemistry, Faculty of Sciences, University of A Coruña, Campus de A Coruña, s/n. 15071 A Coruña, Spain.

[2] Department of Applied Sciences, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK.

* Corresponding author: Professor John R. Dean, Department of Applied Sciences, Northumbria University, Newcastle upon Tyne NE1 8ST, UK. email: John.Dean@northumbria.ac.uk

Abstract

Global concern exists regarding human exposure to organic pollutants derived from public open spaces and indoor dust. This study has evaluated the occurrence of 18 polycyclic aromatic hydrocarbons (PAHs), 11 organophosphorus flame retardants (OPFRs) and bisphenol A (BPA). To achieve this, a new simple, efficient and fast multi-residue analytical method based on a fully automated pressurised liquid extraction (PLE) and subsequent quantification by gas chromatography coupled to electron ionisation-mass spectrometry (GC-EI-MS) in selected ion

monitoring (SIM) mode was developed. The developed method was applied to indoor dust (12 sampling households) and soil derived from two public open spaces (POSs). Among all compounds studied, PAHs were the most ubiquitous contaminants detected in POS soils and indoor dust although some OPFRs and BPA were detected in lower concentrations. An assessment of the incremental lifetime cancer risk (ILCR) was done and indicated a high potential cancer risk from the POS sites and some of the indoor dust sampled sites. However, key variables, such as the actual exposure duration, frequency of contact and indoor cleaning protocols will significantly reduce the potential risk. Finally, the ingestion of soils and indoor dust contaminated with OPFRs and BPA was investigated and noted in almost all cases to be below the USEPA reference doses.

Capsule: The development and application of a new simple, efficient and fast multi-residue analytical method for the investigation of organic pollutants and their risk to human health in public open spaces and indoor environments.

Keywords

Soil; indoor dust; organic pollutants; multi-residue method; health risk assessment.

Introduction

Urbanization and industrialization are accompanied by energy consumption and emission of significant amounts of pollutants in urban areas, especially in developing countries. Chemical properties of several pollutants, such as, polycyclic aromatic hydrocarbons, PAHs; bisphenol A, BPA; and, organophosphorus flame retardants, OPFRs, make them chemicals of global concern due to their adverse effects on health and their widespread occurrence in the

environment (Corrales et al., 2015; Wei et al., 2015; Abdel-Shafy and Mansour, 2016; Xiaolei Wang et al., 2019). Discharged pollutants are transported, dispersed and deposited into outdoor and indoor environments, such as soils and indoor dust, which may pose an important exposure pathway for humans (Deng et al., 2018; Chakraborty et al., 2019; Cristale et al., 2019; Gao et al., 2019; Z. Cao et al., 2019). In this research special attention has been paid to PAHs, BPA and OPFRs because of their ubiquity in various environmental compartments as well as the introduction of some regulatory aspects to address the risk to humans. However, PAHs are often considered ubiquitous in urban and industrial soils (Vane et al., 2014; Gao et al., 2019a; Y. Liu et al., 2019; Sushkova et al., 2019; Yurdakul et al., 2019) and indoor dust (Xianyu Wang et al., 2019; Z. Cao et al., 2019), while OPFRs and BPA have been detected in higher concentrations in indoor dust (Deng et al., 2018; Sugeng et al., 2018; M. Liu et al., 2019; Shoeib et al., 2019; Zhou and Püttmann, 2019; Caban and Stepnowski, 2020).

The most used extraction methodologies for the studied compounds are solid-liquid extraction (SLE) (Mortazavi et al., 2013; Haleyur et al., 2016; Arar and Alawi, 2019; Y. Liu et al., 2019), ultrasonic assisted solvent extraction (UASE) (Cristale and Lacorte, 2013; Brandsma et al., 2014; Gu et al., 2014; Sugeng et al., 2018) and pressurized liquid extraction (PLE) (Benito Quintana et al., 2007; Liu et al., 2011; Yin et al., 2011; Bojakowska et al., 2018; Salgueiro-González et al., 2018) using different organic solvents. In this study, PLE has been selected because of its simplicity in operation, automation and high efficiency in extracting organic contaminants from solid environmental matrices (Andreu and Picó, 2019). The development of multi-residue analytical methods have been reported for the simultaneous extraction and analysis of studied compounds, including 16 PAH and 9 OPFRs in sediments (e.g. Pintado-Herrera et al., 2016) and 14 PAHs, 6 OPFRs and BPA in indoor dust (e.g. Velázquez-Gómez et al., 2018), as well as other compound families. Within this context, the development of an

automated extraction technique followed by chromatographic separation and detection would be ideal for a multi-residue method as it would ultimately lead to a reduction of operating costs, reduced time for analysis, reduced solvent use and applicability to samples were their mass is often limited (e.g. indoor dust).

The aim of this study was to determine the presence of a range of organic pollutants selected due to their risk to humans (i.e. 18 PAHs, 11 OPFRs and BPA) from combustion or industrial products in public open space soils and indoor household dust. To achieve this, a simple, efficient, and fast multi-residue method based on PLE followed by GC-EI-MS was developed for the screening and quantification of the pollutants from soil and indoor dust samples. The long-term toxicity prediction, based on the benzo(a)pyrene equivalency, of exposure to PAHs from POS soil and indoor dust samples has been considered as part of a human health-risk assessment.

Materials and methods

Chemicals and solvents

Tris(1,3-dichloro-2-propyl) phosphate, TDCPP (95%), tetraethyl ethylene diphosphonate, TEEdP (97%), tris (2-ethylhexyl) phosphate, TEHP (97%), tri-m-cresyl phosphate, TCrP (95%), tri-n-butyl phosphate, TnBP (99%), triphenyl phosphate, TPhP (99%), triphenylphosphine oxide, TPPO (98.5%), tripropyl phosphate, TPrP (99%), tris (2-butoxyethyl) phosphate, TBOEP (94%), tris (2-chloroethyl) phosphate, TCEP (97%) and BPA (99%) were all purchased from Sigma-Aldrich (Steinheim, Germany). Tri-iso-butyl phosphate, TiBP (95 %) was purchased from Carbosynth Ltd (Compton, Berkshire, UK). The PAH Calibration Mix (16 compounds) (2000 µg mL^{-1} in methylene chloride was purchased from Restek (Bellefonte, PA, USA). Benzo(e)pyrene, B(e)P (10 µg mL^{-1}) in acetonitrile;

Benzo(j)fluoranthene, B(j)F (10 µg mL^{-1}) in hexane; and Retene, Ret, (10 µg mL^{-1}) in hexane were purchased from Dr. Ehrenstorfer-LGC Standards (Augsburg, Germany).

Hydromatrix was purchased from Thermo Fisher (Hemel Hempstead, UK). Acetone (99.8%), dichloromethane (99.8%) and ethyl acetate (99.5%) were purchased from Fischer Scientific (Loughborough, UK). Mixed standard solutions of OPFRs and BPA were prepared each by weighting individuals and dissolving in ethyl acetate at approximately 1000 µg mL^{-1} level. Mixed standard solution of PAHs was prepared in hexane at 1.0 µg mL^{-1} level by diluting the different commercial standards solutions. All mixed standard solutions were subsequently diluted as necessary.

Samples of soil (10 samples per site) from two open space recreational sites in North East England (Figure S1) were collected. The sites were selected based on their former historical uses as either a landfill site (Public Open Space 1, POS1) or industrial manufacturing (Public Open Space 2, POS2). In addition, 12 indoor dust (ID) samples were collected from a range of dwellings (flat, house or bungalow) across the northern part of the UK (Table S1). All details on the sampling regime, sample collection and storage and pre-treatment are detailed in the Supplementary Information.

Pressurised liquid extraction procedure:

Samples were extracted using an ASE 200 Accelerated Solvent Extractor (Thermo Fisher, Sunnyvale, CA, USA) in 11 mL stainless steel cells. A cellulose filter was placed in the bottom of the cell and was filled until a quarter of the cell volume of Hydromatrix sorbent. Then, 1.0 g of sample, accurately weighed, was added to the cell. Finally, the cell is fully filled of Hydromatrix and is closed. Extraction was performed in a single cycle of a preheating of 5 min

and 10 min static time at 100 °C and 2000 psi using acetone : dichloromethane (50 : 50, v/v) as extraction solvent. Flush volume of 50 % and purge time of 60 s were programmed. Glass ASE collector vial of 60 mL was used to collect the extract. The extract obtained was put into two tubes helping with a glass pipette. ASE collector vials were cleaned with 3 portions of extraction solvent (2 mL approximately) and the wash solvent added to the samples for evaporation. The obtained extract was concentrated to dryness using a sample concentrator (Techne, DB-3, Dri-Block®, Essex, UK) at 35 ºC and a N_2 stream of 10 psi. The residue was dissolved in 1.0 mL of ethyl acetate using a vortex and stored in 2 mL vial in a fridge at 4 ºC until GC-MS analysis. Each sample was extracted in triplicate. All cells were cleaned with acetone and were pre-extracted with cellulose filters inside using the same extraction program in the ASE. Glassware were cleaned with soap, rinsed several times using water, and finally rinsed with acetone.

GC-EI-MS system and operation conditions

Chromatographic separation was achieved using a TG-5MS column (30 m × 0.25 mm ID, 0.25 µm film thickness) from Thermo Scientific (Hemel Hempstead, UK). The chromatographic system consisted of a Trace 1300 gas chromatograph, TriPlus RSH with liquid sampling tool and an ISQ 7000 Single Quadrupole Mass Spectrometer (Thermo Scientific). Sample volume injection was 1.0 µL in splitless mode with a split flow of 30 mL min^{-1}, 1.0 min of splitless time and 10 mL min^{-1} of purge flow. The injector temperature was maintained at 300 °C. Helium was used as a carrier gas with a constant flow of 1.0 mL min^{-1}. The oven temperature program was 70 °C held for 1.0 min, followed by an increase by 40 °C min^{-1} to 110 °C, and held 2.0 min. The temperature was the increased to 170 °C by 5 °C min^{-1} and increased to 200 °C by 2.50 °C min^{-1} and held for 3.0 min. Finally, an increase to 310 °C by 5 °C min^{-1} was performed, and the temperature is held for 5.0 min with a total analysis time of 58 minutes.

149 The temperatures of the source and MS transfer line were 300 °C and 280 °C, respectively. The
150 MS was operated in selective ion monitoring (SIM) mode using electron impact ionization (EI).
151 Using above conditions and quantitative m/z shown in Table S2, the separation of 18 PAHs,
152 11 OPFRs and BPA was assessed in a single chromatographic run in 58 min.
153
154 **Method validation**
155 The calibration graphs for the PAHs, OPFRs and BPA identified in this work were constructed
156 using data from three replicates of each standard solution. Calibration data for each pollutant
157 are shown in Table S2. All calibration graphs were linear with correlation coefficients (R^2)
158 greater than 0.99. Limit of detection (LOD) and limit of quantitation (LOQ) were determined,
159 using the slope of the calibration graph and the standard deviation of the intercept, based on
160 the following equations: LOD = 3.3σ/s and LOQ = 10σ/s, where σ is standard deviation of
161 intercept and *s* is the slope. Typical LOD data varied between 3 ng g^{-1} for TEHP to 322 ng g^{-1}
162 for benzo[a]anthracene (BaA), with corresponding LOQ data of 9 ng g^{-1} and 975 ng g^{-1},
163 respectively; where it can be seen that the values are low enough to perform quantification in
164 soil and dust samples. A procedural blank (total number >20) was included in all extraction
165 batches and the average value was subtracted from the samples. Control standards were
166 injected at regular interval throughout the analysis. The results of precision and accuracy of the
167 method are shown in Tables S2 and S3, respectively. All the 30 organic pollutants
168 demonstrated good precision of (RSD $\leqslant$ 16.7%). The precision of the data from the analytical
169 standards varied between 3.5 % for TBOEP to 13.7 % for acenaphthene (Ace) (Table S2). In
170 most cases the precision of the analysed samples was slightly worse ranging from 2.6 % for
171 BPA to 16.7 % for TEHP. The trueness (expressed as percent recovery) of the developed
172 method was studied using spiked soil samples before and after PLE, at two concentration levels
173 (100 or 200 μg L^{-1} for all target compounds) (Table S3). Typical recoveries pre-PLE ranged

from 57–118 % for TPrP and TCEP; post-PLE recoveries ranged from 87 % to 137 % for Ret and TnBP, respectively. Trueness of the method (PLE plus GC-EI-MS quantification) was also assessed for 8 PAHs by analysing CRM 172 (sandy loam soil, AccuStandard Inc., New Haven, CT, USA). Concentrations found (Table S3) are in good agreement with the certified values after statistical evaluation by applying a t-test at 95% confidence level for two degrees of freedom. t_{cal} values for all PAHs (Table S3) are lower than the t_{tab} value of 4.30. These validation results indicated that the PLE−GC-EI-MS method developed in this work was acceptable. Example chromatograms for all the compounds are shown in Figure S2 including an analytical standard and soil and indoor dust extracts.

Results and Discussion

Analysis of pollutants in public open spaces and indoor dust

Two POS have been selected for consideration in this study using the developed multi-residue method of PLE-GC-EI-MS. Both are used for recreational purposes so the exposure to humans can be assessed. It can be observed (Table S4-S5) that the major contaminants are the PAHs; the ΣPAHs across all 10 sampling sites varies between 5.1 μg g^{-1} to 63 μg g^{-1} for POS1 and 7.1 μg g^{-1} to 166 μg g^{-1} for POS2. Whereas the ΣOPFRs for POS1 vary between 52 ng g^{-1} and 394 ng g^{-1} and for POS2 between 35 ng g^{-1} and 617 ng g^{-1}. As for BPA only in 4 sites from both POS1 and POS2 was it determined; the maximum BPA determined was 90 ng g^{-1}.

In comparison, 12 indoor dust samples (Table S6) were taken and analysed using the developed multi-residue method of PLE-GC-EI-MS, from the living areas of selected homes. It was noted that the concentrations determined of the ΣPAHs across all 12 sampling sites varies between

not detected to 10.5 μg g^{-1}; whereas the ΣOPFRs varied between not detected and 10.4 μg g^{-1}. In addition, the concentration of BPA, in household 2 only, was determined at 4.7 μg g^{-1}.

A comparison of the POS's and Indoor dust sites was done for ΣPAHs (Figure 1(a)) and ΣOPFRs (Figure 1(b)). In terms of the ΣPAHs it is noted that POS2 has significant higher concentrations in sampling sites 3 and 8, compared to POS1. Specifically, in sampling site 3, these elevated concentrations were down to the presence of phenanthrene, Phe (7.8 μg g^{-1}); fluoranthene, Ft (35.9 μg g^{-1}); pyrene, Pyr (5.3 μg g^{-1}); BaA (28.1 μg g^{-1}); chrysene, Chry (4.2 μg g^{-1}); benzo(b,k,j)fluoranthene isomers (3.1 μg g^{-1}); BeP (4.9 μg g^{-1}); indeno(1,2,3-c,d)pyrene, IP (12.5 μg g^{-1}); dibenzo(a,h)anthracene, DBahA (1.8 μg g^{-1}); and benzo(g,h,i)perylene, BghiP (2.2 μg g^{-1}) whereas in sampling site 8, it was from the presence of Ace (1.4 μg g^{-1}); fluorene, Fl (1.7 μg g^{-1}); Phe (55.3 μg g^{-1}); anthracene, Ant (3.5 μg g^{-1}); Chry (18.6 μg g^{-1}); benzo(b,k,j)fluoranthene isomers (11.9 μg g^{-1}); benzo(a)pyrene, BaP (14.4 μg g^{-1}); IP (49.1 μg g^{-1}), and DBahA (9.8 μg g^{-1}). Perhaps as significant was the significantly lower (>10) for the ΣPAHs in indoor dust. In fact, sample ID12 had at least double the ΣPAHs compared to any other indoor dust sample analysed; sample ID12 was from a household with both a high daily hour occupancy (typically 16.9 hours) and was heated exclusively via a wood burning stove.

Toxicity evaluation

PAH toxicity evaluation in public open space soil and indoor house dust samples

For the Public Open Space Residential, POS_{resi}, identified as an area with green open space close to housing, and that includes the possibility of tracking back soil, and of relevance to the two areas considered in this study, the Environment Agency (EA) has identified a provisional Category 4 Screening Level (C4SL) of 10 mg kg^{-1} for BaP (CL:AIRE, 2014). Fortunately, in

POS1 the highest concentration determined was 2.0 µg g^{-1} BaP in sample 10; in POS2 the highest concentration determined was 14.4 µg g^{-1} BaP in sample 8, which was above the C4SL. In terms of the risk from POS2 Sample 8 to the public is most likely from one of the three main pathways, dermal, inhalation and ingestion. As both dermal and ingestion involve physical contact, by the public, with the normally grass-covered soil it is highly probable that the risk is reduced. While the area may well be used by residents for outdoor picnics with the grassed soil will ensure the contact duration, based on an annual estimate, is insignificant. A possibility of transferring the contaminated soil within the home where the contaminants may remain is also minimal. Based on the sampling of indoor dust from other members of the population (Table S1) it is indicated that most residents may clean their floor coverings in the living spaces weekly. Inhalation, while a consideration, is unlikely to the significant as the ambient air temperature is normally <25 °C (even in mid-summer), and often only for brief periods of time. For the indoor dust samples, most homes evaluated had no detectable BaP. For the three with detectable BaP (ID2, ID6 and ID10) the maximum concentration determined was 0.8 µg g^{-1} BaP in sample ID6), which was within the C4SL for a residential home (5.0 µg g^{-1}) (CL:AIRE, 2014).

The cancer potency of each PAH was assessed based on its BaP equivalent (BaP_{eq}) concentration. BaP_{eq} concentration (ng g^{-1}) was calculated in soil and indoor dust samples, based on the measured concentrations of the individual PAH compounds, by using the following equation (Gao et al., 2019b):

$$[BaP_{eq}] = \sum([PAH_i]\ x\ TEF_i)$$

where $[PAH_i]$ represents the concentration (ng g^{-1}) of an individual PAH in samples, and TEF_i (ng g^{-1}) is the toxic equivalence factor of a given PAH (PAH_i) relative to BaP (USEPA, 1994). The TEF approach adopts BaP as the reference compound because of its highly potent

carcinogenic effect. Calculated TEFs for Ace, Fl, Phe, Ant, Ft, Pyr, Ret, BaA, Chry, BbF, BkF, BjF, BeP, BaP, IP, DBahA and BghiP are 0.001, 0.001, 0.01, 0.01, 0.01, 0.001, 0.001, 0.1, 0.01, 0.1, 0.1, 0.1, 1, 1, 0.1, 1 and 0.01, respectively, according to the USEPA (USEPA, 1994; Samburova et al., 2017). The BaP_{eq} concentration values calculated for soil samples (Table S4-S5) varied from 517 to 7150 ng g^{-1}, with an average of 3640 ng g^{-1} at POS1; and from 646 to 31100 ng g^{-1}, with an average of 6440 ng g^{-1} at POS2. The maximum BaP_{eq} concentration values were found at POS1-7 and POS2-8. The BaP_{eq} concentration values calculated for indoor samples (Table S6) varied from <LOQ to 1880 ng g^{-1}, with an average of 449 ng g^{-1}.

The incremental lifetime cancer risk (ILCR) through soil/dust ingestion, inhalation and dermal absorption pathways, has been also applied to quantitatively assess the carcinogenic potential of environmental PAHs to humans. The ILCR refers to the probability of an individual who is exposed to PAHs during his or her lifetime (USEPA, 2005). The ILCR model was applied along with TEFs by using the following equations (Ali et al., 2017; Cao et al., 2017):

$$ILCR_{ing} = CSF_{ing}\ x\ \sqrt[3]{\frac{BW}{70}}\ x\ \frac{[BaP_{eq}]x\ IR_{ing}\ x(EF\ x\ ED\ x\ 10^{-6})}{BW\ x\ AT}$$

$$ILCR_{inh} = CSF_{inh}\ x\ \sqrt[3]{\frac{BW}{70}}\ x\ \frac{[BaP_{eq}]x\ \left(\frac{IR_{inh}}{PEF}\right)\ x(EF\ x\ ED)}{BW\ x\ AT}$$

and

$$ILCR_{derm} = CSF_{derm}\ x\ \sqrt[3]{\frac{BW}{70}}\ x\ \frac{[BaP_{eq}]x\ (SA\ x\ AF)x(EF\ x\ ED\ x\ 10^{-6})\ x\ ABS}{BW\ x\ AT}$$

where $ILCR_{ing}$, $ILCR_{inh}$ and $ILCR_{derm}$ are the incremental lifetime cancer risks resulting from the dust ingestion, inhalation and dermal absorption pathways, respectively; CSF_{ing}, CSF_{inh} and CSF_{derm} are the carcinogenic slope factor (7.3, 3.85 and 25 mg^{-1} kg d) for ingestion, inhalation and dermal absorption pathways, respectively) (Ma et al., 2017); IR_{ing} is the soil/dust ingestion

rate (10 and 200 mg d^{-1} for adult and children, respectively) (USEPA, 2002; Z. Cao et al., 2019); *PEF* is the particle emission factor (1.36×10^9 m^3 kg^{-1}) (USEPA, 2002; Z. Cao et al., 2019): *BW* is the body weight (70 and 15 kg for adult and children, respectively) (Z. Cao et al., 2019); IR_{inh} is the inhalation rate (20 and 10 mg d^{-1} for adult and children, respectively) (USEPA, 2002; Z. Cao et al., 2019); *EF* is the exposure frequency (180 d $year^{-1}$) (Cao et al., 2017; Z. Cao et al., 2019); *ED* is the exposure duration (24 and 6 year for adult and children, respectively) (USEPA, 2002; Z. Cao et al., 2019); *AT* is the average life span (25550 d) (Z. Cao et al., 2019); *SA* is the surface area of dermal exposure (5700 and 2800 cm^2 d^{-1} for adult and children, respectively) (USEPA, 2002; Z. Cao et al., 2019); *AF* is the skin adherence factor (0.07 and 0.2 mg cm^{-2} for adult and children, respectively) (USEPA, 2002; Z. Cao et al., 2019); and *ABS* is the dermal adsorption fraction (0.13, unitless) (USEPA, 2002; Z. Cao et al., 2019).

The sum of ILCR values via ingestion, inhalation and dermal absorption is defined as incremental lifetime cancer risk sum ($ILCR_s$):

$$ILCR_s = \sum (ILCR_{ing} + ILCR_{inh} + ILCR_{derm})$$

When $ILCR_s \leqslant 10^{-6}$ suggests a negligible risk under most regulatory programmes, $ILCR_s$ among 10^{-6} and 10^{-4} suggests a potential risk and $ILCR_s > 10^{-4}$ imply potentially high risk (Ali et al., 2017).

ILCR values through dust ingestion, inhalation and dermal absorption pathways achieved for adults and children are shown in Figure 2 (Table S7. The results (Figure 2, and Table S7) indicated that the exposure pathways of PAHs for both adults and children follow the order: dermal > ingestion >>> inhalation (ingestion and dermal absorption were the most dominant exposure pathways when compared with inhalation pathway). The ILCR through inhalation

varies from 7.1 x 10^{-8} to 9.8 x 10^{-7} (for adult) and 2.6 x 10^{-8} to 3.6 x 10^{-7} (for child) at POS1 and varies from 8.8 x 10^{-8} to 4.3 x 10^{-6} (for adult) and 3.2 x 10^{-8} to 1.6 x 10^{-6} (for child) at POS2; indicating the inhalation-induced cancer risk was almost negligible. On the contrary, high ILCR values through ingestion (9.1 x 10^{-4} − 1.3 x 10^{-2} (for adult) and 9.1 x 10^{-4} − 1.8 x 10^{-2} (for child) at POS1 and 1.1 x 10^{-3} − 5.5 x 10^{-2} (for adult) and 1.1 x 10^{-3} − 8.0 x 10^{-2} (for child) at POS2) were achieved. High $ILCR_{derm}$ values were also achieved (1.6 x 10^{-3} − 2.2 x 10^{-2} (for adult) and 1.7 x 10^{-3} − 2.3 x 10^{-2} (for child) at POS1; 2.0 x 10^{-3} − 9.7 x 10^{-2} (for adult) and 2.1 x 10^{-3} − 1.0 x 10^{-1} (for child) at POS2). Low ILCR values through all pathways were obtained for indoor house dust samples with $ILCR_{inh}$ average of 6.2 x 10^{-8} (for adults) and 2.2 x 10^{-8} (for child), $ILCR_{ing}$ average of 7.9 x 10^{-4} (for adults) and 1.2 x 10^{-3} (for child) and $ILCR_{derm}$ average of 1.4 x 10^{-3} (for adults and child) for dermal absorption. Also, there was a small difference in the levels of cancer risk through dermal absorption between adults and child. Total cancer risk achieved at both POS sites and in specific indoor house dust samples ($ILCR_s$ average of 1.8 x 10^{-2} (for adults) and 2.1 x 10^{-2} (for child) at POS1, 3.2 x 10^{-2} (for adults) and 3.7 x 10^{-2} (for child) at POS2, and 2.2 x 10^{-3} (for adults) and 2.6 x 10^{-3} (for child) for indoor house dust samples), exceed the safety level a high potential cancer risk to exposed adults and children. However, these lifetime calculations need to be considered against the habits of individuals in the POS sites including their actual frequency of visitation and contact with the soil, whereas in the case of the indoor dust samples the weekly cleaning of the living spaces (Table S1) will significantly lower the cancer risk.

In comparing with the literature (Table 1), a higher risk was estimated for industrial soils and dust rather than urban or agricultural soils and household dust. Regarding exposure pathways, $ILCR_{inh}$ shown the lower contribution to $ILCR_s$ as obtained in this study, except for the study conducted by Hanedar et al. (Hanedar et al., 2020). Furthermore, dermal and ingestion

exposure pathways represent similar contributions to $ILCR_s$, showing the higher values for dermal exposure to indoor dusts and soil ingestion (both for a child). In general, the $ILCR_s$ (as well as $ILCR_{ing}$, $ILCR_{der}$ and $ILCR_{ing}$) achieved in this study for soils and indoor dust samples are higher than those previously reported in the literature (Table 1). However, it is important to point out that $ILCR_s$ are strongly influenced by the number of target PAHs considered, sampling period times, TEFs values and environmental exposure factors selected. Then, the lack of consensus on $ILCR_s$ parameters makes comparisons between studies more difficult.

OPFRs toxicity evaluation in indoor house dust samples

OPFR toxicity in indoor house dust samples was calculated through daily intake via dust ingestion. Human intake of OPFRs via dust ingestion was estimated for adults and child using the following equation (USEPA, 2017):

$$DI_i = \frac{EC\ x\ DIR}{BW}$$

where *DI* is the daily intake (μg kg_{BW}^{-1} d^{-1}) as determined in the indoor dust sample; *EC* is the exposure concentration of OPFR (μg g^{-1}); *DIR* is the indoor settled dust ingestion rate (0.060 and 0.100 g d^{-1} for adult and children, respectively) obtained from the United States Environmental Protection Agency (USEPA, 2017); and *BW* is the adult body weight (70 and 15 kg for adult and children, respectively). The sum of DI_i values is defined as daily intake sum (DI_s):

$$DI_s = \sum (DI_i)$$

Estimated exposure to OPFRs from dust ingestion (DI_i) (Table 2) ranged for individual OPFRs between <0.007 to 9.0 μg kg_{BW}^{-1} d^{-1} for TEHP and adults; and between <0.05 to 69.7 μg kg_{BW}^{-1} d^{-1} for TEHP and child. Results shown in Table 2 were compared with the reference dose (RfD)

values (μg kg_{BW}^{-1} d^{-1}) for some OPFRs (2.4, 2.2, 1.5, 1.5 and 7.0 for μg kg_{BW}^{-1} d^{-1} for TnBP, TCEP, TDCPP, TBOEP and TPhP, respectively) (Van den Eede et al., 2011; Shoeib et al., 2019). The estimated DI for children were below RfD values, except for TnBP in sample 8 and TBOEP in samples 2, 5, 6, 7 and 11. By the same way, estimated DI for adults were lower than RfDs for all samples and target OPFRs, except for TBOEP in dust samples 6, 9 and 12. Finally, the sum of DI_i values for adults (DI_s^{adult}) and child (DI_s^{child}) listed in Table 2 shown values into the range of 0.095 to 9.0 μg kg_{BW}^{-1} d^{-1} for adults and 0.74 to 69.7 μg kg_{BW}^{-1} $d^{-1}$for children.

BPA toxicity evaluation in indoor house dust samples

In terms of the risk from the endocrine disruptor BPA in indoor house dust sample ID2 (determined concentration of 4.7 μg g^{-1}) it is possible to calculate the maximum estimated daily intake through indoor dust ingestion (DI) using the above equation (USEPA, 2017). The DI of BPA through indoor dust ingestion was 0.004 and 0.031 μg kg_{BW}^{-1} d^{-1} for adults and children, respectively; which is considerably lower than the temporary tolerable daily intake of 4.0 μg kg_{BW}^{-1} d^{-1} as part of a dietary exposure and low health concern from aggregated exposure (including dust) study (EFSA, 2015). For samples ID1 and ID3-12, DI through indoor dust ingestion are lower than 0.034 and 0.27 μg kg_{BW}^{-1} d^{-1} for adult and child, respectively.

Conclusions

Our developed multi-residue PLE-GC-EI-MS method has been successfully applied to analyse PAHs, OPFRs and BPA in public open space soil and indoor dust samples. Almost all determined concentrations are within regulatory requirements (in England), an exception is BaP (Sample 8, POS2). While the cancer risk, as determined by the ILCRs for dermal, ingestion and inhalation exposure indicated a high potential risk this needs to be considered in terms of actual exposure and soil contact in POSs and the frequency of cleaning in the home which will

remove the indoor dust. Finally, ingestion of OPFRs and BPA were investigated against the reference dose; in almost all cases ingestion rates were within regulatory guidance (USEPA).

Acknowledgments

This work was supported by Ministerio de Ciencia, Innovación y Universidades (MCIU), Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER) (Programa Estatal de I+D+i Orientada a los Retos de la Sociedad, ref: RTI 2018-101116-B-I00) and Xunta de Galicia (Programa de Consolidación y Estructuración de Unidades de Investigación Competitivas ref: ED431C 2017/28-2017-2020). Joel Sánchez-Piñero acknowledges the Xunta de Galicia and the European Union (European Social Fund - ESF) for a predoctoral grant (ED481A-2018/164). Financial support from the host (Northumbria University) is also acknowledged.

CRediT author statement

John R. Dean: Conceptualization, Methodology, Writing – Reviewing and Editing; Joel Sánchez-Piñero: Data curation, Writing - Original draft preparation; Samantha Bowerbank: Methodology, Data curation; Jorge Moreda-Piñeiro: Supervision; Purificación López-Mahía: Supervision.

References

Abdel-Shafy, H.I., Mansour, M.S.M.M., 2016. A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egypt. J. Pet. 25, 107–123. https://doi.org/10.1016/j.ejpe.2015.03.011

Ali, N., Ismail, I.M.I., Khoder, M., Shamy, M., Alghamdi, M., Al Khalaf, A., Costa, M., 2017. Polycyclic aromatic hydrocarbons (PAHs) in the settled dust of automobile workshops, health and carcinogenic risk evaluation. Sci. Total Environ. 601–602, 478–484. https://doi.org/10.1016/j.scitotenv.2017.05.110

393 Andreu, V., Picó, Y., 2019. Pressurized liquid extraction of organic contaminants in
394 environmental and food samples. TrAC Trends Anal. Chem. 118, 709–721.
395 https://doi.org/10.1016/J.TRAC.2019.06.038
396 Arar, S., Alawi, M., 2019. A new solvent extraction method with gas chromatography–mass
397 spectrometry for bisphenol A determination in canned foods. Acta Chromatogr. 31, 71–
398 78. https://doi.org/10.1556/1326.2017.00388
399 Benito Quintana, J., Rodil, R., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez,
400 D., 2007. Optimisation of a selective method for the determination of
401 organophosphorous triesters in outdoor particulate samples by pressurised liquid
402 extraction and large-volume injection gas chromatography-positive chemical ionisation-
403 tandem mass spectrometry. Anal. Bioanal. Chem. 388, 1283–1293.
404 https://doi.org/10.1007/s00216-007-1338-4
405 Bojakowska, I., Tomassi-Morawiec, H., Markowski, W., 2018. PAHs and DDTs in soil and
406 sediment of inland water bodies of Warsaw city and its surroundings. J. Geochemical
407 Explor. 187, 57–71. https://doi.org/10.1016/j.gexplo.2017.07.013
408 Brandsma, S.H., de Boer, J., van Velzen, M.J.M., Leonards, P.E.G., 2014. Organophosphorus
409 flame retardants (PFRs) and plasticizers in house and car dust and the influence of
410 electronic equipment. Chemosphere 116, 3–9.
411 https://doi.org/10.1016/j.chemosphere.2014.02.036
412 Caban, M., Stepnowski, P., 2020. Determination of bisphenol A in size fractions of indoor
413 dust from several microenvironments. Microchem. J. 153, 104392.
414 https://doi.org/10.1016/j.microc.2019.104392
415 Cao, W., Yin, L., Zhang, D., Wang, Y., Yuan, J., Zhu, Y., Dou, J., 2019. Contamination,
416 sources, and health risks associated with soil PAHs in rebuilt land from a Coking Plant,
417 Beijing, China. Int. J. Environ. Res. Public Health 16, 670.

https://doi.org/10.3390/ijerph16040670

Cao, Z., Wang, M., Chen, Q., Zhu, C., Jie, J., Li, X., Dong, X., Miao, Z., Shen, M., Bu, Q., 2019. Spatial, seasonal and particle size dependent variations of PAH contamination in indoor dust and the corresponding human health risk. Sci. Total Environ. 653, 423–430. https://doi.org/10.1016/j.scitotenv.2018.10.413

Cao, Z., Zhao, L., Shi, Y., Feng, J., Wang, S., Zhang, Y., Yan, G., Zhang, X., Wang, X., Shen, M., Wang, Y., 2017. PAH contamination in road dust from a moderate city in North China: The significant role of traffic emission. Hum. Ecol. Risk Assess. An Int. J. 23, 1072–1085. https://doi.org/10.1080/10807039.2017.1300768

Chakraborty, P., Sampath, S., Mukhopadhyay, M., Selvaraj, S., Bharat, G.K., Nizzetto, L., 2019. Baseline investigation on plasticizers, bisphenol A, polycyclic aromatic hydrocarbons and heavy metals in the surface soil of the informal electronic waste recycling workshops and nearby open dumpsites in Indian metropolitan cities. Environ. Pollut. 248, 1036–1045. https://doi.org/10.1016/j.envpol.2018.11.010

CL:AIRE, 2014. Development of Category 4 Screening Levels for Assessment of Land Affected by Contamination: Appendix E Provisional C4SLs for Benzo(a)pyrene as a surrogate marker for PAHs.

Corrales, J., Kristofco, L.A., Baylor Steele, W., Yates, B.S., Breed, C.S., Spencer Williams, E., Brooks, B.W., 2015. Global assessment of bisphenol a in the environment: Review and analysis of its occurrence and bioaccumulation. Dose-Response 13. https://doi.org/10.1177/1559325815598308

Cristale, J., Aragão Belé, T.G., Lacorte, S., de Marchi, M.R.R., 2019. Occurrence of flame retardants in landfills: A case study in Brazil. Environ. Res. 168, 420–427. https://doi.org/10.1016/j.envres.2018.10.010

Cristale, J., Lacorte, S., 2013. Development and validation of a multiresidue method for the

443 analysis of polybrominated diphenyl ethers, new brominated and organophosphorus
444 flame retardants in sediment, sludge and dust. J. Chromatogr. A 1305, 267–275.
445 https://doi.org/10.1016/J.CHROMA.2013.07.028
446 Deng, W.J., Li, N., Wu, R., Richard, W.K.S., Wang, Z., Ho, W., 2018. Phosphorus flame
447 retardants and Bisphenol A in indoor dust and PM2.5 in kindergartens and primary
448 schools in Hong Kong. Environ. Pollut. 235, 365–371.
449 https://doi.org/10.1016/j.envpol.2017.12.093
450 EFSA, 2015. Scientific Opinion on the risks to public health related to the presence of
451 bisphenol A (BPA) in foodstuffs, EFSA Journal.
452 https://doi.org/10.2903/j.efsa.2015.3978
453 Gao, P., da Silva, E.B., Townsend, T., Liu, X., Ma, L.Q., 2019a. Emerging PAHs in urban
454 soils: Concentrations, bioaccessibility, and spatial distribution. Sci. Total Environ. 670,
455 800–805. https://doi.org/10.1016/j.scitotenv.2019.03.247
456 Gao, P., Liu, D., Guo, L., He, C., Lin, N., Xing, Y., Yao, C., Wu, B., Zheng, Z., Wang, Y.,
457 Hang, J., 2019b. Ingestion bioaccessibility of indoor dust-bound PAHs: Inclusion of a
458 sorption sink to simulate passive transfer across the small intestine. Sci. Total Environ.
459 659, 1546–1554. https://doi.org/10.1016/J.SCITOTENV.2018.12.459
460 Gu, Y. yun, Yu, X. jun, Peng, J. feng, Chen, S. bing, Zhong, Y. ying, Yin, D. qiang, Hu, X.
461 lin, 2014. Simultaneous solid phase extraction coupled with liquid chromatography
462 tandem mass spectrometry and gas chromatography tandem mass spectrometry for the
463 highly sensitive determination of 15 endocrine disrupting chemicals in seafood. J.
464 Chromatogr. B Anal. Technol. Biomed. Life Sci. 965, 164–172.
465 https://doi.org/10.1016/j.jchromb.2014.06.024
466 Haleyur, N., Shahsavari, E., Mansur, A.A., Koshlaf, E., Morrison, P.D., Osborn, A.M., Ball,
467 A.S., 2016. Comparison of rapid solvent extraction systems for the GC-MS/MS

468 characterization of polycyclic aromatic hydrocarbons in aged, contaminated soil.
469 MethodsX 3, 364–370. https://doi.org/10.1016/j.mex.2016.04.007
470 Hanedar, A., Güneş, E., Kaykioğlu, G., Çelik, S.Ö., Cabi, E., 2020. Determination of
471 polycyclic aromatic hydrocarbons in the soil, atmospheric deposition and biomonitor
472 samples in the Meric-Ergene River Basin, Turkey. Environ. Dev. Sustain. 22, 3389–
473 3406. https://doi.org/10.1007/s10668-019-00350-3
474 Kumar, B., Verma, V.K., Kumar, S., Sharma, C.S., 2013. Probabilistic health risk assessment
475 of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in urban soils from a
476 tropical city of India. J. Environ. Sci. Heal. Part A 48, 1253–1263.
477 https://doi.org/10.1080/10934529.2013.776894
478 Liu, J., Wang, R., Huang, B., Lin, C., Wang, Y., Pan, X., 2011. Distribution and
479 bioaccumulation of steroidal and phenolic endocrine disrupting chemicals in wild fish
480 species from Dianchi Lake, China. Environ. Pollut. 159, 2815–2822.
481 https://doi.org/10.1016/j.envpol.2011.05.013
482 Liu, M., Jia, S., Dong, T., Han, Y., Xue, J., Wanjaya, E.R., Fang, M., 2019. The occurrence
483 of bisphenol plasticizers in paired dust and urine samples and its association with
484 oxidative stress. Chemosphere 216, 472–478.
485 https://doi.org/10.1016/j.chemosphere.2018.10.090
486 Liu, Y., Gao, P., Su, J., da Silva, E.B., de Oliveira, L.M., Townsend, T., Xiang, P., Ma, L.Q.,
487 2019. PAHs in urban soils of two Florida cities: Background concentrations,
488 distribution, and sources. Chemosphere 214, 220–227.
489 https://doi.org/10.1016/j.chemosphere.2018.09.119
490 Ma, Y., Liu, A., Egodawatta, P., McGree, J., Goonetilleke, A., 2017. Quantitative assessment
491 of human health risk posed by polycyclic aromatic hydrocarbons in urban road dust. Sci.
492 Total Environ. 575, 895–904. https://doi.org/10.1016/j.scitotenv.2016.09.148

493 Mortazavi, S., Bakhtiari, A.R., Sari, A.E., Bahramifar, N., Rahbarizadeh, F., 2013.
494 Occurrence of endocrine disruption chemicals (Bisphenol A, 4-nonylphenol, and
495 octylphenol) in muscle and liver of, Cyprinus carpino common, from Anzali Wetland,
496 Iran. Bull. Environ. Contam. Toxicol. 90, 578–584. https://doi.org/10.1007/s00128-013-
497 0964-0
498 Peng, C., Chen, W., Liao, X., Wang, M., Ouyang, Z., Jiao, W., Bai, Y., 2011. Polycyclic
499 aromatic hydrocarbons in urban soils of Beijing: Status, sources, distribution and
500 potential risk. Environ. Pollut. 159, 802–808.
501 https://doi.org/10.1016/j.envpol.2010.11.003
502 Pintado-Herrera, M.G., González-Mazo, E., Lara-Martín, P.A., 2016. In-cell clean-up
503 pressurized liquid extraction and gas chromatography-tandem mass spectrometry
504 determination of hydrophobic persistent and emerging organic pollutants in coastal
505 sediments. J. Chromatogr. A 1429, 107–118.
506 https://doi.org/10.1016/j.chroma.2015.12.040
507 Salgueiro-González, N., Castiglioni, S., Zuccato, E., Turnes-Carou, I., López-Mahía, P.,
508 Muniategui-Lorenzo, S., 2018. Recent advances in analytical methods for the
509 determination of 4-alkylphenols and bisphenol A in solid environmental matrices: A
510 critical review. Anal. Chim. Acta 1024, 39–51. https://doi.org/10.1016/j.aca.2018.02.081
511 Samburova, V., Zielinska, B., Khlystov, A., 2017. Do 16 polycyclic aromatic hydrocarbons
512 represent PAH air toxicity? Toxics 5, 17. https://doi.org/10.3390/toxics5030017
513 Shoeib, T., Webster, G.M., Hassan, Y., Tepe, S., Yalcin, M., Turgut, C., Kurt-Karakuş, P.B.,
514 Jantunen, L., 2019. Organophosphate esters in house dust: A comparative study between
515 Canada, Turkey and Egypt. Sci. Total Environ. 650, 193–201.
516 https://doi.org/10.1016/j.scitotenv.2018.08.407
517 Škrbić, B., Đurišić-Mladenović, N., Živančev, J., Tadić, Đ., 2019. Seasonal occurrence and

cancer risk assessment of polycyclic aromatic hydrocarbons in street dust from the Novi Sad city, Serbia. Sci. Total Environ. 647, 191–203. https://doi.org/10.1016/j.scitotenv.2018.07.442

Slezakova, K., Oliveira, M., Madureira, J., Fernandes, E. de O., Delerue-Matos, C., Morais, S., Pereira, M. do C., 2017. Polycyclic aromatic hydrocarbons (PAH) in Portuguese educational settings: a comparison between preschools and elementary schools. J. Toxicol. Environ. Heal. - Part A Curr. Issues 80, 630–640. https://doi.org/10.1080/15287394.2017.1286931

Sugeng, E.J., de Cock, M., Leonards, P.E.G., van de Bor, M., 2018. Electronics, interior decoration and cleaning patterns affect flame retardant levels in the dust from Dutch residences. Sci. Total Environ. 645, 1144–1152. https://doi.org/10.1016/j.scitotenv.2018.07.127

Sushkova, S., Minkina, T., Deryabkina, I., Rajput, V., Antonenko, E., Nazarenko, O., Yadav, B.K., Hakki, E., Mohan, D., 2019. Environmental pollution of soil with PAHs in energy producing plants zone. Sci. Total Environ. 655, 232–241. https://doi.org/10.1016/j.scitotenv.2018.11.080

Tarafdar, A., Sinha, A., 2019. Health risk assessment and source study of PAHs from roadside soil dust of a heavy mining area in India. Arch. Environ. Occup. Heal. 74, 252–262. https://doi.org/10.1080/19338244.2018.1444575

USEPA, 2017. Update for Chapter 5 of the Exposure Factors Handbook: Soil and Dust Ingestion. Expo. Factors Handb. 1–100.

USEPA, 2005. Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities. US Environmental Protection Agency. Washington, DC.

USEPA, 2002. Supplemental Guidance for developing soil screening levels for Superfund sites. Office of Solid Waste and Emergency Response (OSWER).

543 USEPA, 1994. Benzo[a]pyrene (BaP). U.S.: Environmental Protection Agency. Washington,
544 DC.
545 Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and
546 preliminary assessment of human exposure to organophosphate flame retardants from
547 indoor dust. Environ. Int. 37, 454–461. https://doi.org/10.1016/j.envint.2010.11.010
548 Vane, C.H., Kim, A.W., Beriro, D.J., Cave, M.R., Knights, K., Moss-Hayes, V., Nathanail,
549 P.C., 2014. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls
550 (PCB) in urban soils of Greater London, UK. Appl. Geochemistry 51, 303–314.
551 https://doi.org/10.1016/J.APGEOCHEM.2014.09.013
552 Velázquez-Gómez, M., Hurtado-Fernández, E., Lacorte, S., 2018. Comprehensive method for
553 the analysis of multi-class organic micropollutants in indoor dust. Sci. Total Environ.
554 635, 1484–1494. https://doi.org/10.1016/J.SCITOTENV.2018.04.186
555 Wang, J., Zhang, X., Ling, W., Liu, R., Liu, J., Kang, F., Gao, Y., 2017. Contamination and
556 health risk assessment of PAHs in soils and crops in industrial areas of the Yangtze
557 River Delta region, China. Chemosphere 168, 976–987.
558 https://doi.org/10.1016/j.chemosphere.2016.10.113
559 Wang, Xianyu, Banks, A.P.W., He, C., Drage, D.S., Gallen, C.L., Li, Y., Li, Q., Thai, P.K.,
560 Mueller, J.F., 2019. Polycyclic aromatic hydrocarbons, polychlorinated biphenyls and
561 legacy and current pesticides in indoor environment in Australia – occurrence, sources
562 and exposure risks. Sci. Total Environ. 693, 133588.
563 https://doi.org/10.1016/j.scitotenv.2019.133588
564 Wang, Xiaolei, Zhong, W., Xiao, B., Liu, Q., Yang, L., Covaci, A., Zhu, L., 2019.
565 Bioavailability and biomagnification of organophosphate esters in the food web of Taihu
566 Lake, China: Impacts of chemical properties and metabolism. Environ. Int. 125, 25–32.
567 https://doi.org/10.1016/j.envint.2019.01.018

568 Wei, G.L., Li, D.Q., Zhuo, M.N., Liao, Y.S., Xie, Z.Y., Guo, T.L., Li, J.J., Zhang, S.Y.,
569 Liang, Z.Q., 2015. Organophosphorus flame retardants and plasticizers: Sources,
570 occurrence, toxicity and human exposure. Environ. Pollut. 196, 29–46.
571 https://doi.org/10.1016/j.envpol.2014.09.012
572 Yang, Q., Chen, H., Li, B., 2015. Polycyclic aromatic hydrocarbons (PAHs) in indoor dusts
573 of guizhou, southwest of china: Status, sources and potential human health risk. PLoS
574 One 10. https://doi.org/10.1371/journal.pone.0118141
575 Yin, H., Tan, Q., Chen, Y., Lv, G., Hou, X., 2011. Polycyclic aromatic hydrocarbons (PAHs)
576 pollution recorded in annual rings of gingko (Gingko biloba L.): Determination of PAHs
577 by GC/MS after accelerated solvent extraction. Microchem. J. 97, 138–143.
578 https://doi.org/10.1016/j.microc.2010.08.008
579 Yurdakul, S., Çelik, I., Çelen, M., Öztürk, F., Cetin, B., 2019. Levels, temporal/spatial
580 variations and sources of PAHs and PCBs in soil of a highly industrialized area. Atmos.
581 Pollut. Res. 10, 1227–1238. https://doi.org/10.1016/j.apr.2019.02.006
582 Zhou, L., Püttmann, W., 2019. Distributions of organophosphate flame retardants (OPFRs) in
583 three dust size fractions from homes and building material markets. Environ. Pollut. 245,
584 343–352. https://doi.org/10.1016/j.envpol.2018.11.023
585
586
587

588

589 **Table 1. PAH literature values of $ILCR_{ing}$, $ILCR_{inh}$, $ILCR_{derm}$ and $ILCR_s$ (in bold) for adult and child found in soils and indoor dust.**

Environmental media	Country	No. PAH	$ILCR_{ing}^{adult}$	$ILCR_{inh}^{adult}$	$ILCR_{derm}^{adult}$	$ILCR_s^{adult}$	$ILCR_{ing}^{child}$	$ILCR_{inh}^{child}$	$ILCR_{derm}^{child}$	$ILCR_s^{child}$	Reference
Industrial soil	Turkey	16	2.6×10^{-8}	2.1×10^{-3}	9.0×10^{-8}	$\mathbf{2.1 \times 10^{-3}}$	3.8×10^{-8}	3.79×10^{-4}	2.34×10^{-8}	$\mathbf{3.8 \times 10^{-4}}$	(Hanedar et al., 2020)
Industrial + residential soil	Turkey	16	3.4×10^{-8}	2.7×10^{-3}	1.2×10^{-7}	$\mathbf{2.7 \times 10^{-3}}$	4.9×10^{-8}	4.9×10^{-4}	3.0×10^{-8}	$\mathbf{4.9 \times 10^{-4}}$	(Hanedar et al., 2020)
Agricultural soil	Turkey	16	2.9×10^{-8}	2.4×10^{-3}	1.0×10^{-7}	$\mathbf{2.4 \times 10^{-3}}$	4.2×10^{-8}	4.2×10^{-4}	2.6×10^{-8}	$\mathbf{4.2 \times 10^{-4}}$	(Hanedar et al., 2020)
Urban soil	China	16	3.4×10^{-7}	3.2×10^{-11}	1.4×10^{-6}	$\mathbf{1.7 \times 10^{-6}}$	5.5×10^{-7}	5.5×10^{-12}	3.4×10^{-7}	$\mathbf{8.9 \times 10^{-7}}$	(Peng et al., 2011)
Urban soil	India	16	1.8×10^{-5}				9.3×10^{-5}				(Kumar et al., 2013)
Industrial soil	China	16	5.1×10^{-5}	7.4×10^{-9}	2.3×10^{-5}	$\mathbf{7.4 \times 10^{-5}}$	2.3×10^{-5}	1.8×10^{-9}	8.5×10^{-6}	$\mathbf{3.2 \times 10^{-5}}$	(Wang et al., 2017)
Industrial soil	China	16	2.9×10^{-6}	4.4×10^{-7}	1.7×10^{-5}	$\mathbf{5.4 \times 10^{-5}}$	2.7×10^{-6}	1.2×10^{-7}	1.7×10^{-6}	$\mathbf{4.4 \times 10^{-6}}$	(Cao et al., 2019)
Soil dust mining area	India	13	4.6×10^{-6}	5.0×10^{-10}	1.3×10^{-5}	$\mathbf{1.8 \times 10^{-5}}$	4.9×10^{-6}	2.0×10^{-10}	1.4×10^{-5}	$\mathbf{1.9 \times 10^{-5}}$	(Tarafdar and Sinha, 2019)
Indoor dust	Portugal	18						1.0×10^{-9}-5.0×10^{-8}			(Slezakova et al., 2017)
Street dust	Serbia	16	4.5×10^{-5}	3.7×10^{-9}	8.4×10^{-5}	$\mathbf{1.3 \times 10^{-4}}$	6.1×10^{-5}	1.2×10^{-9}	7.6×10^{-5}	$\mathbf{1.4 \times 10^{-4}}$	(Škrbić et al., 2019)
Indoor dust (industrial area)	Saudi Arabia	12	2.4×10^{-3}	1.9×10^{-7}	1.8×10^{-4}	$\mathbf{2.5 \times 10^{-3}}$	-	-	-	-	(Ali et al., 2017)

Indoor dust (city)	China	18	2.1×10^{-6}	1.7×10^{-10}	3.8×10^{-6}	$\mathbf{5.9 \times 10^{-6}}$	2.7×10^{-6}	5.3×10^{-11}	3.4×10^{-6}	$\mathbf{6.1 \times 10^{-6}}$	(Yang et al., 2015)
Indoor dust (town)	China	18	1.7×10^{-6}	2.7×10^{-10}	3.1×10^{-6}	$\mathbf{4.8 \times 10^{-6}}$	2.2×10^{-6}	4.3×10^{-11}	2.8×10^{-6}	$\mathbf{5.0 \times 10^{-6}}$	(Yang et al., 2015)
Indoor dust (village)	China	18	1.1×10^{-6}	8.3×10^{-11}	1.9×10^{-6}	$\mathbf{3.0 \times 10^{-6}}$	1.4×10^{-6}	2.7×10^{-11}	1.7×10^{-6}	$\mathbf{3.1 \times 10^{-6}}$	(Yang et al., 2015)
Indoor dust (orefield)	China	18	2.1×10^{-6}	1.6×10^{-10}	3.7×10^{-6}	$\mathbf{5.8 \times 10^{-6}}$	2.7×10^{-6}	5.2×10^{-11}	3.3×10^{-6}	$\mathbf{6.0 \times 10^{-6}}$	(Yang et al., 2015)

590

591

592

593 **Table 2. OPFR daily intakes for adult and child (numbers in parenthesis) expressed as μg kg_{BW}^{-1} d^{-1} in indoor house dust samples**

	Indoor Dust: Sample identifier											
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**	**#11**	**#12**
TPrP	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	<0.05 (<0.39)	0.18 (1.4)	<0.05 (<0.39)
TiBP	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	0.77 (6.0)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)	<0.06 (<0.49)
TnBP	0.26 (2.1)	<0.04 (<0.29)	<0.04 (<0.29)	<0.04 (<0.29)	0.15 (1.2)	<0.04 (<0.29)	<0.04 (<0.29)	0.70 (5.4)	0.095 (0.74)	0.13 (1.0)	0.27 (2.1)	<0.04 (<0.29)
TCEP	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	<0.15 (<1.2)	0.23 (1.8)
TEEdP	0.72 (5.6)	<0.02 (<0.12)	<0.02 (<0.12)	<0.02 (<0.12)	<0.02 (<0.12)	<0.02 (<0.12)	<0.02 (<0.12)	0.26 (2.4)	<0.02 (<0.12)	<0.02 (<0.12)	<0.02 (<0.12)	0.12 (0.89)
TDCPP	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)	<0.01 (<0.11)
TPhP	<0.08 (<0.61)	0.44 (3.4)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)	<0.08 (<0.61)
TBOEP	<0.36 (<2.8)	1.5 (11.9)	<0.36 (<2.8)	<0.36 (<2.8)	0.80 (6.2)	2.1 (16.0)	9.0 (69. 6)	<0.36 (<2.8)	<0.36 (<2.8)	<0.36 (<2.8)	1.9 (15.0)	<0.36 (<2.8)
TEHP	0.81 (6.3)	0.72 (5.6)	<0.007 (<0.05)	<0.007 (<0.05)	0.28 (2.1)	<0.007 (<0.05)	<0.007 (<0.05)	<0.007 (<0.05)	<0.007 (<0.05)	<0.007 (<0.05)	<0.007 (<0.05)	1.9 (14.4)
TPPO	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)	<0.08 (<0.63)
TCrP	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)	<0.03 (<0.25)
DI_s^{adult}	1.8	2.7	-[a]	-[a]	1.2	2. 1	9.0	1.7	0.095	0.13	2. 4	2.2
DI_s^{child}	13.9	20.9	-[a]	-[a]	9.5	16.0	69. 7	13.4	0.74	1.0	17.1	17.1

Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Total OPFR daily intake (DI_s)

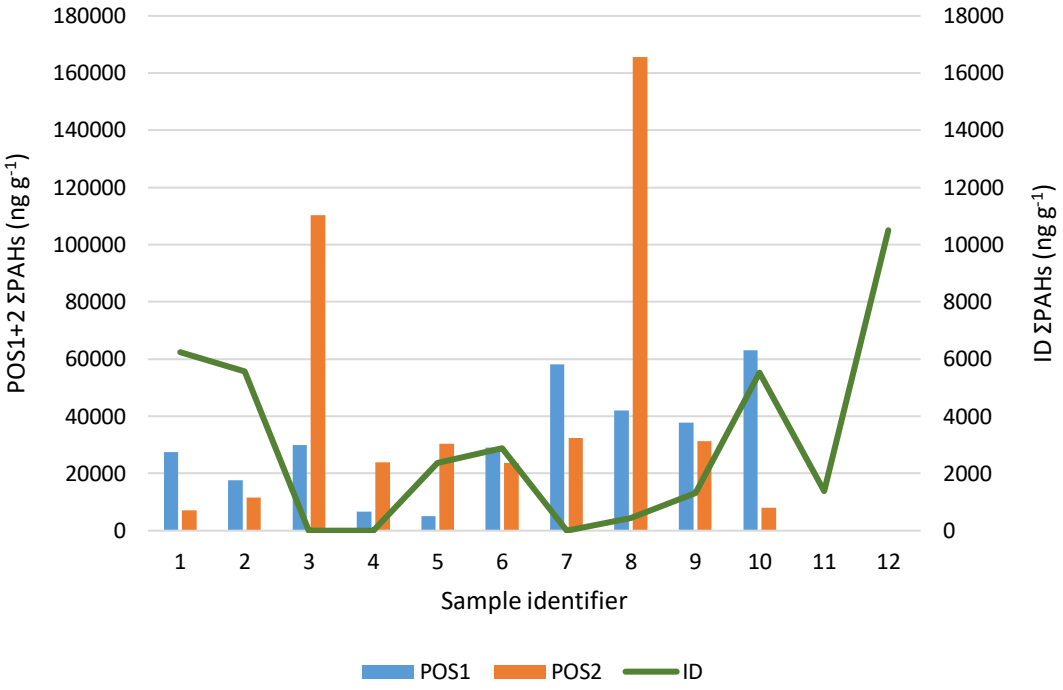
[a] Not calculated (OPFR concentrations are lower than LOQ)

594

595

Figure 1. Comparison of concentrations (ng g^{-1}) from Public Open Space 1, Public Open Space 2 and indoor Dust sampling sites. A plot of the (a) ΣPAHs and (b) ΣOPFRs.

(a)



(b)

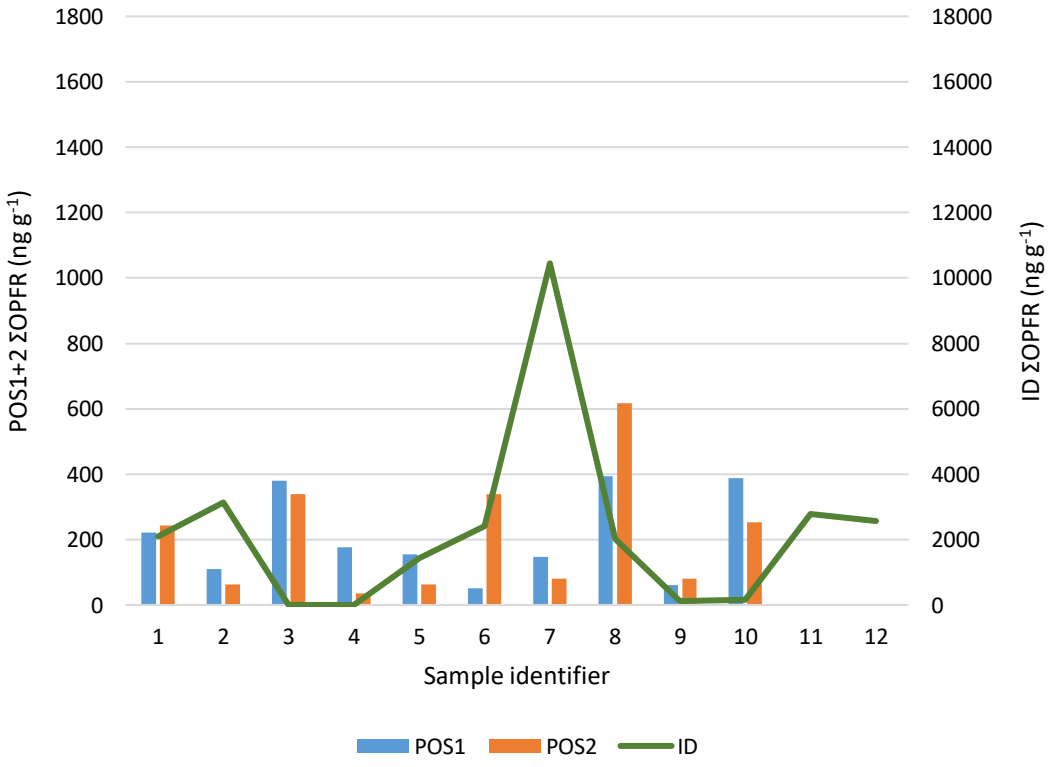
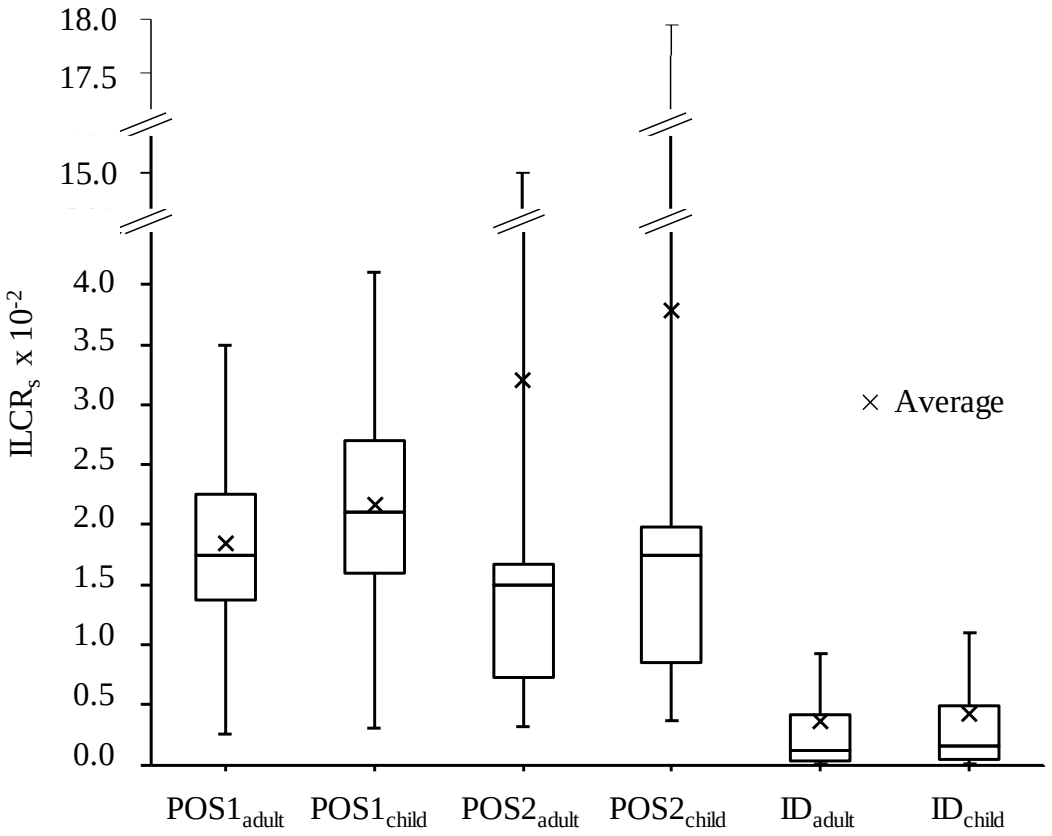


Figure 2. PAH incremental lifetime cancer risk (ILCR) considering adult and child exposure for Public Open Space 1 (POS1), Public Open Space 2 (POS2) and Indoor Dust (ID) samples. Each box represents lower and upper quartiles, the band within the box shows the median value and whiskers represents maximum and minimum values obtained.



The Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons, Bisphenol A and Organophosphate Flame Retardants in Indoor Dust and Soils from Public Open Spaces: Implications for Human Exposure

Joel Sánchez-Piñero[1], Samantha L. Bowerbank[2], Jorge Moreda-Piñeiro[1], Purificación López-Mahía[1] and John R. Dean[2]

[1] Grupo de Química Analítica Aplicada (QANAP), University Institute of Research in Environmental Studies (IUMA), Centro de Investigacións Científicas Avanzadas (CICA), Department of Chemistry, Faculty of Sciences, University of A Coruña, Campus de A Coruña, s/n. 15071 A Coruña, Spain.

[2] Department of Applied Sciences, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK.

Supplementary Information

Chemical standards with CAS numbers

Bisphenol A (BPA) (80-05-7); tris(1,3-dichloro-2-propyl) phosphate, TDCPP (13674-87-8); tetraethyl ethylene diphosphonate, TEEdP (995-32-4); tris (2-ethylhexyl) phosphate, TEHP (78-42-2); tri-m-cresyl phosphate, TCrP (563-04-2); tri-n-butyl phosphate, TnBP (126-73-8); triphenyl phosphate, TPhP (115-86-6); triphenylphosphine oxide, TPPO (791-28-6); tripropyl phosphate, TPrP (513-08-6); tris (2-butoxyethyl) phosphate, TBOEP (78-51-3); tris (2-chloroethyl) phosphate, TCEP (115-96-8); and, tri-iso-butyl phosphate, TiBP (126-71-6).

Soils from public open spaces and indoor dust samples

Public Open Space 1, POS1 (Figure S1a) was based in Jarrow, South Tyneside (approximately 4.3 hectares). Historically the site was used as a landfill site (pre-1920) for commercial and household waste, and subsequently (to 1982) as an allotment garden. Since 1982 the site is maintained as public recreational space. Most of the site is a level grassed open space, interspersed with overgrown grassed areas. The site is currently used for leisure, although there are no formal picnic facilities available (such as benches or litter bins) and a tarmac path crosses the site allowing access to and from surrounding residential areas and local facilities. Ten shallow soil samples (0.02-0.20 cm^2) were collected from across the site using a stratified sampling grid (Figure S1a). Soil samples were collected using a stainless-steel trowel; the sampling equipment was cleaned with acetone after each sample was collected to avoid cross contamination. The samples were transferred into suitable containers (i.e. kraft bags) and then transported to the laboratory for subsequent analyses. All soil samples were then subsequently dried (typically <40 °C for a minimum of 4 days), disaggregated and sieved through a 2 mm nylon mesh followed by a 250 µm nylon mesh and stored in sealed containers for subsequent analysis.

Public Open Space 2, POS2 (Figure S1b) was based in the Walker area of Newcastle upon Tyne. Historically the site was a former Lead Works (from the 1860's to 1940) based adjacent to the river Tyne. Since the 1960's the site has been maintained as public recreational space. The site has level grassed open space, interspersed with overgrown steep grassed / shrub areas. The site is currently used for leisure and is interspersed with a network of tarmac paths which cross the site allowing access to and from surrounding residential areas and the river boundary. Samples of soil were collected from 10 sample points on the site by digging a square hole of about 10 cm^2 from the topsoil. The grass on the top of the soil was removed. The topsoil collected was put inside a paper geochemical (Kraft) bag and labelled. During sampling, sample handling and sample preparation polyethylene gloves were worn. The soil samples were dried in the sample bags in an oven at a temperature of <40 ^oC for 6 days. The dried soil samples were gently disaggregated in a porcelain pestle and mortar and passed through a plastic sieve of mesh size 2 mm, followed by a sieve <250 µm and stored in sealed containers for subsequent analysis.

Household dust samples were collected from a range of domestic dwellings using a portable corded vacuum cleaner (Hoover, Jovis+, 550 W, SM550AC, Brugherio, Italy) with inter-changeable microfiber filter (Hoover, type S105). Each household (flat, house, bungalow), reviewed in terms of its age, was considered in terms of the number of occupants (their age and smoking habits) and the living spaces (identified as the normally occupied daytime spaces) in terms of the total area occupied. The heating methods available, the type of floor covering, whether outdoor footwear was worn in the living spaces, and the presence of any animals, against the frequency of cleaning and the typical number of hours occupied per day. Information on geographical location, occupancy and living areas are summarised in Table S1. The filters were washed after each sample collection, air dried and re-used. After collection,

each sample was sieved and the fraction below 250 µm was collected and stored in sealed containers for subsequent analysis.

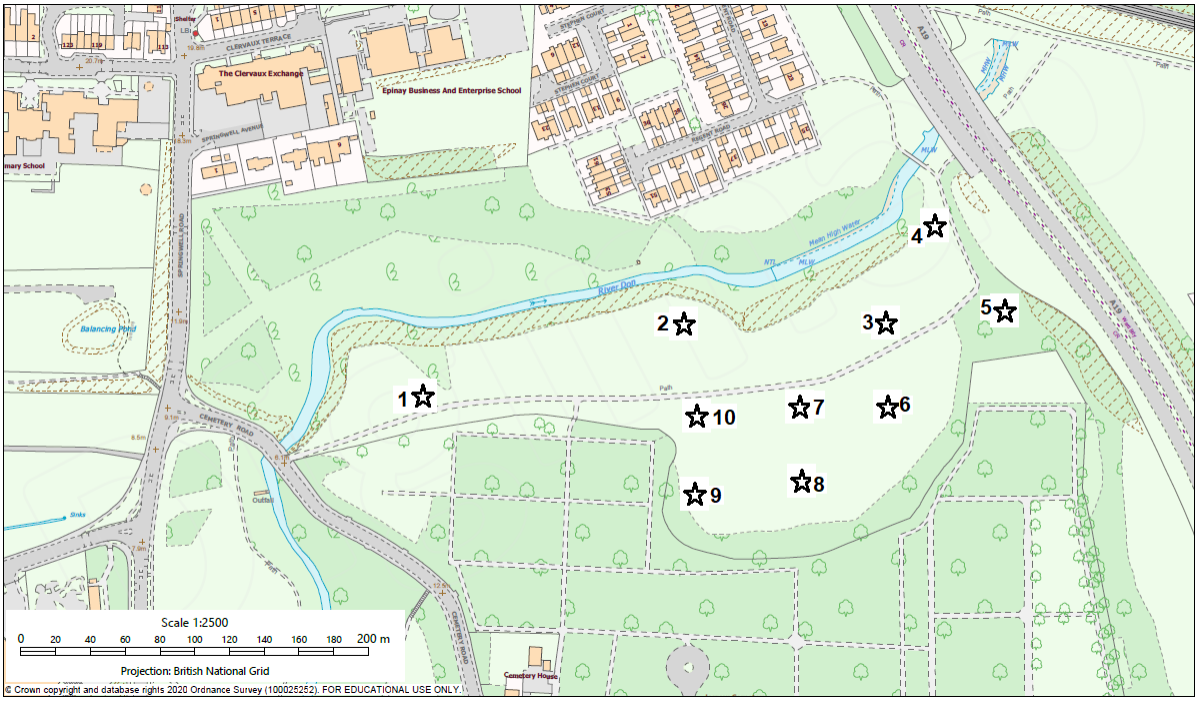
Determination of soil properties

Soil pH was determined by taking 10 g (accurately weighed) and suspending in deionised water in the ratio 1 : 2.5 w/v. After agitation (30 rpm for 10 min) the sample was left to stand for 10 min and the pH recorded, using a previously calibrated pH probe. Soil organic matter was determined, based on the Loss of Ignition (LoI) method. In this method 5 g of the soil sample (W) (accurately weighed) was placed in a pre-weighed crucible. The weight of soil and crucible (W_1) were also recorded. The sample-containing crucible was placed in a pre-heated muffle furnace at 400 °C for 4 hours. After heating the crucible was then allowed to cool in a desiccator. The sample-containing crucible was then re-weighed (W_2); the % LoI was then calculated:

$$\%LOI = \frac{W_1 - W_2}{W} \, x \, 100$$

Figure S1. Schematic diagram of (a) Public Open Space 1 and (b) Public Open Space 2 with sampling points.

(a)



(b)

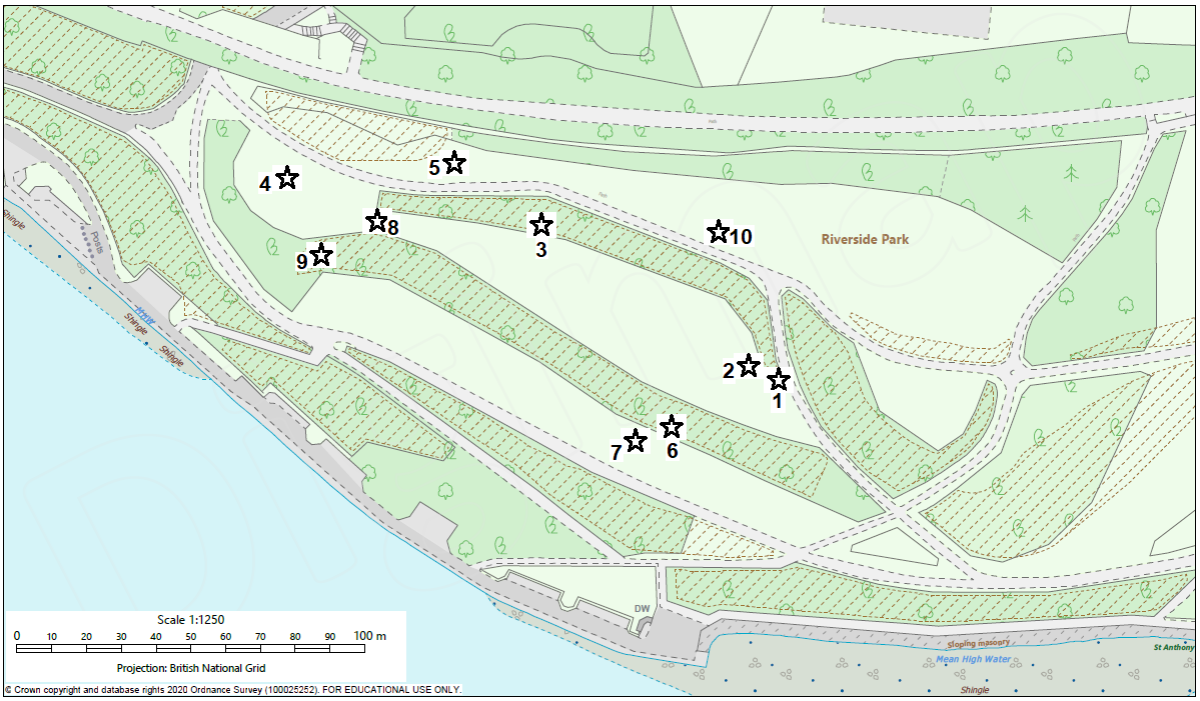


Table S1. Indoor sampling: Information on geographical location, occupancy and living areas

Sample	Postcode	Approximate age of house (years)	Number of occupants				Living areas						
			adults	under 12		Number of smokers	Total area (m^2)	Heating method[a]	Floor covering[b]	Outdoor footwear	Animals: number / type	Frequency of cleaning	Hours occupied per day
				Male	Female								
#1	NE42	54	3	0	0	0	61.4	GCH	C	yes	1 / dog	weekly	8.0
#2	PH15	118	2	0	0	0	49.3	WBS / HP	C, W, T	no	1 / dog	weekly	7.0
#3	NE42	4	1	0	0	0	42.7	ECH	C, V	occasionally	0	occasionally	6.9
#4	KY12	55	2	0	0	0	51.2	HP	W	yes	0	weekly	3.3
#5	NE5	55	3	0	1	0	51.4	GCH	W, T	yes	2 / dog + cat	Daily / every 2 days	6.6
#6	NE20	30	2	0	0	0	79.1	GCH / WBS	C, W	yes	1 / dog	weekly	16.0
#7	NE6	2	1	0	0	1	38.7	GCH	C, V	no	1 / cat	weekly	7.1
#8	NE5	50	5	0	1	0	59.9	GCH / WBS	W, L, T	no	0	weekly	8.6
#9	NE41	60	2	0	0	0	46.5	GCH / WBS	W	no	1 / dog	weekly	12.0
#10	DH8	55	3	1	0	0	27.9	GCH	C, L	no	0	Twice per week	4.1
#11	CA12	34	5	0	0	0	68.5	GCH	C, L, V	yes	1 / dog	weekly	4.3
#12	DH7	120	4	0	0	0	34.8	WBS	C, L, V	no	1 / dog	occasionally	16.9

[a] GCH = gas central heating; WBS = wood burning stove; HP = air source heat pump; ECH = electric central heating

[b] C = carpet; W = wood; T = tiles; V = vinyl; L = laminate

Table S2. Analytical figures of merit for analysis of compounds in soil from public open spaces and indoor house dust

Compound	Retention time (min)	Qualitative m/z	Quantitative m/z	Calibration range (ng mL^{-1})	Nº of data points	Calibration graph	R^2	Precision RSD (%)		LOD (ng g^{-1})	LOQ (ng g^{-1})
								Standard solution[a]	Soil sample		
HAPs											
Acy	10.98	153, 76	152	0-250	5	Y=1188.3x + 171618	0.9943	12.6	4.9	132	399
Ace	12.37	76, 80	153	0-500	6	Y=1946x - 12786	0.9993	13.7	7.6	17	52
Fl	14.57	165, 139	166	0-500	6	Y=1342.1x - 14772	0.9979	11.6	14.5	50	153
Phe	19.06	160, 176	178	0-500	5	Y=1278.7x - 15257	0.9981	10.6	13	43	130
Ant	19.21	160, 176	178	0-500	6	Y=960.4x - 20679	0.9917	9.3	9.9	6	17
Ft	26.56	101, 106.5	202	0-500	5	Y=984.8x - 23588	0.9935	9.2	9.3	220	667
Pyr	28.07	101, 106.5	202	0-500	5	Y=1124.9x - 26961	0.9946	9.2	-[b]	29	89
Ret	31.80	234, 203.5	219	0-500	5	Y=211.12x – 6652.7	0.9908	8.8	-[b]	31	94
BaA	38.06	113.5, 236	228	0-500	5	Y=326.73x - 14585	0.9924	8.5	4.2	322	975
Chry	38.29	113.5, 236	228	0-500	5	Y=840.54x - 21553	0.9919	8.1	9.7	142	432
BjF+BkF+BbF	44.01	101, 141	252	0-500	5	Y=1366.5x - 61960	0.9958	10.7	6.3	103	312
BeP	45.08	125, 132	252	0-500	5	Y=578.01x - 24037	0.9978	7.3	7.5	75	228
BaP	45.34	125, 132	252	0-500	5	Y=804.64x - 37335	0.9974	8.4	12	134	405
IP	49.82	276, 138	292	0-500	4	Y=239.63x - 12987	0.9936	6.3	11.2	16	49

DBahA	50.00	138, 126	278	0-500	5	Y=394.3x - 16402	0.9982	8.4	6.5	6	19
BghiP	50.67	228, 138	276	0-500	5	Y=474.79x - 21269	0.9918	8.8	13.9	18	54
OPFRs											
TPrP	9.96	182, 141	99	0-2000	8	Y=1226.6x -63137	0.9925	13.4	13.9	19	58
TiBP	13.02	155, 138.6	99	0-1000	7	Y=928.57x - 22323	0.9965	11.4	15.3	225	74
TnBP	16.00	168, 157	99	0-1000	7	Y=897.9x - 24569	0.9954	9.9	-[b]	15	44
TCEP	18.67	249, 205	143	0-1000	6	Y=230.63x – 816.4	0.9962	9.1	11.9	59	178
TEEdP	21.49	173, 165	109	0-1000	7	Y=123.51x – 8106.6	0.9950	3.8	11.5	9	18
TDCPP	35.64	209.5, 99	99	0-2000	5	Y=280.76x - 36833	0.9922	6.2	4.3	5	16
TPhP	37.17	169, 215	326	0-1000	5	Y=197.96x - 18386	0.9964	8	16.8	30	91
TBOEP	37.77	198.8, 125	101	0-1000	4	Y=51.848x – 6243.5	0.9873	3.5	5.9	138	418
TEHP	39.07	113, 112	99	0-1000	6	Y=389.46x - 20509	0.9940	3.8	16.7	3	8
TPPO	39.7	227, 199	152	0-2000	5	Y=49.607x – 5377.3	0.9967	5.9	-[b]	31	95
TCrP	42.30	367.5, 261	165	0-1000	5	Y=205.77x - 18393	0.9877	4.9	7.5	12	38
BPA	30.38	228, 119	213	0-2000	5	Y=111.92x - 10480	0.9977	5.2	2.6	13	40

Acenaphthene (Ace); Acenaphtylene (Acy); Anthracene (Ant); Benzo(a)anthracene (BaA); Benzo(a)pyrene (BaP); Benzo(b)fluoranthene (BbF); Benzo(a)pyrene (BeP); Benzo(g,h,i)perylene (BghiP); Benzo(j)fluoranthene (BjF); Benzo(k)fluoranthene (BkF); Bisphenol A (BPA); Chrysene (Chry); Dibenzo(a,h)anthracene (DBahA); Fluorene (Fl); Fluoranthene (Ft); Indeno(1,2,3-c,d)pyrene (IP); Phenanthrene (Phe); Retene (Ret); Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Pyrene (Pyr).

[a] 100 µg L^{-1}

[b] Not calculated (target compound concentration < LOQ)

Table S3. Analytical recovery (pre- and post-PLE) for a soil sample and analysis of a soil certified reference material for PAHs (CRM 172)

Compound	Analytical Recovery (%) (n = 3)		CRM172 (Sandy loam soil)		
	Pre-PLE[a]	Post-PLE[b]	Certified value (ng g^{-1})	Found value (ng g^{-1}) (n = 3)	$\|t_{exp}\|$[c]
HAPs					
Acy	86 ± 7	96 ± 8	55.6 ± 18.1	-[d]	
Ace	87 ± 1	93 ± 7	94.9 ± 24.7	-[d]	
Fl	97 ± 1	90 ± 4	66.4 ± 11.2	-[d]	
Phe	96 ± 3	98 ± 1	168 ± 7.6	170.4 ± 4.6	0.74
Ant	103 ± 1	112 ± 1	17.7 ± 2.7	13.6 ± 0.2	4.14
Ft	87 ± 4	92 ± 6	634 ± 82.4	670.2 ± 30.2	1.70
Pyr	95 ± 3	123 ± 1	86.5 ± 13	73.9 ± 4.8	3.71
Ret	95 ± 3	87 ± 4			
BaA	107 ± 2	101 ± 5	303 ± 47.7	-[d]	
Chry	85 ± 3	105 ± 8	154 ± 20.8	146.5 ± 3.1	3.42
BjF+BkF+ BbF	84 ± 2	101 ± 7	-[e]	-[d]	
BeP	96 ± 1	109 ± 9	-[e]	-[d]	
BaP	107 ± 6	97 ± 2	33.9 ± 10.9	-[d]	
IP	116 ± 5	111 ± 7	150.7 ± 30.5	151.3 ± 4.9	0.17
DBahA	105 ± 10	102 ± 2	284 ± 30.5	277.8 ± 16.1	0.55
BghiP	96 ± 1	110 ± 5	452 ± 81.2	392.4 ± 21.2	4.00
OPFRs					
TPrP	57 ± 1	108 ± 5			
TiBP	98 ± 1	114 ± 7			
TnBP	95 ± 2	137 ± 4			
TCEP	118 ± 8	94 ± 6			
TEEdP	90 ± 11	114 ± 4			
TDCPP	104 ± 2	107 ± 2			
TPhP	78 ± 4	102 ± 1			
TBOEP	116 ± 2	87 ± 3			
TEHP	82 ± 1	96 ± 7			
TPPO	82 ± 4	93 ± 2			
TCrP	88 ± 2	95 ± 4			
BPA	101 ± 5	107 ± 8			

Acenaphthene (Ace); Acenaphtylene (Acy); Anthracene (Ant); Benzo(a)anthracene (BaA); Benzo(a)pyrene (BaP); Benzo(b)fluoranthene (BbF); Benzo(a)pyrene (BeP); Benzo(g,h,i)perylene (BghiP); Benzo(j)fluoranthene (BjF); Benzo(k)fluoranthene (BkF); Bisphenol A (BPA); Chrysene (Chry); Dibenzo(a,h)anthracene (DBahA);

Fluorene (Fl); Fluoranthene (Ft); Indeno(1,2,3-c,d)pyrene (IP); Phenanthrene (Phe); Retene (Ret); Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Pyrene (Pyr).

[a] spiked 200 µg L^{-1} on soil.

[b] spiked 100 µg L^{-1} on soil.

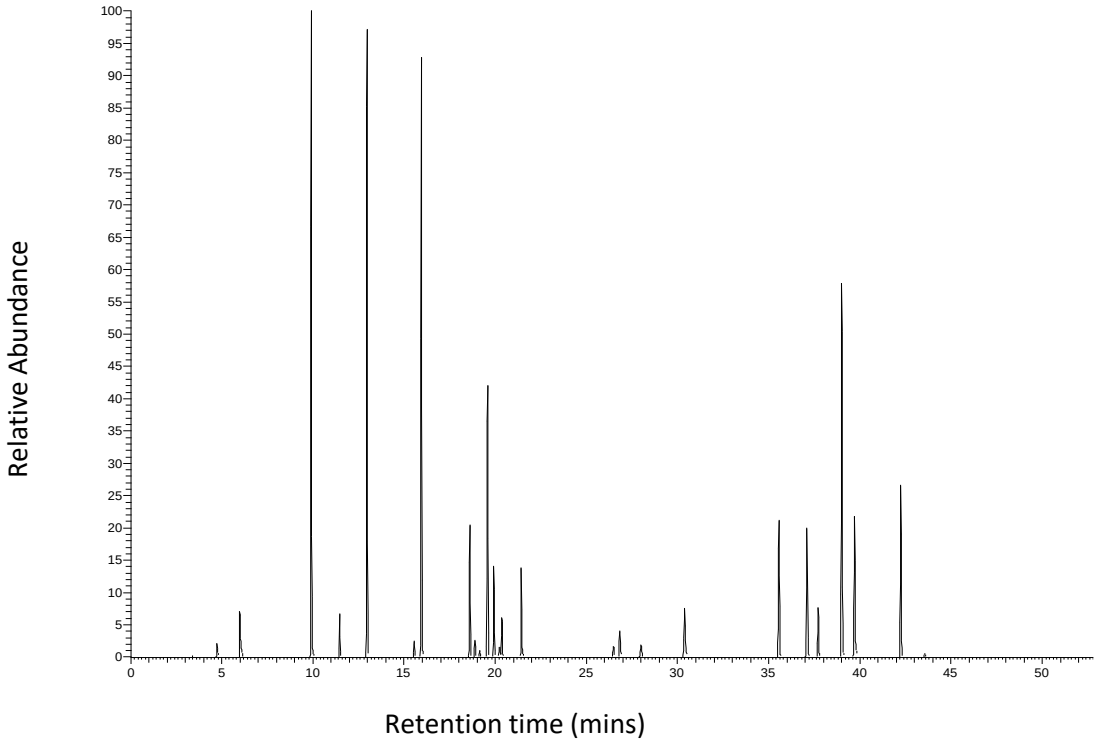
[c] t_{exp} calculated as follows: $t_{exp} = \left|[\,]_{certified} - [\,]_{found}\right| x \frac{\sqrt{n}}{SD}$, $[\,]_{found}$ and SD are the mean and standard deviation values (n = 2) after PL10- GC-EI-MS and $[\,]_{certified}$ is the certified concentration

[d] <LOQ

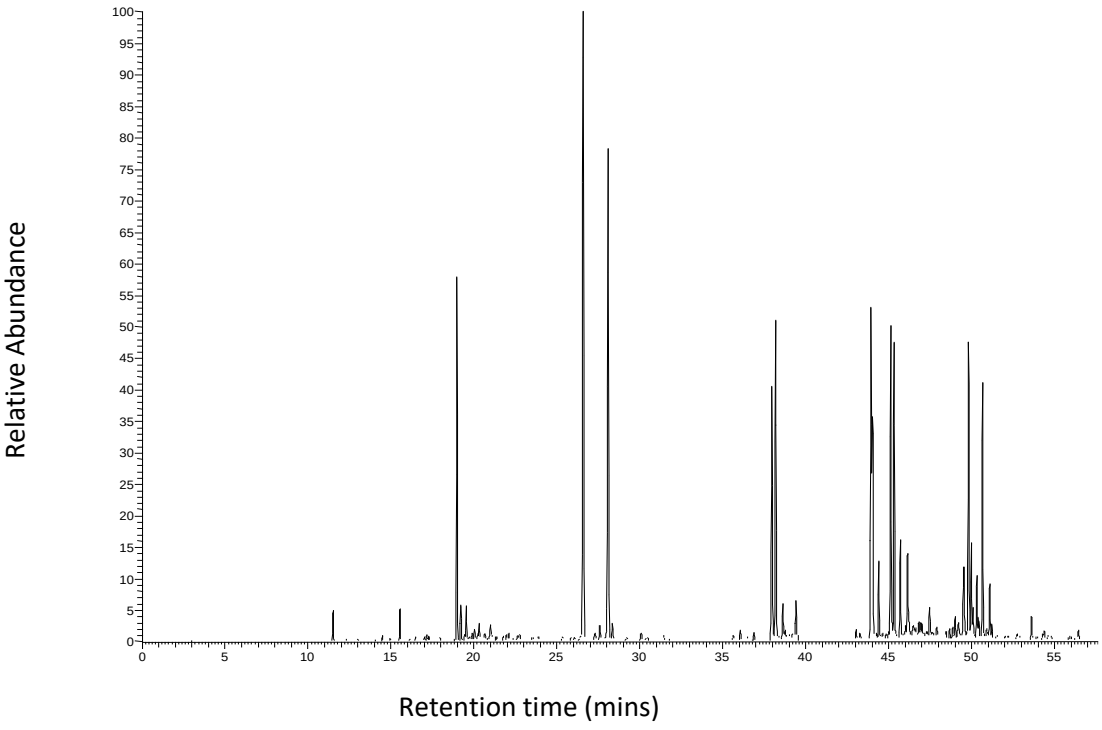
[e] Not certified

Figure S2. GC-EI-MS chromatograms for a mixture of the target compounds (a) A 200 ng mL^{-1} Standard, and PLE extracts from (b) a soil sample from POS1, (c) a soil sample from POS2 and (d) an indoor dust sample, using the optimized conditions.

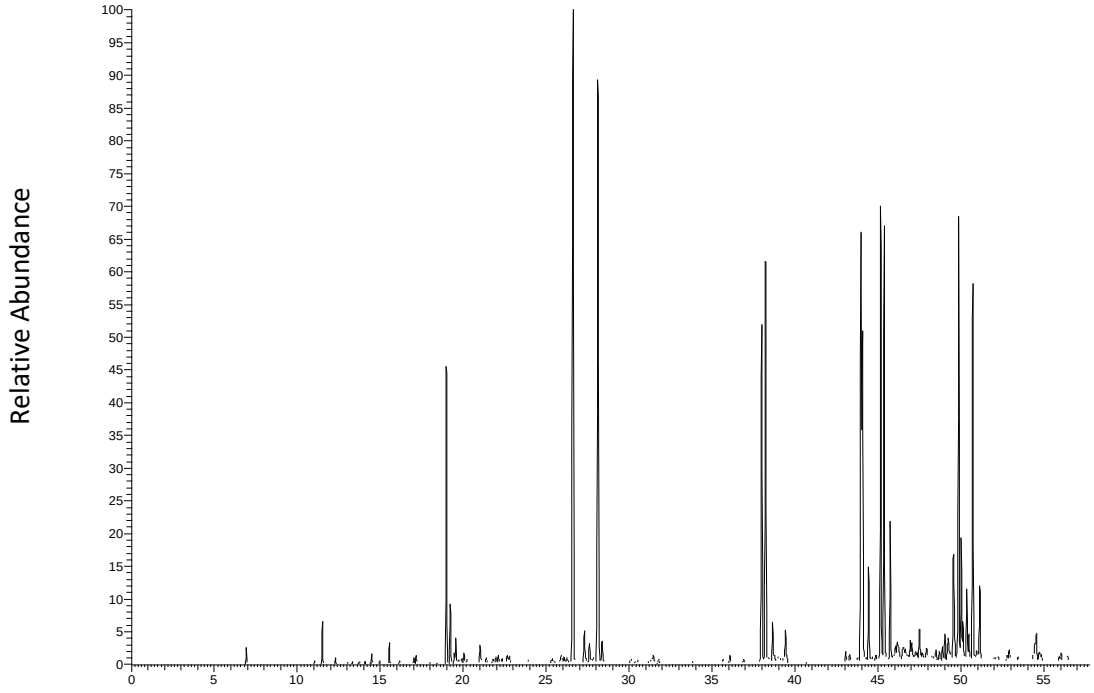
(a)



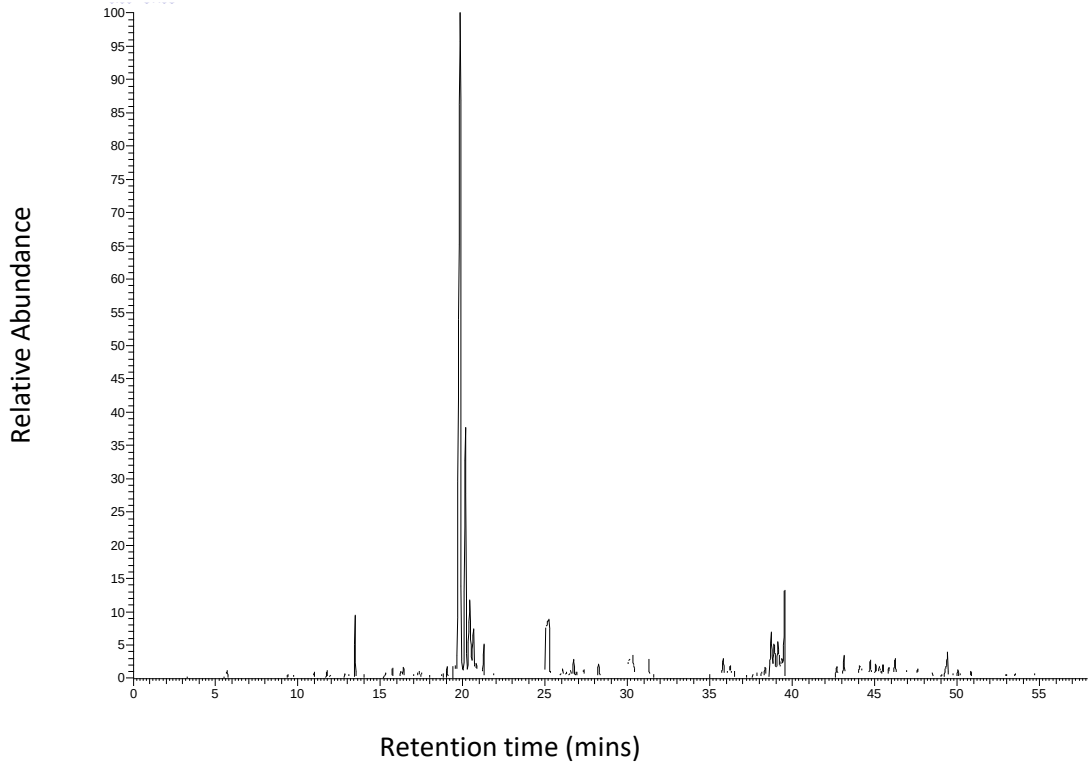
(b)



(c)


Relative Abundance
Retention time (mins)

(d)


Relative Abundance
Retention time (mins)

1

Table S4: Analysis and characterisation of soil at public open space 1

	Public Open Space 1: Sample identifier[a]									
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	#7	**#8**	**#9**	**#10**
Soil pH[e]	7.2	6.7	5.7	7.1	5.7	7.0	6.9	6.7	6.7	6.7
%LOI[e]	17.0	27.5	41.4	18.9	14.2	14.9	15.0	15.5	15.9	15.9
Compound	**Concentration (ng g^{-1}) ± SD (n = 3)**									
HAPs										
Acy	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Ace	20.8 ± 4.6	82.3 ± 12	18.2 ± 1.2	-[b]	-[b]	-[b]	-[b]	-[b]	29.4	21.2 ± 1.8
Fl	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Phe	2250 ± 63	2730 ± 195	3090 ± 175	867 ± 23	619 ± 125	2720 ± 133	4260 ± 547	3640 ± 285	4040 ± 317	5980 ± 1150
Ant	88.7 ± 3.1	72.7 ± 5.5	150 ± 15	27.3 ± 0.5	22.6 ± 0.3	91.7 ± 2.4	127 ± 15	96.6 ± 6.9	101 ± 15	184 ± 13
Ft	9590 ± 440	4390 ± 270	-[b]	2280 ± 66	1700 ± 84	11500 ± 268	22200 ± 285	15600 ± 957	14700 ± 1080	24100 ± 1550
Pyr	1360 ± 47	672 ± 22	2510 ± 140	291 (298, 285)[c]	241 ± 14	1360 ± 24	2690 ± 285	1980 ± 90	1760 ± 144	-[b]
Ret	297 ± 5.9	-[b]	289 ± 4.1	220 ± 3.6	219 ± 2.0	234 ± 10	-[b]	239 ± 6.9	-[b]	311 ± 46
BaA	6990 ± 311	4400 ± 79	13600 ± 1250	1700 ± 97	1340 ± 63	6980 ± 99	14300 ± 1590	10600 ± 588	8680 ± 661	18500 ± 1320
Chry	1000 ± 182	771 ± 20	1960 ± 149	-[b]	-[b]	1040 ± 30	2080 ± 209	1620 ± 72	1360 ± 76	2840 ± 188
BjF+BkF+BbF	633 ± 64	336 ± 27	1080 ± 34	-[b]	-[b]	545 ± 22	1090 ± 94	766 ± 29	747 ± 25	1330 ± 58
BeP	1250 ± 17	921 ± 54	-[b]	121 (122, 120)[c]	294 ± 20	1070 ± 30	2350 ± 186	1710 ± 46	1450 ± 66	-[b]
BaP	773 ± 16	493 ± 20	1080 ± 34	-[b]	-[b]	708 ± 16	1650 ± 140	1200 ± 36	973 ± 62	2010 ± 156

IP	2100 ± 92	1660 ± 33	4080 ± 33	681 ± 52.5	417 ± 6.1	1800 ± 85	4770 ± 433	3300 ± 112	2630 ± 67	5030 ± 314
DBahA	366 ± 20	431 ± 6.8	750 ± 151	123 ± 4.3	50.7 ± 0.6	339 ± 6.8	829 ± 94	189 ± 46	372 (381, 363)[c]	1120 ± 66
BghiP	801 ± 13	647 ± 14	1380 ± 88	278 ± 19.1	188 ± 4.3	666 ± 19	1640 ± 141	1110 ± 38	934 ± 50	1680 ± 109
ΣPAHs	27500 ± 2710[d]	17600 ± 1460[d]	30000 ± 3550[d]	6600 ± 723[d]	5100 ± 538[d]	29100 ± 3200[d]	58100 ± 6350[d]	42100 ± 4450[d]	37800 ± 4070[d]	63100 ± 7460[d]
BaP_{eq}	3500	2570	3780	517	546	3210	7150	4790	4210	6080
OPFRs										
TPrP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TiBP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TnBP	22.1 ± 1.6	109 ± 5	20.8 ± 1.2	-[b]	17.9 ± 0.7	19.8 ± 2.0	ND	16.7 ± 0.9	25.5 ± 5.4	28.8 ± 4.1
TCEP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TEEdP	32.5 ± 1.5	-[b]	38.0 ± 1.0	26.3 ± 0.1	-[b]	32.6 ± 0.5	-[b]	-[b]	34.2 ± 1.3	76.5 ± 15
TDCPP	167 (139, 195)[c]	-[b]	73.3 (64.8, 81.9)[c]	-[b]	-[b]	-[b]	110 ± 10	87.0 (83.0, 91.0)[c]	-[b]	56.5 ± 2.1
TPhP	-[b]	-[b]	-[b]	109 ± 1.0	87.2 ± 0.8	-[b]	-[b]	127 ± 3.1	-[b]	101 ± 15
TBOEP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TEHP	-[b]	-[b]	128 ± 13	40.9 ± 1.8	49.4 ± 1.3	-[b]	35.6 ± 5.8	53.1 ± 1.1	-[b]	125 ± 8.0
TPPO	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TCrP	-[b]	-[b]	120 ± 8.0	-[b]	-[b]	-[b]	-[b]	110 ± 1.0	-[b]	-[b]
ΣOPFR	222 ± 66[d]	109[d]	380 ± 43[d]	176 ± 36[d]	155 ± 28[d]	52.4 ± 6.4[d]	146 ± 37[d]	394 ± 40[d]	59.7 ± 4.3[d]	388 ± 34[d]
BPA	41.4 ± 1.3	-[b]	-[b]	49.9 ± 2.7	-[b]	-[b]	-[b]	49.6 ± 1.2	-[b]	89.7 ± 4.1

Acenaphthene (Ace); Acenaphtylene (Acy); Anthracene (Ant); Benzo(a)anthracene (BaA); Benzo(a)pyrene (BaP); Benzo(b)fluoranthene (BbF); Benzo(a)pyrene (BeP); Benzo(g,h,i)perylene (BghiP); Benzo(j)fluoranthene (BjF); Benzo(k)fluoranthene (BkF); Bisphenol A (BPA); Chrysene (Chry); Dibenzo(a,h)anthracene (DBahA); Fluorene (Fl); Fluoranthene (Ft); Indeno(1,2,3-c,d)pyrene (IP); Phenanthrene (Phe); Retene (Ret); Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Pyrene (Pyr).

[a] All Public Open Space soil samples were determined on the <250 µm fraction

[b] <LOQ

[c] n = 2; mean (individual values)

[d] $SD_{sum} = \sqrt{\sum SD_i^2}$, SD_i is the SD PAH_i or the SD of the $OPFR_i$

[e] methods are detailed in the Supplementary Information.

2

3

4

Table S5: Analysis and characterisation of soil at public open space 2

	Public Open Space 2: Sample identifier[a]									
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**
Soil pH[e]	6.6	7.5	7.4	6.5	6.6	7.7	7.6	7.0	7.9	6.9
%LOI[e]	10.1	10.9	11.5	9.1	16.1	11.6	9.4	10.6	9.6	10.7
Compound	**Concentration (ng g^{-1}) ± SD (n = 3)**									
PAHs										
Acy	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Ace	-[b]	-[b]	91.2 (87.2, 95.2)[c]	126 (112, 141)[c]	120 ± 3.3	253 (300, 206)[c]	122 ± 14	1380 ± 201	-[b]	-[b]
Fl	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	1750 ± 151	-[b]	-[b]
Phe	741 ± 117	1250 (1250, 1250)[c]	7790 (7760, 7820)[c]	2705 ± 486	3490 ± 292	3940 ± 462	4200 ± 291	55300 ± 2920	2680 ± 47	918 ± 202
Ant	25.5 ± 1.4	42.3 ± 7.4	326 (388, 264)[c]	91.2 ± 17	145 ± 17	108 ± 12	151 ± 11	3460 ± 198	97.7 ± 20	25.8 ± 4.3
Ft	2680 ± 437	4580 ± 272	35900 ± 11200	8530 ± 1230	10500 ± 873	6760 ± 764	12200 ± 722	-[b]	12800 ± 1190	3810 ± 299
Pyr	390 ± 72	661 ± 27	5330 (4670, 6000)[c]	1220 ± 159	1530 ± 147	1050 ± 95	1660 ± 110	-[b]	1830 ± 170	527 ± 40
Ret	-[b]	-[b]	-[b]	529 ± 342	288 ± 13	593 ± 11	325 ± 5.2	-[b]	293 ± 41	-[b]
BaA	1770 ± 258	2910 ± 37	28100 (28100, 28100)[c]	5730 ± 712	7860 ± 638	5730 ± 330	7580 ± 495	-[b]	7050 (6990, 7100)[c]	1780 ± 163
Chry	339 ± 60	497 ± 3.7	4200 ± 1160	864 ± 89	1140 ± 77	1030 ± 41	1110 ± 88	18600 ± 758	1140 ± 209	-[b]
BjF+BkF+BbF	-[b]	-[b]	3110 (3260, 2970)[c]	369 ± 24	484 ± 43	342 ± 22	436 ±61	11900 ± 681	507 (495, 518)[c]	-[b]

BeP	330 ± 65	506 ± 4.3	4930 (5090, 4780)[c]	883 ± 103	1110 ± 72	1020 ± 61	1060 ± 77	-[b]	1220 ± 140	282 ± 9.3
BaP	-[b]	-[b]	3940 (3820, 4060)[c]	597 ± 70	780 ± 67	519 ± 32	716 ± 50	14400 ± 708	758 (752, 764)[c]	-[b]
IP	512 ± 98	764 ± 13	12500 (12200, 12900)[c]	1410 ± 156	1840 ± 133	1350 ± 158	1760 ± 141	49100 ± 2390	1930 ± 396	403 ± 51
DBahA	119 ± 13	155 ± 1.8	1780 (1970, 1580)[c]	268 ± 28	333 ± 24	317 ± 32	324 ± 21	9790 ± 402	224 (243, 204)[c]	95.5 ± 17
BghiP	224 ± 39	331 ± 5.5	2190 (2450, 1920)[c]	564 ± 59	743 ± 41	606 ± 37	695 ± 59	-[b]	816 ± 100	183 ± 18
ΣPAHs	7130 ± 804[d]	11700 ± 1380[d]	110000 ± 10600[d]	23900 ± 2370[d]	30400 ± 3040[d]	23600 ± 2078[d]	32300 ± 3360[d]	166000 ± 18900[d]	31300 ± 3470[d]	8020 ± 1150[d]
BaP_{eq}	718	1100	15500	2630	3400	2760	3260	31100	3320	646
OPFRs										
TPrP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TiBP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	256 ± 24	-[b]	-[b]
TnBP	242 (227, 258)[c]	-[b]	-[b]	-[b]	-[b]	75.1 (74.8, 75.4)[c]	-[b]	-[b]	-[b]	186 (158, 214)[c]
TCEP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TEEdP	-[b]	29.9 ± 5.3	55.8 ± 12	35.3 ± 8.4	34.0 ± 0.6	82.6 ± 6.0	38.1 ± 5.7	90.7 ± 3.7	32.5 ± 0.9	-[b]
TDCPP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TPhP	-[b]	-[b]	175 ± 30	-[b]	-[b]	106 ± 1.5	-[b]	-[b]	-[b]	-[b]
TBOEP	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
TEHP	-[b]	32.6 (32.9, 32.3)[c]	107 ± 14.4	-[b]	28.1 (29.4, 26.7)[c]	75.7 ± 12	43.3 ± 2.2	270 (272, 267)[c]	48.7 ± 0.6	66.4 ± 1.3
TPPO	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]

TCrP	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]
ΣOPFR	242[d]	62.5 ± 1.4[d]	338 ± 49[d]	35.3[d]	62.1 ± 3.0[d]	339 ± 13[d]	81.4 ± 2.6[d]	617 ± 81[d]	81.2 ± 8.1[d]	252 ± 60[d]
BPA	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]	_[b]

Acenaphthene (Ace); Acenaphtylene (Acy); Anthracene (Ant); Benzo(a)anthracene (BaA); Benzo(a)pyrene (BaP); Benzo(b)fluoranthene (BbF); Benzo(a)pyrene (BeP); Benzo(g,h,i)perylene (BghiP); Benzo(j)fluoranthene (BjF); Benzo(k)fluoranthene (BkF); Bisphenol A (BPA); Chrysene (Chry); Dibenzo(a,h)anthracene (DBahA); Fluorene (Fl); Fluoranthene (Ft); Indeno(1,2,3-c,d)pyrene (IP); Phenanthrene (Phe); Retene (Ret); Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Pyrene (Pyr).

[a] All Pubic Open Space soil samples were determined on the <250 µm fraction

[b] <LOQ

[c] n = 2; mean (individual values)

[d] $SD_{sum} = \sqrt{\sum SD_i^2}$, SD_i is the SD PAH_i or the SD of the $OPFR_i$

[e] methods are detailed in the Supplementary Information.

Table S6: Analysis and characterisation of indoor house dust

	Indoor Dust: Sample identifier											
	ID1	**ID2**	**ID3[a]**	**ID4**	**ID5[a]**	**ID6[a]**	**ID7[a]**	**ID8**	**ID9[a]**	**ID10[a]**	**ID11**	**ID12**
Compound	**Concentration (ng/g) ± SD (n = 3)**											
PAHs												
Acy	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
Ace	110 (94, 127)[c]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	62.5 (66, 59)	-[b]	64.2 ± 0.5
Fl	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	159 ± 9.7
Phe	-[b]	1200 ± 60	-[b]	-[b]	379 (328, 431)	465 (343, 587)	-[b]	-[b]	-[b]	-[b]	-[b]	5270 ± 275
Ant	119 ± 4.3	83.7 ± 3.4	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	366 (379, 354)	112 (113, 110)	227 (232, 223)[c]	359 ± 47
Ft	2160 ± 281	1780 ± 139	-[b]	-[b]	1020 (991, 1060)	1060 (959, 1160)	-[b]	-[b]	938 (933, 942)	-[b]	1156 ± 17	1460 ± 100
Pyr	-[b]	-[b]	-[b]	-[b]	457 (438, 476)	-[b]	-[b]	187 ± 2.5	-[b]	-[b]	-[b]	-[b]
Ret	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
BaA	3850 ± 149	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	3866 (3838, 3895)	-[b]	-[b]
Chry	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	1570 ± 119
BjF+BkF+BbF	-[b]	516 ± 20	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]
BeP	-[b]	533 ± 16	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	-[b]	397 (414, 381)	-[b]	-[b]
BaP	-[b]	534 ± 18	-[b]	-[b]	-[b]	781 (802, 761)	-[b]	-[b]	-[b]	533 (549, 517)	-[b]	-[b]
IP	-[b]	448 ± 13	-[b]	-[b]	515 (505, 526)	577 (474, 680)	-[b]	-[b]	-[b]	-[b]	-[b]	1360 (1390, 1340)[c]

DBahA	–[b]	484 ± 20	–[b]	–[b]	–[b]	–[b]	–[b]	251 ± 23	–[b]	559 (545, 574)	–[b]	–[b]
BghiP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	261 ± 61
ΣPAHs	6240 ± 1560[c]	5570 ± 498[c]	–[b]	–[b]	2370 ± 253[c]	2880 ± 226[c]	–[b]	438 ± 32[c]	1300 ± 286[c]	5530 ± 1330[c]	1380 ± 465[c]	10500 ± 1610[c]
BaP_{eq}	408	1678	–[e]	–[e]	66.0	854	–[e]	251	13.0	1880	13.8	226
OPFRs												
TPrP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	215 ± 24	–[b]
TiBP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	896 (897, 896)[c]	–[b]	–[b]	–[b]	–[b]
TnBP	308 ± 5.9	–[b]	–[b]	–[b]	175 (204, 146)	–[b]	–[b]	811 (740, 883)[c]	111 (107, 116)	152 (113, 188)	310 (340, 280)[c]	–[b]
TCEP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	271 ± 51
TEEdP	834 (852, 817)[c]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	307 (309, 306)[c]	–[b]	–[b]	–[b]	134 ± 6.4
TDCPP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]
TPhP	–[b]	515 ± 11	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]
TBOEP	–[b]	1780 ± 29	–[b]	–[b]	930 (916, 944)	2410 (1930, 2890)	10400 (9910, 11000)	–[b]	–[b]	–[b]	2256 ± 63	–[b]
TEHP	946 ± 7.7	838 ± 19	–[b]	–[b]	321 (306, 335)	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	2150 (2140, 2170)[c]
TPPO	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]
TCrP	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]
ΣOPFR	2090 ± 278[c]	3130 ± 536[c]	–[b]	–[b]	1430 ± 327[c]	2410[c]	10400[c]	2010 ± 260[c]	111[c]	152[c]	2780 ± 941[c]	2560 ± 921[c]
BPA	–[b]	4750 ± 215	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]	–[b]

Acenaphthene (Ace); Acenaphtylene (Acy); Anthracene (Ant); Benzo(a)anthracene (BaA); Benzo(a)pyrene (BaP); Benzo(b)fluoranthene (BbF); Benzo(a)pyrene (BeP); Benzo(g,h,i)perylene (BghiP); Benzo(j)fluoranthene (BjF); Benzo(k)fluoranthene (BkF); Bisphenol A (BPA); Chrysene (Chry); Dibenzo(a,h)anthracene (DBahA); Fluorene (Fl); Fluoranthene (Ft); Indeno(1,2,3-c,d)pyrene (IP);

Phenanthrene (Phe); Retene (Ret); Tetraethyl ethylene diphosphonate (TEEdP); Tri-m-cresyl phosphate (TCrP); Triphenylphosphine oxide (TPPO); Tris (2-butoxyethyl) phosphate (TBOEP); Tris(2-chloroethyl) phosphate (TCEP); Tri(2-ethylhexyl) phosphate (TEHP); Tris(1,3-dichloro-2-propyl) phosphate (TDCPP); Tri-iso-butyl phosphate (TiBP); Tri-n-butyl phosphate (TnBP); Triphenyl phosphate (TPhP); Tripropyl phosphate (TPrP); Pyrene (Pyr).

[b] <LOQ

[c] n = 2; mean (individual values)

[d] $SD_{sum} = \sqrt{\sum SD_i^2}$, SD_i is the SD PAH_i or the SD of the $OPFR_i$

[e] Not calculated (PAHs concentration are lower than LOQ)

8

9

Table S7. PAH incremental lifetime cancer risk for adult and child in soil and indoor house dust samples

	Public Open Space 1: Sample identifier									
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**
$ILCR_{ing}^{adult}$	6.2×10^{-3}	4.5×10^{-3}	6.7×10^{-3}	9.1×10^{-4}	9.6×10^{-4}	5.7×10^{-3}	1.3×10^{-2}	8.4×10^{-3}	7.4×10^{-3}	1.1×10^{-2}
$ILCR_{inh}^{adult}$	4.8×10^{-7}	3.5×10^{-7}	5.2×10^{-7}	7.1×10^{-8}	7.5×10^{-8}	4.4×10^{-7}	9.8×10^{-7}	6.6×10^{-7}	5.8×10^{-7}	8.3×10^{-7}
$ILCR_{derm}^{adult}$	1.1×10^{-2}	8.1×10^{-3}	1.2×10^{-2}	1.6×10^{-3}	1.7×10^{-3}	1.0×10^{-2}	2.2×10^{-2}	1.5×10^{-2}	1.3×10^{-2}	1.9×10^{-2}
$ILCR_{s}^{adult}$	**1.7×10^{-2}**	**1.3×10^{-2}**	**1.8×10^{-2}**	**2.5×10^{-3}**	**2.7×10^{-3}**	**1.6×10^{-2}**	**3.5×10^{-2}**	**2.3×10^{-2}**	**2.1×10^{-2}**	**3.0×10^{-2}**
$ILCR_{ing}^{child}$	9.0 x 10-^{3}	6.6×10^{-3}	9.7×10^{-3}	1.3×10^{-3}	1.4×10^{-3}	8.3×10^{-3}	1.8×10^{-2}	1.2×10^{-2}	1.1×10^{-2}	1.6×10^{-2}
$ILCR_{inh}^{child}$	1.7×10^{-7}	1.3×10^{-7}	1.9×10^{-7}	2.6×10^{-8}	2.7×10^{-8}	1.6×10^{-7}	3.6×10^{-7}	2.4×10^{-7}	2.1×10^{-7}	3.0×10^{-7}
$ILCR_{derm}^{child}$	1.1×10^{-2}	8.2×10^{-3}	1.2×10^{-2}	1.7×10^{-3}	1.8×10^{-3}	1.0×10^{-2}	2.3×10^{-2}	1.5×10^{-2}	1.4×10^{-2}	1.9×10^{-2}
$ILCR_{s}^{child}$	**2.0×10^{-2}**	**1.5×10^{-2}**	**2.2×10^{-2}**	**3.0×10^{-3}**	**3.2×10^{-3}**	**1.9×10^{-2}**	**4.1×10^{-2}**	**2.8×10^{-2}**	**2.4×10^{-2}**	**3.5×10^{-2}**
	Public Open Space 2: Sample identifier									
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**
$ILCR_{ing}^{adult}$	1.3×10^{-3}	1.9×10^{-3}	2.7×10^{-2}	4.6×10^{-3}	6.0×10^{-3}	4.9×10^{-3}	5.8×10^{-3}	5.5×10^{-2}	5.9×10^{-3}	1.1×10^{-3}
$ILCR_{inh}^{adult}$	9.8×10^{-8}	1.5×10^{-7}	2.1×10^{-6}	3.6×10^{-7}	4.7×10^{-7}	3.8×10^{-7}	4.5×10^{-7}	4.2×10^{-6}	4.5×10^{-7}	8.8×10^{-8}
$ILCR_{derm}^{adult}$	2.2×10^{-3}	3.4×10^{-3}	4.9×10^{-2}	8.2×10^{-3}	1.1×10^{-2}	8.6×10^{-3}	1.0×10^{-2}	9.7×10^{-2}	1.0×10^{-2}	2.0×10^{-3}
$ILCR_{s}^{adult}$	**3.5×10^{-3}**	**5.4×10^{-3}**	**7.6×10^{-2}**	**1.3×10^{-2}**	**1.7×10^{-2}**	**1.4×10^{-2}**	**1.6×10^{-2}**	**1.5×10^{-1}**	**1.6×10^{-2}**	**3.2×10^{-3}**
$ILCR_{ing}^{child}$	1.8×10^{-3}	2.8×10^{-3}	4.0×10^{-2}	6.8×10^{-3}	8.7×10^{-3}	7.1×10^{-3}	8.4×10^{-3}	8.0×10^{-2}	8.5×10^{-3}	1.7×10^{-3}
$ILCR_{inh}^{child}$	3.6×10^{-8}	5.5×10^{-8}	7.7×10^{-7}	1.3×10^{-7}	1.7×10^{-7}	1.4×10^{-7}	1.6×10^{-7}	1.5×10^{-6}	1.7×10^{-7}	3.2×10^{-8}

$ILCR_{derm}^{child}$	2.3 x 10^{-3}	3.5 x 10^{-3}	5.0 x 10^{-2}	8.4 x 10^{-3}	1.1 x 10^{-2}	8.8 x 10^{-3}	1.0 x 10^{-2}	1.0 x 10^{-1}	1.1 x 10^{-2}	2.1 x 10^{-3}
$ILCR_s^{child}$	**4.1 x 10^{-3}**	**6.3 x 10^{-3}**	**9.0 x 10^{-2}**	**1.5 x 10^{-2}**	**2.0 x 10^{-2}**	**1.6 x 10^{-2}**	**1.9 x 10^{-2}**	**1.8 x 10^{-1}**	**1.9 x 10^{-2}**	**3.7 x 10^{-3}**

Indoor Dust: Sample identifier

	#1	**#2**	**#3[a]**	**#4[a]**	**#5**	**#6**	**#7[a]**	**#8**	**#9**	**#10**	**#11**	**#12**
$ILCR_{ing}^{adult}$	7.2 x 10^{-4}	3.0 x 10^{-3}			1.2 x 10^{-4}	1.5 x 10^{-3}		4.4 x 10^{-4}	2.3 x 10^{-5}	3.3 x 10^{-3}	2.4 x 10^{-5}	4.0 x 10^{-4}
$ILCR_{inh}^{adult}$	5.6 x 10^{-8}	2.3 x 10^{-7}			9.0 x 10^{-9}	1.2 x 10^{-7}		3.4 x 10^{-8}	1.8 x 10^{-9}	2.6 x 10^{-7}	1.9 x 10^{-9}	3.1 x 10^{-8}
$ILCR_{derm}^{adult}$	1.3 x 10^{-3}	5.3 x 10^{-3}			2.1 x 10^{-4}	2.7 x 10^{-3}		7.9 x 10^{-4}	4.1 x 10^{-5}	5.9 x 10^{-3}	4.3 x 10^{-5}	7.1 x 10^{-4}
$ILCR_s^{adult}$	**2.0 x 10^{-3}**	**8.2 x 10^{-3}**			**3.2 x 10^{-4}**	**4.2 x 10^{-3}**		**1.2 x 10^{-3}**	**6.4 x 10^{-5}**	**9.2 x 10^{-3}**	**6.8 x 10^{-5}**	**1.1 x 10^{-3}**
$ILCR_{ing}^{child}$	1.0 x 10^{-3}	4.3 x 10^{-3}			1.7 x 10^{-4}	2.2 x 10^{-3}		6.5 x 10^{-4}	3.4 x 10^{-5}	4.8 x 10^{-3}	3.6 x 10^{-5}	5.8 x 10^{-4}
$ILCR_{inh}^{child}$	2.0 x 10^{-8}	8.4 x 10^{-8}			3.3 x 10^{-9}	4.3 x 10^{-8}		1.3 x 10^{-8}	6.5 x 10^{-10}	9.4 x 10^{-8}	6.9 x 10^{-10}	1.1 x 10^{-8}
$ILCR_{derm}^{child}$	1.3 x 10^{-3}	5.4 x 10^{-3}			2.1 x 10^{-4}	2.7 x 10^{-3}		8.1 x 10^{-4}	4.2 x 10^{-5}	6.0 x 10^{-3}	4.4 x 10^{-5}	7.2 x 10^{-4}
$ILCR_s^{child}$	**2.4 x 10^{-3}**	**9.7 x 10^{-3}**			**3.8 x 10^{-4}**	**4.9 x 10^{-3}**		**1.5 x 10^{-3}**	**7.5 x 10^{-5}**	**1.1 x 10^{-2}**	**8.0 x 10^{-5}**	**1.3 x 10^{-3}**

PAH incremental lifetime cancer risk via ingestion ($ILCR_{ing}$); PAH incremental lifetime cancer risk via inhalation ($ILCR_{inh}$); PAH incremental lifetime cancer risk via dermal absorption ($ILCR_{derm}$); Total incremental lifetime cancer risk ($ILCR_s$): negligible risk $\leq 10^{-6}$; potential risk 10^{-6} to 10^{-4}; potentially high risk $>10^{-4}$.

[a] Not calculated (BaP_{eq} concentrations are lower than LOQ)

10

11