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# Cancer risk assessments of Hong Kong soils contaminated by polycyclic aromatic hydrocarbons

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## HIGHLIGHTS

- High levels of soil organic matter in soils render PAHs more resistant to degradation.
- Open burning site contain high concentrations of PAHs in Hong Kong.
- Car dismantling workshop can increase potential cancer risk on human.

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## ABSTRACT

The aim of this study was to evaluate soils from 12 different land use types on human cancer risks, with the main focus being on human cancer risks related to polycyclic aromatic hydrocarbons (PAHs). Fifty-five locations were selected to represent 12 different types of land use (electronic waste dismantling workshop (EW (DW)); open burning site (OBS); car dismantling workshop (CDW) etc.). The total concentrations of 16 PAHs in terms of total burden and their bioaccessibility were analysed using GC/MS. The PAHs concentrations were subsequently used to establish cancer risks in humans via three exposure pathways, namely, accident ingestion of soil, dermal contact soil and inhalation of soil particles. When the 95th centile values of total PAH concentrations were used to derive ingestion and dermal cancer risk probabilities on humans, the CDW land use type indicated a moderate potential for cancerous development ($244 \times 10^{-6}$ and $209 \times 10^{-6}$, respectively). Bioaccessible PAHs content in soil samples from CDW ($3.60 \times 10^{-6}$) were also classified as low cancer risk. CDW soil possessed a higher carcinogenic risk based on PAH concentrations. Bioremediation is recommended to treat the contaminated soil.



## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are usually produced via the incomplete combustion of organic substances and comprised of a diverse group of organic compounds. Their general structure consists of two or more fused aromatic rings arranged in different structural configurations [1]. Polycyclic aromatic hydrocarbons in the environment have drawn much attention due to their toxicity and potential carcinogenic effects on humans [2]. They may be released into the surroundings by anthropogenic pathways, such as incomplete combustion, or via pyrolysis of organic materials that are commonly used as energy sources [3].

Soil serves as an enormous sink for the accumulation of organic contaminants and may allow the entry of PAHs into food chains [4]. A number of studies have focused on the variation of PAH concentrations in different soil types. In general, it has been found that PAH concentrations in soil increase with the degree of anthropogenic impact, in both industrial and domestic land use [5].

Hong Kong's rapid industrial development and expeditious urbanization since the 1970s have led to a shift in rural land use pattern. The massive decline in agricultural products supplied by local farms in the 1950s have been attributed to increased profit margins, which have been gained from converting fish ponds and agricultural land to other uses such as electronic waste (e-waste)

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recycling sites, open burning sites and car dismantling workshops [6,7]. Man et al. [8], demonstrated that the absence of non-cancer risk and very low cancer risk may be exerted on humans associated with 1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethanes (DDTs) and hexachlorocyclohexanes (HCHs) contents after changing the use of agricultural land in Hong Kong. However, Lopez et al. indicated that e-waste recycling activities including dismantling and open burning have generated a large amount of heavy metals (e.g. arsenic (As), chromium (Cr), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb)) and persistent toxic substances (polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and PAHs) on existing abandoned farm soils in Hong Kong. In addition, Man et al. revealed that e-waste dismantling workshops can be detrimental to both adults and children, and car dismantling workshops may also prove to be harmful to children, based on metal concentrations. Furthermore, e-waste recycling activities have been shown to exert relatively high cancer risks on humans after exposure to PBDE and PCB contaminated soils [9]. Hence, agricultural land use conversions to other purposes are potentially jeopardizing the health of residents in Hong Kong. Elevation of PAH concentrations resulting from these practices have caused scientific concern as these increased concentrations in soil will increase human health risk as a consequence of exposure [10].

We hypothesize that soils from different types of land use may generate different levels of PAHs to the surrounding environment, leading different degree of cancer risk exert on humans. This study aimed to assess cancer risk that is attributable to PAHs in soil of different land use types in order to evaluate the potential health hazards of the PAHs from the soil samples. Therefore, a cancer risk assessment was conducted to examine the potential risks that may be exerted upon human health via PAHs through 3 exposure pathways, namely ingestion, dermal contact and inhalation.

## 2. Materials and methods

### 2.1. Sampling, preparation and analysis

The soil PAH concentrations of the e-waste sites and open burning sites [11], human health risk assessments of heavy metals (As, Cr, Cu, Zn, Cd and Pb) [non-cancer risks], DDTs and HCHs [non-cancer and cancer risks], and PCBs and PBDEs [cancer risks] at the same locations have been previously reported [8,9,12]. For this study, 275 composite soil samples were collected from existing and former agricultural land in Hong Kong. Each site was grouped according to their current land use, resulting in 12 identified soil types: (i) agricultural (A); (ii) abandoned agricultural (Ab); (iii) organic farm (OF); (iv) container storage (CS); (v) construction waste (CW); (vi) e-waste storage (EW (S)); (vii) e-waste dismantling workshop (EW (DW)); (viii) e-waste open burning site (EW (OBS)); (ix) open burning site (OBS); (x) petrol station (PS); (xi) metal recycling workshop (MRW); and (xii) car dismantling workshop (CDW). Descriptions of each type of land use and the number of sites investigated were also shown in Man et al. [8,9,12]. The soils of existing (A and OF) and abandoned (Ab) farmlands were used to compare with other types of land use. Soil sampling, preparation and analysis of texture and soil organic matter used in this study are described in Man et al. [9].

### 2.2. Extraction and analysis of total PAHs

Soxhlet extraction was performed according to the US EPA Standard Method 3540C [13] in which 5 g of soil sample was added to 10 g of anhydrous sodium sulphate (S6264, Sigma Chemical Co.). The mixture was transferred into a cellulose extraction thimble and inserted into a Soxhlet fitted with a 250 mL flask. Dichloromethane and acetone (v:v 1:1) (150 mL) was added and the whole set up then heated for 18 h in a water bath at 69 °C. The extracts were concentrated to 10 mL by a rotary evaporator and used for subsequent clean ups. In order to remove the organic and inorganic constituents other than those of interest, clean up steps were performed before analysis. Florisil column clean up was thus applied for purification of the concentrated extract (US EPA Standard Method 3620B) [14]. The extracts were concentrated to less than 5 mL by a rotary evaporator afterwards, and then n-hexane (10 mL) was added and concentrated to less than 2 mL. Subsequently, deuterated PAHs (acenaphthene-$_{d10}$, phenanthrene-$_{d10}$, chrysene-$_{d12}$, and perylene-$_{d12}$) were injected into the sample extracts as internal standards for quantitation. Finally, the extract was topped up to 2 mL with n-hexane for the analysis of PAHs.

GC-MS analysis was carried out on a Hewlett Packard 6890 GC system, equipped with a mass selective detector and a 30 m × 0.25 mm × 0.25 μm DB-5 capillary column (J & W Scientific Co., Ltd., USA). The US EPA Standard Method 8270C [15] was applied for the determination of the following 16 PAHs of naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (IcdP), dibenz(a,h)anthracene (DahA) and benzo(g,h,i)perylene (BghiP). The peaks of BbF and BkF were close together and difficult to separate, therefore these two compounds were regarded as one and referred to as BbkF.

### 2.3. Quality control

Every 20th sample of the 275 composite soil samples used for analysing PAH concentrations were run in duplicate to check data consistency. A standard reference material (SRM), 1941b – organics in marine sediment (National Institute of Standards and Technology (NIST, USA)) and an analytical blank were included in every batch of extraction to assess the performance and recoveries of the entire analytical process. No detectable PAH concentrations were found in any of the analytical blanks, whilst the mean recoveries of PAHs ranged from 82 ± 10% for Ant to 118 ± 9% for BghiP.

### 2.4. Exposure scenarios and cancer risk equations

In this study, potential cancer risk imposed on workers or farmers as a result of being in contact with contaminated soil was assumed to occur via 3 major exposure pathways. These included: accidental ingestion of soil particles; dermal absorption of pollutants via soil particle contact; and inhalation of fugitive soil particle, with potential cancer risks via these means estimated using the following Eqs. (1) and (2) [16] and (3) [17].

$$\text{Cancer risk}_{\text{ingest}} = \frac{C_{\text{soil}} \times \text{IngR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \times \text{SFO} \quad (1)$$

where Cancer risk$_{\text{ingest}}$ is the cancer risk via ingestion of soil particles; $C_{\text{soil}}$ is the concentration of the pollutant in soil (mg/kg); IngR is the ingestion rate of soil (mg/day); EF is the exposure frequency (days/year); ED is the exposure duration (years); BW is the average body weight (kg); AT is the averaging time (days); CF is the conversion factor ($1 \times 10^{-6}$ kg/mg); SFO is the oral slope factor $(\text{mg/kg/day})^{-1}$.

$$\text{Cancer risk}_{\text{dermal}} = \frac{C_{\text{soil}} \times \text{SA} \times \text{AF}_{\text{soil}} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \times \text{SFO} \times \text{GIABS} \quad (2)$$

where Cancer risk$_{\text{dermal}}$ is the cancer risk via dermal contact of soil particles; SA is the surface area of the skin that contacts soil ($\text{cm}^2$/day); AF$_{\text{soil}}$ is the skin adherence factor for soil ($\text{mg/cm}^2$);

**Table 1**
Parameters for estimating human cancer risk.

| Exposure factors | Adult |
|---|---|
| Ingestion rate, IngR (mg/day) | 100 |
| Exposed skin area, SA ($cm^2$) | 3300 |
| Skin adherence factor, $AF_{soil}$ ($mg/cm^2$) | 0.2 |
| Exposure frequency, EF (days/year) | 313 |
| Exposure duration, ED (year) | 25 |
| Exposure time, ET (h/day) | 8 |
| Body weight, BW (kg) | 60 |
| Averaging time, AT (days) = (70 years × 365 days/year) | 25,550 |
| Averaging time, AT* (h) = (70 years × 365 days/year × 24 h/day) | 613,200 |

*Note*: IngR was taken from Calabrese et al. [26]; ED from the US EPA [28]; $AF_{soil}$, AT from the US EPA [29]; SA of adult from the US EPA [31]; BW from Lee et al. [30] and AT*, ET from US EPA [17].

ABS is the dermal absorption factor (chemical specific); GIABS is the gastrointestinal absorption factor.

$$\text{Cancer risk}_{\text{inhale}} = \frac{C_{soil} \times EF \times ET \times ED}{PET \times AT*} \times IUR \quad (3)$$

where Cancer $risk_{inhale}$ is the cancer risk via inhalation of soil particles; ET is the exposure time (h/day); IUR is the inhalation unit risk $(mg/m^3)^{-1}$; AT* is the averaging time (h); PEF is the particle emission factor = $1.36 \times 10^9$ $m^3/kg$.

PEF is the inhalation of pollutants that are adsorbed to respirable particles ($PM_{10}$) and relates the concentration of a pollutant in soil with the concentration of respirable particles in the air, due to fugitive dust emissions from contaminated soils [18].

The parameters for estimating human cancer risk are listed in Table 1. Qualitative descriptions of lifetime cancer risks are as follows: very low when the estimated value is $\leq 10^{-6}$; low from $10^{-6}<$ to $<10^{-4}$, moderate from $10^{-4} \leq$ to $<10^{-3}$, high from $10^{-3} \leq$ to $<10^{-1}$ and very high when the value is $\geq 10^{-1}$ [19]. Seven carcinogenic PAH concentrations and their respective toxic equivalency factors (TEFs) including BaP (1), BaA (0.1), BbF (0.1), BkF (0.01), Chr (0.001), DahA (1) IcdP (0.1) were used to conduct the cancer risk assessment applying BaP toxicity equivalence [20]. Since, BbF (0.1) and BkF (0.01) were combined to form BbkF, the conservative TEF of BbkF (0.1) was used [20]. Oral slope factor $(mg/kg/day)^{-1}$, SFO × GIABS $(mg/kg\text{-}day)^{-1}$ and and IUR $(mg/m^3)^{-1}$ of BaP, are listed in Table 2.

### 2.5. In vitro digestion model to extract bioaccessible PAHs

The physiologically based extraction test described in Ruby et al. [21] and Tang et al. [22] were used as the in vitro digestion model, to evaluate the bioaccessible PAHs in this study. This test simulates the conditions of both the stomach and intestine in humans for extracting the samples for 1 h and 4 h, respectively. Gastric solution was used in this study and prepared by adding 17.55 g of NaCl (S9888, Sigma Chemical Co.), 1.0 g of citrate (C1909, Sigma Chemical Co.), 1.0 g of malate (63190, Fluka Chemical Co.), 0.85 mL of lactic acid (L6661, Sigma Chemical Co.), 1.0 mL of acetic acid (33309, RDH Chemical Co.), and 2.5 g of pepsin (P7000, Sigma Chemical Co.) to 2 L of deionised water, which was then adjusted to pH 1.5 with 12 M HCl. Subsequently, 1 g of soil was added to a 50 mL Teflon centrifuge tubes followed by 30 mL of gastric solution and this mixture was then shaken in a shaking incubator (SHEL LAB 1575 R) at 55 rpm for 1 h at 37 °C. The simulated gastric conditions were altered to intestinal conditions via the adjustment of pH to 7.0 using 1 M NaOH. Meanwhile, 0.06 g of porcine bile extract (B8631, Sigma Chemical Co.) and 0.018 g of porcine pancreatin (P1500, Sigma Chemical Co.) were added to each Teflon centrifuge tubes (50 mL). During the simulated intestinal conditions, the samples were also shaken with a shaking incubator at 55 rpm for 4 h at 37 °C. The samples were then centrifuged at 3300 rpm for 10 min at 37 °C and filtered with an Advantec 5C filter paper. Finally, the filtrate was diluted and made up to 35 mL with deionised water.

Extraction of bioaccessible PAHs was subsequently performed using a liquid–liquid extraction method. The filtrate (35 mL) was extracted with dichloromethane (35 mL) and acetone (v:v 1:1) for 2 min in a separatory funnel and left standing for half an hour. The organic sample extracts were then collected and any water left in the extracts was absorbed with anhydrous sodium sulphate (S6264, Sigma Chemical Co.). The sample extracts were concentrated to 10 mL by a rotary evaporator and the same clean up and analytical procedure was used as described for total PAHs (Section 2.2).

### 2.6. Selection of soil samples for the in vitro digestion model and the recoveries and risk assessment of bioaccessible PAHs

The minimum, median and maximum BaP equivalent lifetime cancer risks via the ingestion pathway for each type of land use were selected for testing bioaccessible PAH concentrations. This yielding 3 (minimum, median and maximum) × 12 types of land use = 36 soil samples, with each of them tested in duplicate. CRM140-100 Resource Technology Corporation Lot 010572 and an analytical blank were included in extraction. Mean bioaccessible PAH recoveries of CRM140-100 Resource Technology Corporation Lot 010572 ranged from 0.506 ± 0.12% for BaP to 53.7 ± 2.22% for Nap. The bioaccessible PAH concentrations were used to conduct cancer risk assessments using the same method for assessing total PAHs.

### 2.7. Statistical analysis

Statistical analyses including variance analysis, Pearson correlation and percentile rank were achieved using SPSS 16.0 for windows. Variance analysis ($p < 0.05$) of total PAH concentrations and cancer risk of bioaccessible PAHs via ingestion of soil particles amongst 12 different types of land use were performed using one-way ANOVA test.

## 3. Results

### 3.1. Concentrations of total PAHs of the 12 different types of land use

Tables 3 and S1 (supplementary data) show the mean concentrations of PAHs. Total PAHs in OBS, EW (DW) and CDW (7006, 2306 and 8042 μg/kg) were significantly higher ($p < 0.05$) than the other land use types. In addition, the sum of the 10 PAHs mean concentrations in OBS, EW (DW) and CDW (5592, 1973 and 7210 μg/kg) far exceeded the Dutch target values (1000 μg/kg) [23]. Furthermore, the BaP TEQ concentrations of some of the soil samples from CDW exceeded the Canadian Environmental Quality Guidelines for agricultural and industrial uses (5300 μg/kg) [24], as demonstrated by the standard deviation (4931 ± 16715 μg/kg).

### 3.2. Correlation of PAHs with SOM

The mean values of soil organic matter (SOM) in OBS, EW (DW), EW (OBS) and CDW (6.11, 8.63, 6.30 and 9.91%) were significantly higher ($p < 0.05$) than other types of land use (Table S2 (supplementary data)). In addition, SOM significantly correlated with most PAH concentrations such as the sum of 10 PAHs, BaP TEQ and total PAHs ($r = 0.302$, $r = 0.232$ and $r = 0.332$ at $p < 0.01$, respectively (Table S3 (supplementary data)).

**Table 2**
Slope factors (SFs) of BaP for ingestion, dermal contact and inhalation and dermal absorption factor (ABS) of BaP [32].

| Contaminants | Cancer risk | | | |
|---|---|---|---|---|
| | Ingestion | Dermal contact | Inhalation | Dermal absorption factor (ABS) (chemical-specific) |
| | SFO $(mg/kg\text{-}day)^{-1}$ | SFO × GIABS $(mg/kg\text{-}day)^{-1}$ | IUR $(mg/m^3)^{-1}$ | |
| BaP | 7.30E+00 | 7.30E+00 | 1.10E−06 | 0.13 |

SFO = oral slope factor, GIABS = gastrointestinal absorption factor, IUR = inhalation unit risk, RfDo = reference dose for ingestion, RfCi = reference dose for inhalation, all the contaminants GIABS = 1.

**Table 3**
Concentrations of PAHs (μg/kg) for 12 different soils.

| Sampling sites | Sum of the 10 PAHs | BaP TEQs | Total PAHs |
|---|---|---|---|
| Organic farm | 155 ± 105 a | 5.01 ± 6.22 a | 174 ± 118 a |
| Agricultural | 167 ± 131 a | 11.7 ± 12.9 a | 192 ± 149 a |
| Abandoned agricultural | 145 ± 141 a | 8.03 ± 15.6 a | 166 ± 161 a |
| E-waste storage | 260 ± 64.0 a | 6.26 ± 1.77 a | 289 ± 68.5 a |
| Container storage | 285 ± 147 a | 7.81 ± 5.51 a | 318 ± 159 a |
| Metal recycling workshop | 435 ± 278 a | 89.2 ± 62.3 a | 504 ± 323 a |
| Construction waste | 257 ± 256 a | 20.6 ± 32.9 a | 298 ± 299 a |
| Petrol station | 127 ± 54.8 a | 21.8 ± 13.5 a | 147 ± 62.6 a |
| Open burning site | 5592 ± 6049 ab | 401 ± 272 a | 7006 ± 6073 b |
| E-waste dismantling workshop | 1973 ± 2027 ab | 329 ± 349 a | 2306 ± 2352 ab |
| E-waste open burning site | 847 ± 268 a | 78.2 ± 59.5 a | 1008 ± 311 a |
| Car dismantling workshop | 7210 ± 19,277 b | 4931 ± 16,715 a | 8042 ± 19,953 b |
| The New Dutch list (Dutch target value) | 1000 | | |
| The New Dutch list (Dutch intervention value) | 40,000 | | |
| Canadian environmental quality guidelines (agricultural and industrial) | | 5300 | |

Sum of the10 PAHs = sum of Nap, Phe, Ant, Fla, BaA, Chr, BbkF, BaP, IcdP and BghiP BaP TEQs = seven carcinogenic PAHs (BaP, BaA, BbF, BkF Chr, DahA, IcdP) toxic equivalent concentration to BaP.
PAHs concentrations amongst the 12 different types of soil followed by the same letter on the same column are not significantly different at the 0.05 probability level according to the Duncan's Multiple Range Test.
*Note*: The New Dutch list (Dutch target value and intervention value) [23] and Canadian environmental quality guidelines of BaP TEQs for agricultural and industrial land use have been applied for the protection of the value of human health in $1 \times 10^{-5}$ incremental lifetime cancer risk [24].

### 3.3. Cancer risk of PAHs via ingestion, dermal contact and inhalation of soils

Table 4 shows that when only the lowest 5% of the samples were considered, all samples possessed very low carcinogenic risk via the ingestion pathway. At the 95th centile, only 7 types of land use (OF, A, Ab, EW(S), CS, CW, PS) registered very low cancer risk. Another 4 sites, namely MRW, OBS, EW (DW), EW (OBS) showed low cancer risk ($1.08 \times 10^{-6}$, $5.63 \times 10^{-6}$, $5.46 \times 10^{-6}$ and $1.27 \times 10^{-6}$, respectively). The highest cancer risk amongst all sites was a moderate cancer risk calculated for CDW ($244 \times 10^{-6}$). In addition, the cancer risk to humans resulting from carcinogenic PAHs via dermal contact as an exposure route was also assessed. Similar to the ingestion pathway, all of the sampling sites showed very low cancer risk at the 5th centile of samples. At the 95th centile, the same 7 sampling sites (OF, A, Ab, EW(S), CS, CW, PS) registered very low cancer risk and sampling sites of MRW, OBS, EW (DW), EW (OBS) showed low cancer risk of $1.20 \times 10^{-6}$, $4.83 \times 10^{-6}$, $4.68 \times 10^{-6}$ and $1.10 \times 10^{-6}$, respectively. Only CDW showed moderate cancer risk ($209 \times 10^{-6}$) again. However, when considering inhalation as an exposure pathway, the data revealed that even at the 95th centile, all soil samples registered very low cancer risk values for all land use types ($<10^{-6}$).

### 3.4. Cancer risk of bioaccessible PAHs via the ingestion of soils

Table S4 (supplementary data) shows the percentage in fractions of bioaccessible carcinogenic PAHs to total PAHs. According to Table 5, the mean cancer risk of soil samples from OBS, EW (DW),

**Table 4**
Cancer risk in humans via ingestion, dermal contact and inhalation of 12 different soils based upon the total BaP toxicity equivalence concentration at the 5th, median and 95th centile.

| Sampling sites | Cancer risk via ingestion | | | Cancer risk via dermal contact | | | Cancer risk via inhalation | | |
|---|---|---|---|---|---|---|---|---|---|
| | 5th Centile | Median | 95th Centile | 5th Centile | Median | 95th Centile | 5th Centile | Median | 95th Centile |
| Organic farm | 0.000400 | 0.0104 | 0.186 | 0.00100 | 0.00900 | 0.159 | 2.69E−15 | 7.68E−14 | 1.37E−12 |
| Agricultural | 0.00130 | 0.0322 | 0.289 | 0.00100 | 0.0280 | 0.248 | 9.64E−15 | 2.38E−13 | 2.13E−12 |
| Abandoned agricultural | 0.000200 | 0.0125 | 0.222 | 0.00100 | 0.0110 | 0.190 | 1.71E−15 | 9.20E−14 | 1.64E−12 |
| E-waste storage | 0.0275 | 0.0485 | 0.0900 | 0.0240 | 0.0420 | 0.100 | 2.03E−13 | 3.58E−13 | 6.29E−13 |
| Container storage | 0.0439 | 0.0844 | 0.120 | 0.0380 | 0.0720 | 0.100 | 3.24E−13 | 6.23E−13 | 8.54E−14 |
| Metal recycling workshop | 0.272 | 0.542 | **1.08** | 0.234 | 0.465 | **1.20** | 2.01E−12 | 4.00E−12 | 1.04E−11 |
| Construction waste | 0.00300 | 0.0800 | 0.630 | 0.00300 | 0.069 | 0.540 | 2.19E−14 | 5.91E−13 | 4.65E−12 |
| Petrol station | 0.0466 | 0.140 | 0.408 | 0.0400 | 0.120 | 0.350 | 3.44E−13 | 1.04E−12 | 3.01E−12 |
| Open burning site | 0.818 | **1.17** | **5.63** | 0.702 | **1.01** | **4.83** | 6.04E−12 | 8.66E−12 | 4.16E−11 |
| E-waste dismantling workshop | 0.143 | 0.625 | **5.46** | 0.122 | 0.536 | **4.68** | 1.05E−12 | 4.62E−12 | 4.03E−11 |
| E-waste open burning site | 0.0133 | 0.378 | **1.27** | 0.0110 | 0.324 | **1.10** | 9.84E−14 | 2.79E−12 | 9.35E−12 |
| Car dismantling workshop | 0.141 | **1.50** | **244** | 0.121 | **1.29** | **209** | 1.04E−12 | 1.11E−11 | 1.80E−09 |

*Note*: Type in bold indicates potential cancer risk (all cancer risks are presented in units of $10^{-6}$).

**Table 5**
Cancer risk in humans via the ingestion of 12 different soils. based on the minimum, medium, maximum and mean bioaccessible BaP toxic equivalent concentrations.

| Sampling sites | Cancer risk via ingestion | | | |
|---|---|---|---|---|
| | Min | Median | Max | Mean |
| Organic farm (OF) | 0.000289 | 0.00147 | 0.0209 | 0.00754 ± 0.0116 a |
| Agricultural (A) | 0.000583 | 0.00249 | 0.0114 | 0.00482 ± 0.00576 a |
| Abandoned agricultural (Ab) | 0.000147 | 0.00152 | 0.0420 | 0.0144 ± 0.0235 a |
| E-waste storage (EW (S)) | 0.00540 | 0.0039 | 0.00243 | 0.00391 ± 0.00146 a |
| Container storage (CS) | 0.00113 | 0.00269 | 0.00380 | 0.00255 ± 0.00136 a |
| Metal recycling workshop (MRW) | 0.00950 | 0.0190 | 0.0320 | 0.0202 ± 0.0113 a |
| Construction waste (CS) | 0.00236 | 0.00201 | 0.0225 | 0.00895 ± 0.0117 a |
| Petrol station (PS) | 0.0099 | 0.0108 | 0.0188 | 0.0132 ± 0.00489 a |
| Open burning site (OBS) | 0.0750 | 0.131 | 0.510 | 0.239 ± 0.238 ab |
| E-waste dismantling workshop (EW (DW)) | 0.0065 | 0.034 | 0.420 | 0.152 ± 0.230 ab |
| E-waste open burning site (EW (OBS)) | 0.00120 | 0.0320 | 0.0690 | 0.0344 ± 0.0341 ab |
| Car dismantling workshop (CDW) | 0.0420 | 0.0850 | **10.7** | **3.60 ± 6.11 c** |

Min = minimum and max = maximum.
Cancer risk amongst the 12 different types of soil followed by the same letter on the same column are not significantly different according to the Duncan's Multiple Range Test at the 0.05 probability level.
*Note*: Type in bold indicates potential cancer risk (all cancer risks are presented in units of $10^{-6}$).

EW (OBS) and CDW ($0.239 \times 10^{-6}$, $0.152 \times 10^{-6}$ and $0.0344 \times 10^{-6}$ and $3.60 \times 10^{-6}$) were significantly higher than others types of land use. However, only soil samples from CDW ($3.60 \times 10^{-6}$) were classified as low cancer risk.

## 4. Discussion

Based on the concentrations of PAHs, changing agricultural land use to OBS, EW (DW) and CDW may result in potential human health risks. In addition, SOM is able to bind to PAHs after their deposition on soils [5], which will render PAHs more resistant to degradation and leaching from soils due to this strong sorption [25]. Activities such as open burning and car dismantling conducted on former farmland would release a large amount of PAHs and bind with SOM, which would potentially jeopardize environmental and human health.

There is a wide range of soil ingestion rates available in published data, however, there are significant uncertainties such as multiple sources of error, bias and artefacts associated with tracer element studies. For example, a typical tracer element study was conducted in Calabrese et al. [26] who suggested 100 mg/day conservative soil ingestion rate (IngR) for adult. In 2009, the US EPA drafted an updated handbook on exposure factors for better incorporation in human health risk assessments [27]. However, this document is still an external draft. The highlight in the updated handbook on exposure factors is the emphasis on age group specific exposure factors. The new ingestion rate of 50 mg/day for adult was based on 9 studies, of which 4 of them were in consensus which may introduce a bias [27]. After taking everything into consideration, a conservative soil ingestion rate (IngR) of 100 mg/day was chosen for an adult [26] in this study. However, it is important to note that the weather conditions in different areas will impact on the local population in having different tendencies and behaviours to accidentally ingesting soil particles. For example, winter snow storms are common in the United States therefore residents are expected to have minimal contact with soil [27], unlike residents in Hong Kong where snow is not normally associated with the winters. Specific soil ingestion rates for adults should be determined in the rural areas of Hong Kong in order to further improve this study.

"Exposure duration (ED) is assumed to be equivalent to job tenure for receptors in the non-residential soil screening scenario". United States EPA has selected a value of 25 years as the default for the ED of outdoor workers [28], however, no such data is currently available Hong Kong. Hence, the exposure duration (ED) chosen was 25 years [28], with exposure frequency (EF) assumed to be 313 days/year, whereby workers and farmers are working or farming on the farms all year round except for 1 day of holiday per week.

"The duration of a lifetime has traditionally been assigned the nominal value of 70 years as a reasonable approximation" for carcinogenic chemical exposure and cancer risk evaluation [27]. Hence, the average working time (AT) has been estimated as 25,550 days [70 years × 365 days/year] [29]. In addition, US EPA has added an exposure time (ET) of 8 h/day for continuous chronic exposure via occupation when assessing the risk of soil via the inhalation pathway [17]. Hence, 8 h/day was chosen for the inhalation pathway and the average working time (AT*) estimated to be 613,200 h [70 years old × 365 days/year × 24 h/day]. In this study, the body weight of 60 kg for an adult was chosen based on statistics of the local population [30]. In addition, the surface area of skin that contacts the soil (*SA*) was assumed to be 3300 $cm^2$/day for an adult worker and 5700 $cm^2$/day for an adult resident [31]. In this study, the target population was either workers or farmers, hence, SA of 3300 $cm^2$/day for an adult was chosen. The skin adherence factor of soil ($AF_{soil}$) (0.2 mg/$cm^2$) for an adult worker was a default value set by the [29].

It is important to note that one of the limitations of this study is that all the exposure factors, such as IngR and SA of adults via ingestion, and dermal contact were fixed by default values [26,31]. Fixed exposure factors are commonly used in risk assessment because of their convenience for screening large numbers of potentially contaminated sites. However, they may not be sufficiently accurate in portraying the reality as the exposure factors change during various stages of life and environmental conditions, due to different physiological and behavioural factors, especially in children [27]. Furthermore, according to the Human Health Evaluation Manual published in 2009 [17], which did not recommend the inclusion of ventilation rate and body weight in equation (3), as "the amount of the chemical that reaches the target site of the chemical via the inhalation pathway is not the simple function of the ventilation rate and body weight". Therefore, ventilation rate and body weight were excluded in equation (3) [17]. Adversely, it is important to note that the IUR value for benzo[*a*]pyrene in the MidAtlantic Risk Assessment Regional Screening Level Summary Table used in this study has not received agency-wide review and endorsement [32], as the US EPA currently has no official IUR value for benzo[*a*]pyrene [33]. However, using the IUR value for benzo[a]pyrene in the Mid Atlantic Risk Assessment Regional Screening Level Summary Table may still provide some risk information when assessing cancer risk of PAHs via inhalation in this study.

It is worth mentioning that cancer risk calculations were used for screening procedure only and they are interpreted as preliminarily indications of potential cancer risks only. Five percent of CDW soil samples via the ingestion and dermal contact pathways possessed the greatest chance of developing cancer in humans amongst the 12 different types of land use. However, there was only a very low risk in the development of cancer in humans as a result of PAH inhalation. In this investigation, soil samples were collected from 55 sampling sites consisting of 12 different land use types. The possible carcinogenic risks posed to humans from PAHs were investigated through various exposure pathways. Since agricultural activities were practiced at all of the sampling sites prior to their current use, background PAH concentrations identified in the soil may be attributed to such activities including open burning to discarding crop residues, clearing land and providing nutrients for the next growth cycle [34]. Moreover, transportation around the sampling sites may have also contributed to the deposition of PAHs in the soil, as well as, aerial deposition resulting from forest fires and lightning acting as a contributory factor to background PAH concentrations. Higher PAH concentrations were detected at OBS and CDW sites owing to the extensive practice of PAH emitting activities, including open burning on OBS and leaching of substantial fossil fuel residues and engine lubricants, which contain high concentrations of PAHs, from the dismantling of vehicles at the CDW sites.

The observed inhalation cancer risks for PAHs were very low when compared to other exposure routes (ingestion and dermal contact). This may be a consequence of a lack of evaluation of air samples [9]. Man et al. [9] suspected that the major exposure pathway of PBDEs and PCBs contaminated soils was via inhalation in both OBS and EW (OBS) as burning activities tend to generate ultrafine particles less than $PM_{0.1}$, which can penetrate deeply into the lungs and cause adverse health effects. Rovira et al. [35] showed that when air samples of respirable particles ($PM_{10}$) were applied, human inhalation was found to be one of the most important exposure routes in terms of the levels of metals and PCDD/Fs in the vicinity of a cement plant. One of the drawbacks of this study was the use of soil particles of less than 2 mm for the risk assessment evaluation via the inhalation pathway instead of air samples of respirable particles ($PM_{10}$).

It is also worth noting that historically, excess lifetime cancer risk of $\geq 10^{-6}$ has been consistently considered insignificant and $\geq 10^{-4}$ as significant, where actions are usually taken to reduce risk when cancer risk falls within the latter group. There is no consistency with interpreting cancer risk between $10^{-6}$ and $10^{-4}$ in which actions may be taken depending on the locality's jurisdiction (e.g. Canadian soil quality guidelines for the protection of environmental and human health considers cancer risk of $\leq 10^{-5}$ at contaminated sites as insignificant) and circumstances [24]. Therefore, remediation action is recommended to lower the cancer risk in CDW (classified as moderate cancer risk).

Ingestion of bioaccessible PAHs is usually due to accidental consumption of soil especially in children via hand to mouth feeding [36]. Consequently, the total bioaccessible concentration of PAHs may provide crucial information about the risk of PAH intake in humans. An in vitro system mimicking the human digestive system was used to investigate the amount of bioaccessible PAHs in the soil samples. Due to the elevated concentration of total PAHs in the soil of CDW, bioaccessible PAHs concentrations in these sites also indicated a low cancer risk.

It is also worth mentioning that unless an in vitro bioaccessibility test has been "validated" against an in vivo bioavailability test for a chemical, the bioaccessibility results would generally not be accepted for use as part of a risk assessment [37,38]. To date, validation has only been achieved for a few metals (e.g. lead) and a number of in vitro bioaccessibility tests ([37,39]. Development of in vitro testing methods for oral bioaccessibility of organics has not progressed as far as metals and are unlikely to be ready for use in bioavailability adjustment in risk assessment. Hence, the bioaccessible cancer risk of PAHs can be used as a reference only.

Conducting risk assessment by means of total pollutant concentrations always results in the overestimation of the health risk exerted on humans [40]. Using bioavailable pollutant concentrations to evaluate health risk is commonly regarded as the most accurate way, as only the bioavailable portion of the contaminants will ultimately reach the bloodstream and impose adverse effects on the body [41]. However, this method usually involves experiments conducted with the use of animals, raising ethical concerns. Alternately, accessing bioaccessible fractions of pollutants is more realistic than using total pollutant concentrations [40]. In this study, bioaccessible fractions of pollutants were used to estimate the health risk via ingestion by an in vitro digestion model. As the bioaccessible fraction of pollutants were not used to estimate health effects attributed to the other two pathways, namely dermal contact and inhalation, it is important to note that consequent cancer risks were underestimated using bioaccessible BaP TEQ concentrations. Furthermore, owing to uncertainties with using animal data in estimating human health risk, it would still be appropriate for total BaP TEQ concentrations to be used in determining human health risk assessments. Overestimation is usually better than underestimation during risk assessments in order to provide greater protection of human health.

The Environmental Protection Department (EPD) of Hong Kong released a contaminated land standard "Risk-Based Remediation Goals" (RBRGs) in 2007, with the objective of protecting human health, based on four post-restoration land use scenarios (1 urban residential; 2 rural residential; 3 industrial and 4 public parks) [42]. The RBRGs stated that as it is unlikely that local lands will be developed or redeveloped for agricultural purposes, it is not a prerequisite to derive a local standard to protect agricultural soils in Hong Kong [42]. Therefore, there are no existing regulatory frameworks for PAHs concentrations on agricultural soils. However, this study demonstrated potential cancer risk may arise after exposure to PAHs contaminated agricultural soil which indicated the need for establishing a local set of contaminated soil standard, with emphasis on the protection of human health.

## 5. Conclusion

Alteration of agricultural land use to OBS, EW (DW), EW (OBS) and CDW can potentially pose carcinogenic risks based on the PAH concentrations in soils, especially the high PAH concentration found in CDW soil. Remediation such as bioremediation is recommended to lower the PAH concentrations in the soil of CDW. The observed inhalation cancer risks seem very low when compared to other exposure routes. This may be a consequence of a lack of evaluation of air samples of respirable particles ($PM_{10}$). As these contaminants especially ultrafine particles ($PM_{0.1}$) are produced in the sampling sites (OBS and EW (OBS)) as a consequence of burning activities. In order to gain a fuller picture of potential cancer risks after changing agricultural land use, future studies using air sampling of respirable particles ($PM_{10}$) to evaluate cancer risk via the exposure pathway of inhalation in open burning sites is essential.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2012.11.067.

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# Cancer risk assessments of Hong Kong soils contaminated by polycyclic aromatic hydrocarbons

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## Abstract

The aim of this study was to evaluate soils from 12 different land use types on human cancer risks, with the main focus being on human cancer risks related to polycyclic aromatic hydrocarbons (PAHs). Fifty-five locations were selected to represent 12 different types of land use (electronic waste dismantling workshop (EW (DW)); open burning site (OBS); car dismantling workshop (CDW) etc.). The total concentrations of 16 PAHs in terms of total burden and their bioaccessibility were analysed using GC/MS. The PAHs concentrations were subsequently used to establish cancer risks in humans via three exposure pathways, namely, accident ingestion of soil, dermal contact soil and inhalation of soil particles. When the $95^{th}$ centile values of total PAH concentrations were used to derive ingestion and dermal cancer risk probabilities on humans, the CDW land use type indicated a moderate potential for cancerous development ($244 \times 10^{-6}$ and $209 \times 10^{-6}$, respectively). Bioaccessible PAHs content in soil samples from CDW ($3.60 \times 10^{-6}$) were also classified as low cancer risk. CDW soil possessed a higher carcinogenic risk based on PAH concentrations. Bioremediation is recommended to treat the contaminated soil.

Keywords: Car dismantling workshop; Open burning; Farm soil; Lifetime cancer risk; Bioaccessible PAHs

# Supplementary data

Table S1 Concentration of 16 individuals PAH (μg/kg) of 12 different soils..

| Sampling site | No. of samples | Naphthalene | | Acenaphthylene | | Acenaphthene | | Fluorene | |
|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| | | Concentration in soils (μg/kg) | | | | | | | |
| Organic farm | 25 | 90.5 ± 81.2a | [10.9 - 258] | 2.7 ± 3.12a | [0.220 - 12.0] | 0.695 ± 0.509a | [0.120 - 1.89] | 4.51 ± 3.63a | [0.340 - 10.9] |
| Agricultural | 100 | 71.4 ± 77.2a | [N.D. - 313] | 3.69 ± 4.06a | [0.190 - 25.8] | 0.653 ± 0.608a | [N.D. - 2.39] | 4.21 ± 4.44a | [N.D. - 20.9] |
| Abandoned agricultural | 55 | 68.3 ± 79.7a | [1.61 - 364] | 2.75 ± 3.12a | [0.0500 - 15.6] | 0.849 ± 0.893a | [0.0900 - 4.25] | 4.57 ± 6.60a | [0.240 - 35.2] |
| E-waste storage | 5 | 68.3 ± 45.2a | [86.3 - 203] | 2.23 ± 0.903a | [1.06 - 3.57] | 1.04 ± 0.591a | [1.690 - 2.09] | 10.5 ± 2.06a | [8.20 - 13.7] |
| Container storage | 5 | 163 ± 95.1a | [88.9 - 317] | 1.92 ± 0.757a | [0.970 - 2.72] | 1.43 ± 0.915a | [0.660 - 2.44] | 10.9 ± 4.06a | [7.42 - 17.5] |
| Metal recycling workshop | 5 | 13.0 ± 4.95a | [4.89 - 17.2] | 9.18 ± 6.87a | [2.43 - 19.9] | 0.72 ± 0.305a | [0.300 - 1.11] | 2.16 ± 0.930a | [1.30 - 3.70] |
| Constructions waste | 15 | 66.8 ± 73.9a | [4.32 - 245] | 2.96 ± 2.22a | [0.480 - 7.97] | 0.965 ± 0.603a | [0.240 - 2.36] | 4.54 ± 3.88a | [0.530 - 12.4] |
| Petrol station | 10 | 7.63 ± 3.60a | [3.54 - 16.1] | 2.54 ± 1.16a | [1.29 - 5.16] | 0.639 ± 0.179a | [0.360 - 0.970] | 1.15 ± 0.420a | [0.340 - 1.77] |
| Open burning site | 10 | 3276 ± 6363b | [395 - 21210] | 560 ± 726b | [N.D. - 2126] | 59.7 ± 54.3b | [9.67 - 173] | 318 ± 317b | [N.D. - 984] |
| E-waste dismantling workshop | 15 | 40.2 ± 19.2a | [15.1- 66.3] | 20.0 ± 19.7a | [0.330- 62.3] | 5.57 ± 5.48a | [0.180- 18.8] | 21.8 ± 22.8a | [0.105- 75.9] |
| E-waste open burning site | 5 | 173 ± 95.6a | [92.4 - 312] | 31.3 ± 22.6a | [11.2 - 70.1] | 6.72 ± 4.64a | [2.79 - 14.8] | 44.4 ± 50.4a | [17.0 - 134] |
| Car dismantling workshop | 25 | 106 ± 70.3a | [21.0 -255] | 25.4 ± 22.1a | [2.85 -69.7] | 10.9 ± 13.2a | [0.640 -61.2] | 18.2 ± 13.5a | [5.08 - 63.4] |
| Sampling site | No. of samples | Phenanthrene | | Anthracene | | Fluoranthene | | Pyrene | |
| Organic farm | 25 | 29.3 ± 15.9a | [4.93 – 56.3] | 1.14 ± 0.980a | [N.D. – 2.49] | 17.4 ± 12.7a | [3.23 – 40.3] | 12.6 ± 11.8a | [3.24 - 46.3] |
| Agricultural | 100 | 24.6 ± 22.3a | [3.45 - 56.3] | 1.21 ± 0.990a | [N.D. - 3.42] | 15.2 ± 12.2a | [3.23 - 49.7] | 10.9 ± 11.2a | [2.16 - 48.5] |
| Abandoned agricultural | 55 | 24.3 ± 28.9a | [1.99 - 101] | 2.53 ± 3.09a | [N.D. - 16.0] | 20.8 ± 20.8a | [2.28 - 140] | 14.1 ± 13.4a | [1.16 - 68.4] |
| E-waste storage | 5 | 46.6 ± 7.87a | [2.07 - 148] | 2.02 ± 3.17a | [N.D. - 17.8] | 16.4 ± 14.8a | [2.32 - 69.8] | 11.2 ± 10.7a | [0.310 - 52.1] |
| Container storage | 5 | 51.1 ± 20.1a | [36.6 - 57.2] | 1.91 ± 1.39a | [0.430 - 3.36] | 24.9 ± 8.00a | [15.9 - 35.3] | 14.6 ± 5.00a | [9.13 - 21.0] |
| Metal recycling workshop | 5 | 35.1 ± 14.7a | [34.0 - 81.6] | 2.93 ± 1.87a | [0.710 - 5.21] | 32.1 ± 16.7a | [14.9 - 52.9] | 17.3 ± 7.75a | [7.69 - 26.3] |
| Constructions waste | 15 | 44.8 ± 55.3a | [17.0 - 55.8] | 8.50 ± 5.14a | [2.70 - 14.9] | 61.0 ± 48.2ab | [18.3 - 121] | 28.0 ± 19.9a | [10.5 - 55.4] |
| Petrol station | 10 | 10.9 ± 2.10a | [4.11 - 229] | 3.18 ± 2.88a | [N.D. - 10.0] | 59.0 ± 101ab | [4.95 - 395] | 27.1 ± 39.2a | [4.02 - 151] |
| Open burning site | 10 | 481 ± 471c | [7.41 - 14.4] | 2.86 ± 0.917a | [1.56 - 4.46] | 18.2 ± 7.06a | [8.70 - 30.4] | 9.84 ± 3.53a | [5.08 - 17.1] |
| E-waste dismantling workshop | 15 | 169 ± 170b | [80.9 - 1747] | 113 ± 143ab | [12.8 - 493] | 398 ± 367d | [25.9 - 1179] | 462 ± 345b | [42.8 - 1283] |
| E-waste open burning site | 5 | 209 ± 224b | [9.17 - 532] | 119 ± 190ab | [N.D. - 664] | 255 ± 273c | [9.66 - 867] | 238 ± 268ab | [8.01 - 948] |
| Car dismantling workshop | 25 | 183 ± 125b | [81.7 - 607] | 38.3 ± 37.2a | [14.9 - 103] | 110 ± 86.0ab | [31.8 - 235] | 64.3 ± 56.7a | [7.56 - 151] |

Table S1 (Con'd) Concentrations of 16 individuals PAHs of 12 different soils.

| Sampling site | No. of samples | Benz(a)anthracene | | Chrysene | | Benzo(b+k)fluoranthene | | Benzo(a)pyrene | |
|---|---|---|---|---|---|---|---|---|---|
| | | Mean | Range | Mean | Range | Mean | Range | Mean | Range |
| | | Concentration in soils (µg/kg) | | | | | | | |
| Organic farm | 25 | 2.97 ± 2.98a | [0.500 - 10.6] | 4.27 ± 3.38a | [0.710 - 12.7] | 2.78 ± 4.76a | [N.D. - 19.5] | 3.20 ± 3.36a | [N.D. - 13.9] |
| Agricultural | 100 | 4.97 ± 4.95a | [0.550 - 19.7] | 8.60 ± 8.46a | [0.810 - 50.9] | 7.97 ± 13.1a | [N.D. - 93.4] | 6.92 ± 7.39a | [N.D. - 26.5] |
| Abandoned agricultural | 55 | 3.79 ± 6.43a | [0.170 - 42.4] | 5.93 ± 8.23a | [0.320 - 44.1] | 3.94 ± 8.45a | [N.D. - 46.6] | 4.99 ± 9.32a | [N.D. - 58.1] |
| E-waste storage | 5 | 3.30 ± 1.37a | [1.67 - 5.29] | 6.45 ± 2.46a | [3.09 - 9.40] | 0.108 ± 0.242a | [N.D. - 0.540] | 4.76 ± 1.70a | [2.77 - 6.60] |
| Container storage | 5 | 4.12 ± 3.22a | [1.53 - 9.26] | 7.81 ± 4.61a | [2.62 - 12.1] | 1.63 ± 2.46a | [N.D. - 5.55] | 5.15 ± 3.59a | [1.85 - 10.5] |
| Metal recycling workshop | 5 | 32.1 ± 24.4a | [10.3 - 61.7] | 42.2 ± 28.3a | [16.1 - 75.9] | 38.0 ± 27.8a | [13.0 - 70.2] | 43.6 ± 32.2a | [15.0 - 83.9] |
| Constructions waste | 15 | 6.70 ± 10.2a | [0.980 - 40.9] | 9.93 ± 10.8a | [1.04 - 42.7] | 12.5 ± 20.9a | [N.D. - 59.7] | 11.0 ± 16.0a | [0.56 - 61.6] |
| Petrol station | 10 | 8.95 ± 5.36a | [2.44 - 19.6] | 13.3 ± 5.83a | [5.41 - 24.1] | 8.84 ± 5.54a | [2.42 - 19.0] | 11.5 ± 7.09a | [2.90 - 27.7] |
| Open burning site | 10 | 177 ± 229c | [6.24 - 785] | 274 ± 265a | [30.0 - 974] | 270 ± 215abc | [57.7 - 807] | 327 ± 173a | [175 -779] |
| E-waste dismantling workshop | 15 | 150 ± 173c | [1.97 - 521] | 186 ± 177a | [16.4 - 532] | 441 ± 494c | [17.9 - 1581] | 202 ± 211a | [5.39 - 695] |
| E-waste open burning site | 5 | 22.1 ± 17.5a | [3.64 - 48.9] | 48.8 ± 35.2a | [3.19 - 84.8] | 83.7 ± 54.2ab | [3.93 -142] | 48.4 ± 31.7a | [2.81 - 89.4] |
| Car dismantling workshop | 25 | 91.1 ± 80.3b | [15.6 - 342] | 852 ± 1886b | [35.2 - 7095] | 316 ± 776bc | [15.3 - 3841] | 4671 ± 16457a | [2.02 - 80546] |
| Sampling site | No. of samples | Indeno(1,2,3-cd)pyrene | | Dibenz(a,h)anthracene | | Benzo(g,h,i)perylene | | | |
| Organic farm | 25 | 4.88 ± 6.23a | [N.D. - 24.4] | 0.747 ± 1.80a | [N.D. - 7.55] | 4.78 ± 5.44a | [N.D. -18.4] | | |
| Agricultural | 100 | 11.1 ± 11.3a | [N.D. - 44.4 ] | 2.36 ± 3.73a | [N.D. - 26.4] | 9.32 ± 9.66a | [N.D. - 42.0] | | |
| Abandoned agricultural | 55 | 8.41 ± 17.8a | [N.D. - 105] | 1.42 ± 3.70a | [N.D. - 24.9] | 7.26 ± 13.5a | [N.D. - 83.5] | | |
| E-waste storage | 5 | 6.05 ± 1.84a | [3.51 - 7.62] | 0.538 ± 0.522a | [N.D. - 1.18] | 7.38 ± 2.13a | [4.46 - 9.45] | | |
| Container storage | 5 | 6.39 ± 3.51a | [2.62 - 10.3] | 1.44 ± 1.13a | [N.D. - 2.81] | 9.98 ± 5.05a | [4.49 - 16.4] | | |
| Metal recycling workshop | 5 | 95.9 ± 62.6ab | [34.9 - 178] | 29.0 ± 18.7a | [10.4 - 52.3] | 65.5 ± 36.4a | [28.6 - 115] | | |
| Constructions waste | 15 | 22.5 ± 42.8a | [1.37 - 171] | 5.33 ± 10.1a | [N.D. - 40.4] | 20.8 ± 28.6a | [2.82 - 105] | | |
| Petrol station | 10 | 23.6 ± 13.6a | [8.33 - 55.6] | 6.12 ± 4.40a | [0.05 - 15.1] | 21.3 ± 11.3a | [9.27 - 43.1] | | |
| Open burning site | 10 | 152 ± 243ab | [N.D. - 807] | 13.4 ± 38.2a | [N.D. - 121] | 124 ± 193ab | [N.D. - 641] | | |
| E-waste dismantling workshop | 15 | 209 ± 236b | [0.410 - 680] | 46.8 ± 49.2a | [N.D. - 149] | 201 ± 225b | [N.D. - 622] | | |
| E-waste open burning site | 5 | 48.1 ± 54.7ab | [N.D. - 134] | 14.3 ± 17.2a | [N.D. - 43.6] | 65.0 ± 58.2a | [N.D. - 153] | | |
| Car dismantling workshop | 25 | 473 ± 534c | [0.920 - 1696] | 171 ± 307b | [1.48 - 1376] | 335 ± 310c | [1.10 - 827] | | |

PAHs concentration followed by the same letter on the same column are not significantly different at the 0.05 probability level according to the Duncan's Multiple Range Test. N.D. = not detected

Table S2 Soil texture and soil organic matter of 12 different soils.

| Sampling sites | Soil texture | SOM % |
|---|---|---|
| Organic farm | Sandy loam (25) | 2.48 ± 0.827 a |
| Agricultural | Sandy loam (71), loamy sand (19) and loam (10) | 2.98 ± 1.66 a |
| Abandoned agricultural | Sandy loam (44) and loamy sand (11) | 4.07 ± 1.90 a |
| E-waste storage | Sandy loam (5) | 2.65 ± 1.35 a |
| Container storage | Loamy sand (5) | 3.73 ± 0.657 a |
| Metal recycling workshop | Sandy loam (5) | 2.24 ± 0.411 a |
| Construction waste | Sandy loam (10) and loamy sand (5) | 3.90 ± 1.70 a |
| Petrol station | Sandy loam (9) and loamy sand (1) | 3.22 ± 0.972 a |
| Open burning site | Sandy loam (8) and loamy sand (2) | 6.11 ± 3.33 b |
| E-waste dismantling workshop | Sandy loam (13) and sand (2) | 8.63 ± 2.42 c |
| E-waste open burning site | Sandy loam (2) and sand (3) | 6.30 ± 1.98 b |
| Car dismantling workshop | Loamy sand (25) | 9.91 ± 2.83 c |

The number in brackets indicates the number of samples belonging to the particular soil type, SOM = soil organic matter and SOM % followed by the same letter on the same column are not significantly different at the 0.05 probability level according to the Duncan's Multiple Range Test.

Table S3 Correlation matrix of PAHs with soil organic matter.

| | Nap | Any | Ane | Fle | Phe | Ant | Fla | Pyr | BaA | Chr | BbkF | BaP | IcdP | DahA | BghiP | Sum of 10 | BaP TEQ | Total PAHs | SOM |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nap | 1 | 0.184* | 0.302* | 0.304* | 0.162* | 0.091 | 0.1 | 0.027 | 0.045 | 0.007 | 0.046 | -0.002 | -0.003 | -0.009 | -0.004 | 0.218* | -0.002 | 0.218* | 0.034 |
| Any | | 1 | 0.843* | 0.924* | 0.600* | 0.409* | 0.485* | 0.135* | 0.284* | 0.053 | 0.101 | 0.005 | 0.084 | 0.008 | 0.115 | 0.091 | 0.007 | 0.135* | 0.082 |
| Ane | | | 1 | 0.947* | 0.818* | 0.553* | 0.657* | 0.301* | 0.429* | 0.138* | 0.197* | 0.053 | 0.248* | 0.173* | 0.278* | 0.189* | 0.058 | 0.239* | 0.268* |
| Fle | | | | 1 | 0.771* | 0.519* | 0.586* | 0.172* | 0.330* | 0.062 | 0.126* | 0.009 | 0.096 | 0.028 | 0.120* | 0.129* | 0.011 | 0.174* | 0.133* |
| Phe | | | | | 1 | 0.768* | 0.821* | 0.401* | 0.591* | 0.206* | 0.343* | 0.093 | 0.408* | 0.295* | 0.439* | 0.227* | 0.102 | 0.276* | 0.402* |
| Ant | | | | | | 1 | 0.756* | 0.198* | 0.576* | 0.108 | 0.373* | 0.019 | 0.330* | 0.167* | 0.497* | 0.137* | 0.026 | 0.166* | 0.336* |
| Fla | | | | | | | 1 | 0.283* | 0.838* | 0.177* | 0.459* | 0.041 | 0.426* | 0.199* | 0.622* | 0.183* | 0.05 | 0.218* | 0.422* |
| Pyr | | | | | | | | 1 | 0.514* | 0.509* | 0.468* | 0.362* | 0.721* | 0.934* | 0.405* | 0.430* | 0.381* | 0.500* | 0.470* |
| BaA | | | | | | | | | 1 | 0.250* | 0.538* | 0.084 | 0.608* | 0.432* | 0.714* | 0.217* | 0.098 | 0.261* | 0.499* |
| Chr | | | | | | | | | | 1 | 0.802* | 0.845* | 0.776* | 0.589* | 0.339* | 0.871* | 0.850* | 0.877* | 0.356* |
| BbkF | | | | | | | | | | | 1 | 0.836* | 0.745* | 0.563* | 0.559* | 0.881* | 0.842* | 0.886* | 0.405* |
| BaP | | | | | | | | | | | | 1 | 0.596* | 0.516* | 0.279* | 0.964* | 1.000* | 0.953* | 0.220* |
| IcdP | | | | | | | | | | | | | 1 | 0.784* | 0.739* | 0.676* | 0.610* | 0.711* | 0.588* |
| DahA | | | | | | | | | | | | | | 1 | 0.543* | 0.560* | 0.534* | 0.615* | 0.482* |
| BghiP | | | | | | | | | | | | | | | 1 | 0.372* | 0.292* | 0.397* | 0.575* |
| Sum of 10 | | | | | | | | | | | | | | | | 1 | 0.966* | 0.996* | 0.302* |
| BaP TEQ | | | | | | | | | | | | | | | | | 1 | 0.956* | 0.232* |
| Total PAHs | | | | | | | | | | | | | | | | | | 1 | 0.333* |
| SOM | | | | | | | | | | | | | | | | | | | 1 |

Sum of 10 PAHs = sum of Nap, Phe, Ant, Fla, BaA, Chr, BbkF, BaP, IcdP and BghiP, BaP TEQs = seven carcinogenic PAHs (BaP, BaA, BbF, BkF, Chr, DahA IcdP toxic equivalent concentration to BaP), SOM = soil organic matter and values with * correlation is significant at the 0.05 level (2-tailed) (Pearson correlation coefficients), SOM = soil organic matter and N = 275

Table S4 Percentage of bioaccessible carcinogenic PAHs fractions to total PAHs of 12 different soils.

| Sampling sites | Percentage of bioaccessible carciogenic PAHs fractions to total PAHs | | | | | | |
|---|---|---|---|---|---|---|---|
| | BaA | Chr | BbkF | BaP | IcdP | DahA | BghiP |
| Organic farm | 5.45 | 3.60 | 3.26 | 10.10 | 0.72 | 0.17 | 0.37 |
| Agricultural | 5.43 | 6.53 | 1.22 | 2.08 | 1.21 | 0.22 | 0.52 |
| Abandoned agricultural | 5.69 | 2.96 | 2.21 | 3.39 | 1.69 | 0.30 | 0.76 |
| E-waste storage | 8.86 | 5.39 | 4.32 | 4.99 | 2.04 | 0.77 | 1.43 |
| Container storage | 4.85 | 1.81 | 0.92 | 3.69 | 2.03 | 0.65 | 0.75 |
| Metal recycling workshop | 7.41 | 2.04 | 1.89 | 3.54 | 1.32 | 0.23 | 0.38 |
| Construction waste | 10.06 | 5.71 | 0.24 | 1.15 | 1.70 | 0.46 | 0.63 |
| Petrol station | 9.62 | 6.85 | 2.39 | 1.61 | 2.24 | 1.28 | 0.49 |
| Open burning site | 1.86 | 4.84 | 3.08 | 1.72 | 2.55 | 0.15 | 0.82 |
| E-waste dismantling workshop | 3.19 | 3.36 | 1.80 | 2.83 | 1.58 | 0.77 | 0.49 |
| E-waste open burning site | 6.57 | 5.36 | 2.30 | 3.96 | 1.68 | 1.88 | 0.94 |
| Car dismantling workshop | 2.98 | 3.42 | 3.23 | 4.74 | 0.98 | 1.32 | 2.07 |