# Supplementary Material

# Distribution, Sources, and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Agricultural and Dumpsite Soils in Sierra Leone

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Materials and methods

**Text S1**: Study area description

The Republic of Sierra Leone is divided into four Provinces (Southern Province, Northern Province, North-western Province, and Eastern Province), and two Western areas (western urban and western rural) and the provinces are divided into 14 districts which are further divided into 149 chiefdoms. The capital city is Freetown which is 27 meters above sea level. Freetown is situated on the coastline along the Peninsula Mountain extending into the Atlantic Ocean. Freetown is divided into western urban and western rural with a tropical climate.

Kingtom and Waterloo dumpsites are surrounded by residential areas and local agricultural farmland. Kingtom is the most densely populated and traffic congested area in Freetown. Waterloo is a rural community in the east about 30 kilometers from Freetown, which has also increased in size and population in recent years caused by overpopulation in Freetown. These are the two major dumpsites in the western areas, and they are enclosed by local farmers, wood-burning ovens (bakeries), street vendors, and stores. Households and public garbage, such as plastics, automobiles, and tires, is deposited unlawfully in dumpsites in a chaotic manner. As a result, during the dry season, when there is little or no rainfall, waste burning is common; Bonganema is in the southern province, Njala University residential area; Magburaka is in the northern province near agricultural soils along the Rokel River. Kabala, Makeni, and Sinikoro soil samples were all collected around local farmers and agricultural soil areas. In comparison Kingtom and Waterloo, the other cities appear to be less populated see Table S1.

**Text S2**: Chemical Analysis, Analytical Procedures, and Sample Preparation

The soil samples were tested for the following 16 USEPA priority PAHs: Acenaphthene (Ace), Benzo(ghi)perylene (BghiP), Anthracene (Ant), Acenaphthylene (Acy), Benzo(a)anthracene (BaA), Benzo(b)Fluoranthene (BbF), Chrysene (Chr), Dibenzo (a, h) anthracene (DahA), Benzo(k)Fluoranthene (BkF), Fluorene (Flo), Fluoranthene (Fluo), Indeno(1,2,3-cd) Pyrene (IcdP), Benzo(a)Pyrene (BaP), Naphthalene (Nap), Pyrene (Pyr) and Phenanthrene (Phe). Analytical procedures and sample preparation methods in this research were comparable to those mentioned by [5,11,33–35]. A solution of mixture recovery surrogates (Nap-$d_8$, Ace-$d_{10}$, Phe-$d_{10}$, Chr-$d_{12}$, and Perylene-$d_{12}$. 1000 ng of each) was spiked to ca. 10 g of the soil sample and Soxhlet extracted with 150 mL of dichloromethane (DCM) for 24 hrs. During the Soxhlet extraction, copper flacks were added to the solvent in the collection flask to get rid of elemental sulfur in soil samples. After replacing the solvent with n-hexane, the volume of each concentrated sample extract was reduced to 2-3 mL using a rotary evaporator (Heidolph-4000, Germany) before further purification. The extract was loaded onto an alumina-silica gel column (v: v = 2:1) column and rinsed with 30 mL of DCM/n-hexane (v:v = 2:3). A mild nitrogen stream (purity ≥ 99.999%) was subsequently used to reduce the effluent to ca. 0.2 mL. Before the PAHs instrumental analysis, 1000 ng of hexamethylbenzene was added to the eluate as the internal standard. A gas chromatography-mass spectrometry (GC–MS, Agilent 6890N GC–5975 MSD) installed with a DB-5 capillary column was utilized in the analysis of the soil samples for the 16 PAHs. The PAH standard reagents with concentrations of 200, 150, 100, 50, 20, and 10 μg $L^{-1}$ n-hexane solutions were used to build a six-point calibration curve with an internal standard. One

microlitre of each final sample was introduced into GC-MS and the carrier gas was helium (purity ≥ 99.999%) set as constant flow at 1.2 mL $min^{-1}$. The GC oven temperature was set initially at 80ºC (for 2 mins) and then increased to 290ºC at a rate of 4ºC $min^{-1}$ for 25 mins. The mass spectrometry was run in SCAN mode varied from (50-500 m/z) with 70eV Electronic Impact (EI) source, and the temperatures of the EI source and quadruple were 230ºC and 150ºC respectively. The target compounds were recognized by the GC retention time and characteristic ions and quantitated according to the characteristic ions.

**Results**

**Table S1.** Population density and environmental surroundings of the study area

| Sampling sites | Sample ID | Main areas | Population | The environmental surrounding of the study area |
|---|---|---|---|---|
| Kingtom dumpsite | KT | Freetown | 1,955,964 | Landfill, Settlements, Wetland – floodplain. Agriculture |
| Waterloo dumpsite | WL | Freetown | 666,270 | Landfill, Settlements, Thicket, Herbaceous savanna, Agriculture in shallows, and recession. |
| Makeni | MK | Northern Province | 154,970 | Settlements, Herbaceous savanna, Mangrove. Agriculture |
| Magburaka | MB | Northern Province | 42,300 | Savanna, Settlements, Rokel river, Woodland, Gallery. Forest and riparian forest, Mangrove. Agriculture. |
| Kabala | KB | Northern Province | 20,970 | Agriculture, Mangrove, Savanna. |
| Sinikoro | SN | Northern Province | 4,222 | Savanna, Settlements, Mangrove, Woodland, Agriculture, Rocky land in NNE. |
| Bonganema | BG | Southern province | 318,555 | Savanna, Gallery Forest, riparian forest, Water bodies, Mangrove, Agriculture. |

Sierra Leone population density as of 2015 census

**Table S1a.** Relationship between ∑16PAHs concentration and total population

| | ∑16PAHs concentration | Total population |
|---|---|---|
| ∑16PAHs concentration | 1 | 0.953 |
| Total population | 0.953 | 1 |
| A 2-tailed test of significance is used | | |
| *: Correlation is significant at $p < 0.05$ | | |

Spearman's correlation at $p < 0.05$.

**Table S2.** Comparison of worldwide ΣPAH mean concentrations (ng/g dw) in topsoil from selected cities in Sierra Leone

| Research areas (cities) | Main areas | Average | ∑PAHs range in soils (ng/g) | Authors |
|---|---|---|---|---|
| Kingtom (Freetown) | Western urban | 1142.37 | 697.84− 1,749.90 | This research |
| Waterloo (Freetown) | Western rural | 265.12 | 168.3−389.34 | This research |
| Bonganema | Southern province | 54.30 | 42.42−64.31 | This research |
| Magburaka | Northern province | 79.69 | 24.90−123.50 | This research |
| Kabala | Northern province | 54.11 | 25.82−81.42 | This research |
| Makeni | Northern province | 36.55 | 24.1−49.0 | This research |
| Sinikoro | Northern province | 52.34 | 45.54−59.14 | This research |
| Central China | Dajiuhu | 42.4 | 7.3–191.5 | (Xing et al., 2020) |
| Shenyang, China | Urban areas | 2370 | 283−21821 | (Luo et al., 2020) |
| Hong Kong, China | Rural areas | 57.6 | 42.3–410 | (Zhang et al., 2006) |
| Beijing, China | Urban areas | 3917 | 219–27,825 | (Tang et al., 2005) |
| Southern Italy | Caserata provincial territory | 137 | 10−4191 | (Qi et al., 2019) |
| Southern Italy | Urban areas | 84.9 | 7.6–755 | (Thiombane et al., 2019) |
| Turin, Italy | Urban areas | 857 | 148–3,410 | (Morillo et al., 2007) |
| Southern Italy | Rural areas | 333 | 1.87–11,353 | (Thiombane et al., 2019) |
| Moscow, Russia | Urban areas | 1553.9 | 208–9,604 | (Agapkina et al., 2007) |
| Glasgow, UK | Urban areas | 11930 | 48–51,822 | (Morillo et al., 2007) |
| London, UK | Urban areas | 18000 | 400–67,000 | (Vane et al., 2014) |
| Seville, Spain | Urban areas | 807.5 | 89.5–4,004 | (Morillo et al., 2008) |
| Delhi, India | Rural areas | 1910 | 830–3,880 | (Agarwal et al., 2009) |
| Delhi, India | Urban areas | 6838.6 | 81.6–45,017 | (Kumar et al., 2012) |
| Ghana, Kumasi | Kumasi | 442.5 | 14.8-2084 | (Bortey-Sam et al., 2014) |

Total mean concentration in dry weight = ΣPAH (ng/g dw)

**Table S3**. PAHs-ring percentage (%) composition, mean (ng/g dw), and range (ng/g dw) distribution in the topsoil (0–20 cm )profile

| | Kingtom | | | Waterloo | | | Bonganema | | | Magburaka | | | Makeni | | | Kabala | | | Sinikoro | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PAHs-rings** | **Percentage** | **Mean** | **Range** | **Percentage** | **Range** | **Mean** | **Percentage** | **Mean** | **Range** | **Percentage** | **Mean** | **Range** | **Percentage** | **Mean** | **Range** | **Percentage** | **Mean** | **Range** | **Percentage** | **Mean** | **Range** |
| 2-ring | 16.54 | 188.98 | 75.46–268.52 | 25.59 | 35.04–113.46 | 67.83 | 45.49 | 24.41 | 21.11–27.68 | 48.58 | 36.07 | 9.73–62.40 | 53 | 19.25 | 8.75–29.75 | 56.56 | 30.33 | 10.55–50.11 | 57 | 29.83 | 27.54–32.13 |
| 3-ring | 13.04 | 148.91 | 113.97–176.24 | 16.07 | 31.56–49.18 | 42.60 | 34.99 | 1878 | 14.89–20.94 | 16.46 | 12.22 | 10.50–13.93 | 31.24 | 11.34 | 10.05–12.64 | 27.42 | 14.70 | 5.80–20.60 | 25.61 | 13.41 | 11.24–15.57 |
| 4-ring | 30.48 | 348.17 | 219.16–540.77 | 34.74 | 61.80–136.28 | 92.11 | 17.25 | 9.26 | 6.06–11.64 | 18.07 | 13.42 | 3.46–23.37 | 13.54 | 4.62 | 0.80–5.48 | 11.41 | 4.24 | 0.49–12.23 | 13.32 | 5.48 | 2.49–13.95 |
| 5-ring | 29.62 | 338.43 | 221.71–567.80 | 18.07 | 31.69–64.60 | 47.91 | 1.77 | 0.95 | 0.29–1.72 | 12.95 | 9.61 | 1.10–18.13 | 1.53 | 0.55 | 0.21–0.71 | 4.03 | 1.92 | 1.15–4.32 | 2.91 | 1.13 | 0.35–3.05 |
| 6-ring | 10.32 | 117.88 | 70.35–196.07 | 5.53 | 11.34–17.19 | 14.67 | 0.51 | 0.27 | 0.27–0.28 | 3.95 | 2.93 | 0.83–5.03 | 0.69 | 0.25 | 0.06–0.45 | 0.58 | 0.21 | 0.00–0.62 | 1.15 | 0.56 | 0.28–1.21 |

**Tale S4** Spearman's correlation coefficients (r) amongst soil properties and PAHs concentration

| | 2-ring PAHs | 3-ring PAHs | 4-ring PAHs | 5-ring PAHs | 6-ring PAHs | LMWPAHs | HMWPAHs | ∑7PAHs | ∑16PAHs | pH | Silt | Sand | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-ring PAHs | 1 | | | | | | | | | | | | |
| 3-ring PAHs | 0.82 | 1 | | | | | | | | | | | |
| 4-ring PAHs | 0.82 | **0.91** | 1 | | | | | | | | | | |
| 5-ring PAHs | 0.78 | 0.72 | 0.84 | 1 | | | | | | | | | |
| 6-ring PAHs | 0.72 | 0.65 | 0.77 | **0.88** | 1 | | | | | | | | |
| LMWPAHs | **0.97** | **0.90** | **0.89** | 0.76 | 0.74 | 1 | | | | | | | |
| HMWPAHs | 0.79 | 0.87 | **0.99** | **0.90** | 0.81 | **0.86** | 1 | | | | | | |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ∑7PAHs | 0.71 | 0.63 | **0.77** | **0.92** | **0.95** | 0.71 | 0.82 | 1 | | | | | |
| ∑16PAHs | **0.94** | **0.94** | **0.95** | 0.83 | **0.75** | **0.97** | **0.93** | 0.75 | 1 | | | | |
| pH | 0.62 | 0.61 | **0.60** | **0.71** | **0.74** | 0.60 | 0.63 | **0.76** | 0.63 | 1 | | | |
| Silt | -0.32 | -0.46 | -0.50 | -0.59 | -0.70 | -0.39 | -0.55 | **-0.69** | -0.47 | -0.40 | 1 | | |
| Sand | 0.24 | 0.38 | 0.41 | **0.55** | **0.67** | 0.29 | 0.47 | **0.67** | 0.38 | 0.45 | **-0.98** | 1 | |
| Clay | -0.29 | -0.44 | -0.42 | **-0.55** | **-0.65** | -0.32 | -0.47 | **-0.65** | -0.41 | -0.56 | **0.91** | **-0.95** | 1 |

Note: Highest Significance levels at $p < 0.05$* and $p < 0.01$** are indicated in bold italics.

**Table S5**. Soil physico-chemical properties range and geometric mean distribution in the soil profile

| Soil properties | Kingtom | Gmean | Waterloo | Gmean | Bonganema | Gmean | Magburaka | Gmean | Makeni | Gmean | Sinikoro | Gmean | Kabala | Gmean |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Clay content | 12.7–17.2 | 14.9 | 6.4–12.1 | 8.5 | 22.8–39.3 | 30.2 | 17.3.–26.8 | 21.5 | 13.8–31.9 | 21.0 | 8.5.–28.6 | 15.6 | 27.2–36.1 | 31.4 |
| Silt content | 24.3–26.4 | 26.3 | 11.6–20.6 | 15.7 | 36.0–44.5 | 40.7 | 41.1–43.7 | 42.3 | 16.8–38.5 | 25.4 | 22.4–55.3 | 35.2 | 42.0–49.5 | 45.6 |
| Sand content | 55.7–63.0 | 58.5 | 67.3–81.9 | 74.8 | 16.2–41.1 | 26.3 | 29.6–41.7 | 35.1 | 29.7–69.4 | 45.4 | 15.1–69.1 | 33.3 | 14.4–30.8 | 21.0 |
| pH levels | 7.8–8.0 | 7.9 | 5.1–6.6 | 5.6 | 5.2–5.8 | 5.6 | 5.5–6.0 | 5.7 | 6.3–6.8 | 6.6 | 6.3–6.3 | 6.3 | 6.3–6.8 | 6.6 |

Geometric mean=Gmean

**Table S6.** Comparison of Toxicity equivalent quantity $TEQ_{BaP}$ mean values in the soil profile from selected cities in Sierra Leone

| Research areas | Name of regions | *TEQBaP* mean values (ng/g) | References |
|---|---|---|---|
| Kingtom, Freetown | Western urban | 153.6 | This research |
| Waterloo, Freetown | Western rural | 24.9 | This research |
| Bonganema | Southern province | 1.08 | This research |
| Magburaka | Northern Province | 6.67 | This research |
| Kabala | Northern Province | 1.45 | This research |
| Makeni | Northern Province | 0.33 | This research |
| Sinikoro | Northern Province | 1.13 | This research |
| Campania | Rural | 661 | (Thiombane et al., 2019) |

| | | | |
|---|---|---|---|
| Delhi (India) | Urban | 218 | (Agarwal et al., 2006) |
| United Kingdom | Rural | 83.5 | (Nam et al., 2008) |
| Campania | Urban | 54.9 | (Thiombane et al., 2019) |
| Tarragonain (Spain) | Urban | 64 | (Nadal et al., 2007) |
| Gwangju (Korea) | Urban | 14.3 | (Islam et al., 2017) |
| Norway | Rural | 14.3 | (Nam et al., 2008) |
| Poland | Agricultural soil | 11.9 | (Maliszewska-Kordybach et al., 2009) |

Toxicity equivalent quantity =$TEQ_{BaP}$

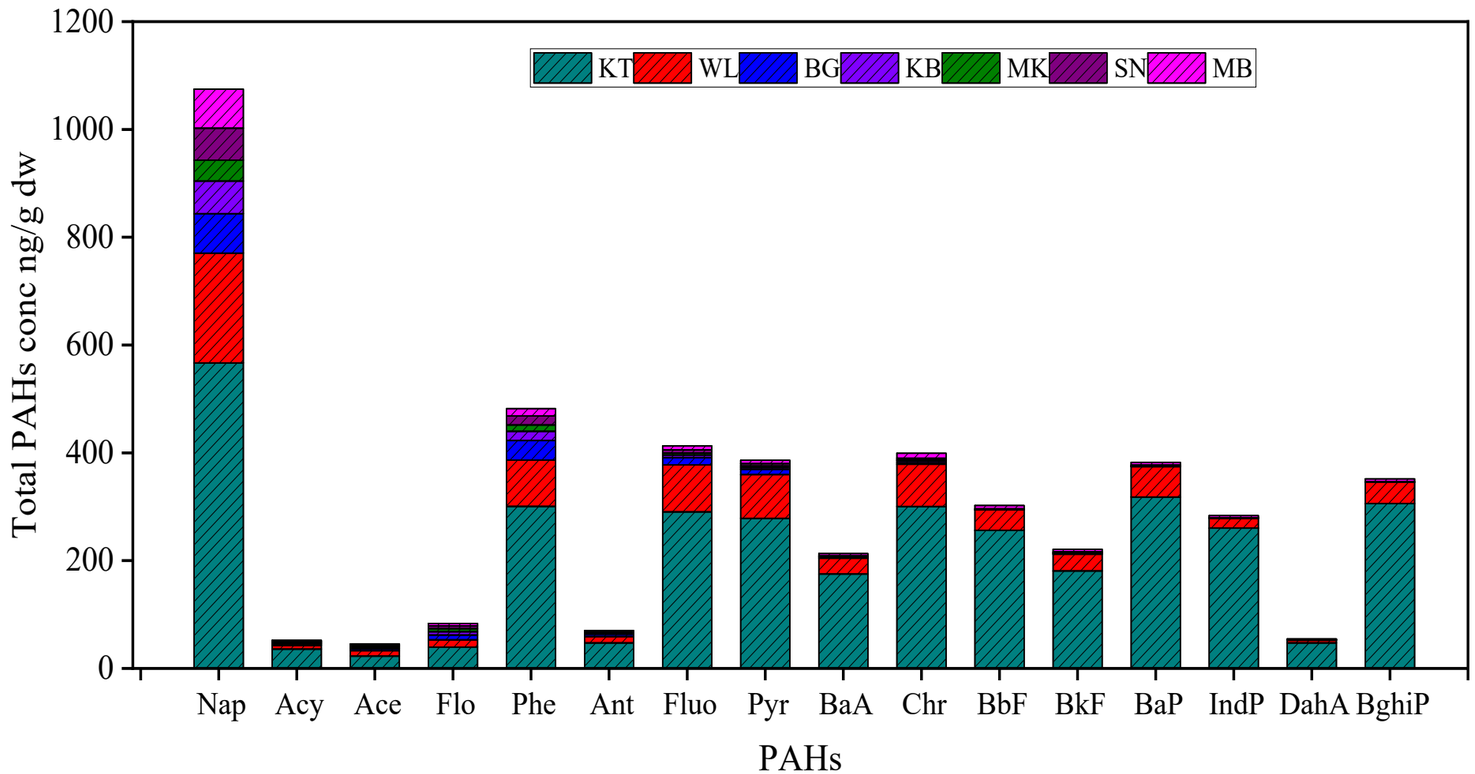

**Figure S1** Total individual PAHs concentration distribution in KT, Kingtom; WL, Waterloo; BG, Bonganema; KB, Kabala; MK, Makeni; SN, Sinikoro, and MB, Magburaka

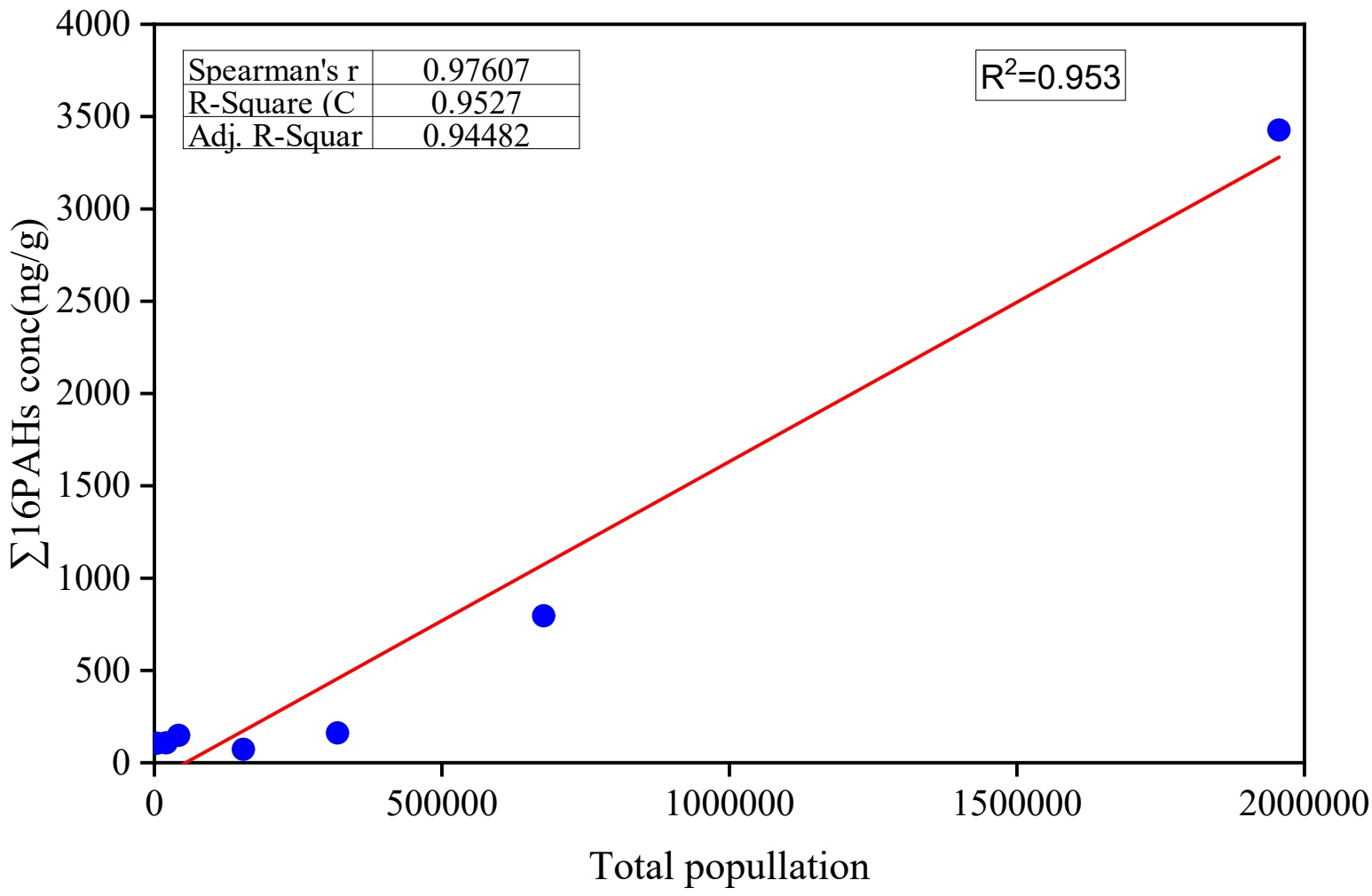


**Figure S2** The relationship between the sum of total PAHs concentration and the total population in each studied area

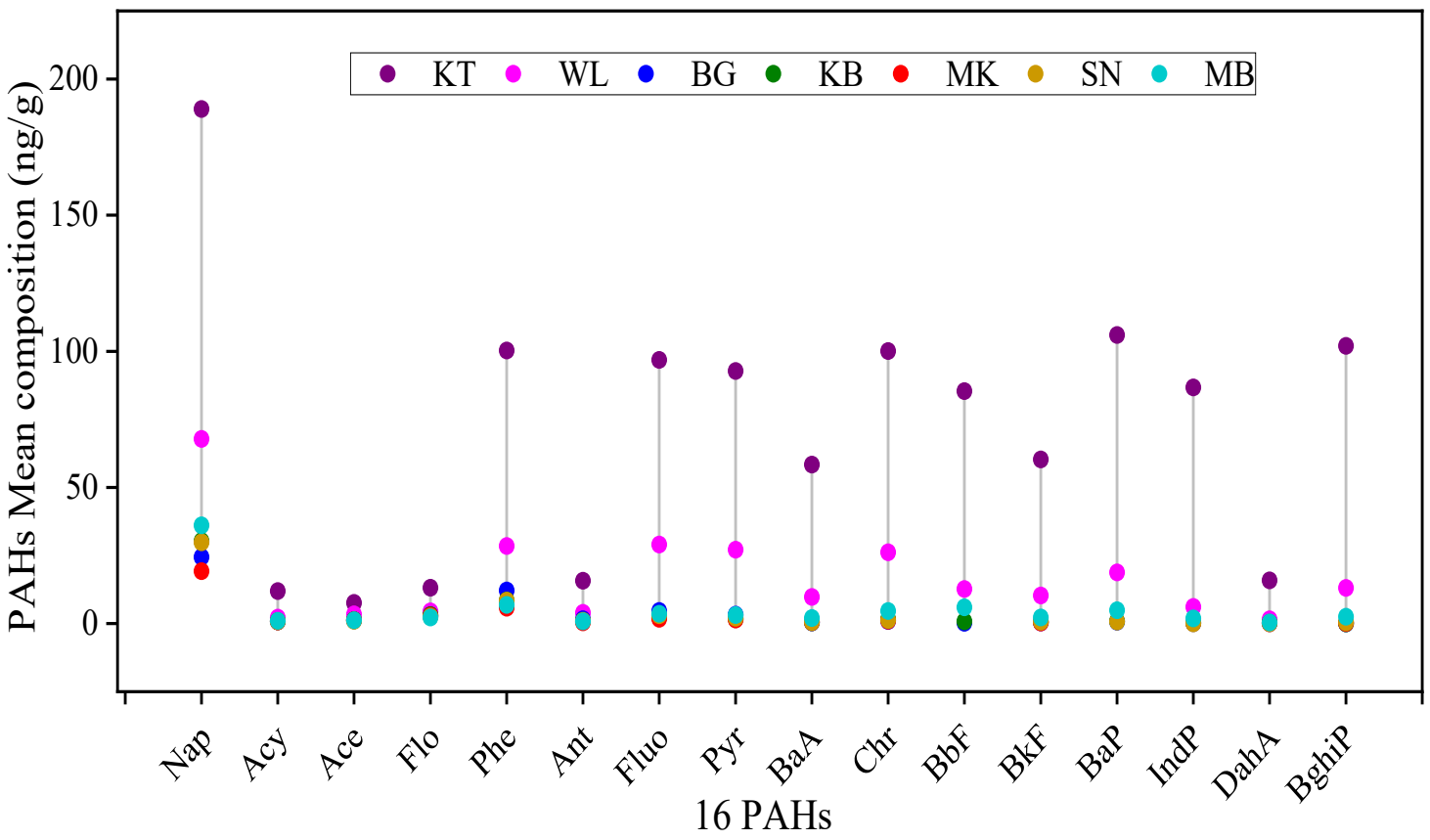


**Figure S3** PAHs mean concentration and distribution in Kingtom; KT, Waterloo; WL, Bonganema; BG, Kabala; KB, Makeni; MK, Sinikoro; SN, and Magburaka; MB

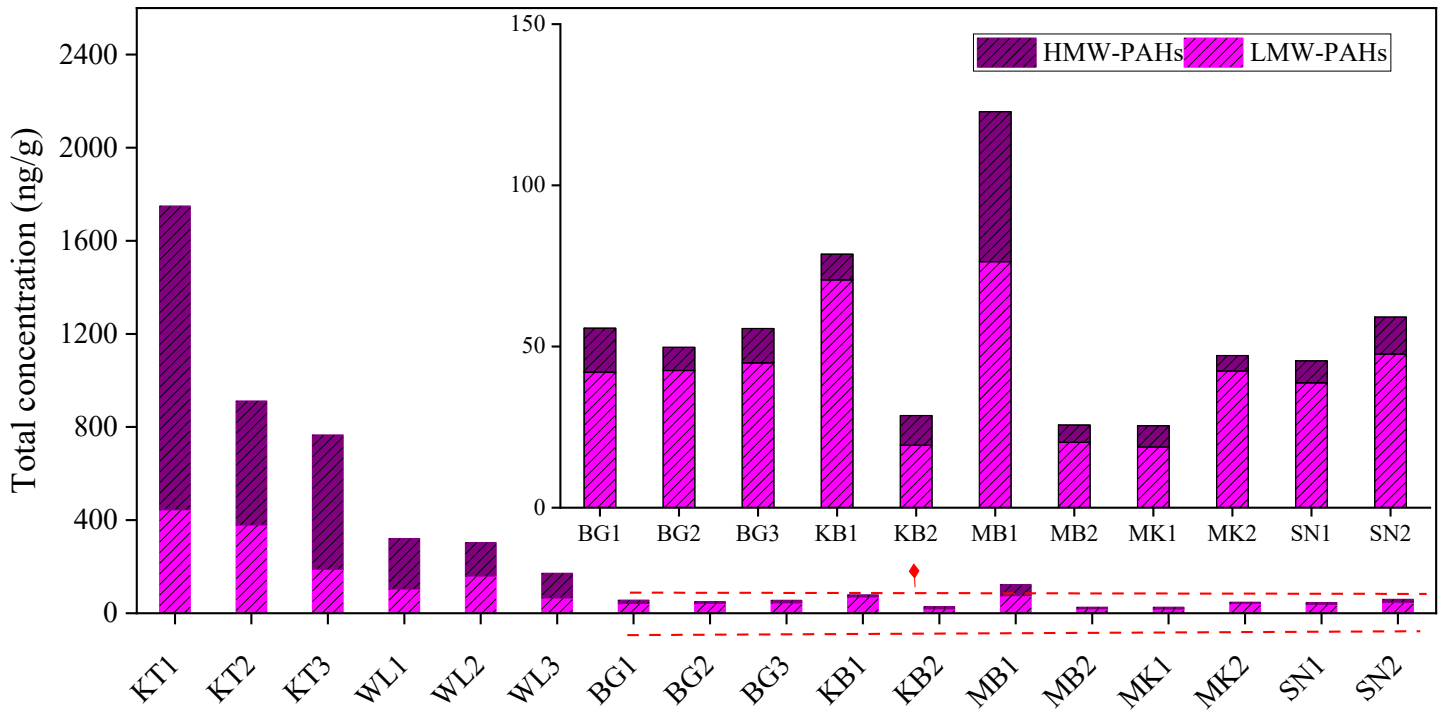


**Figure S4** LMW-PAHs and HMW-PAHs concentrations (ng/g dw) in topsoil of the study area

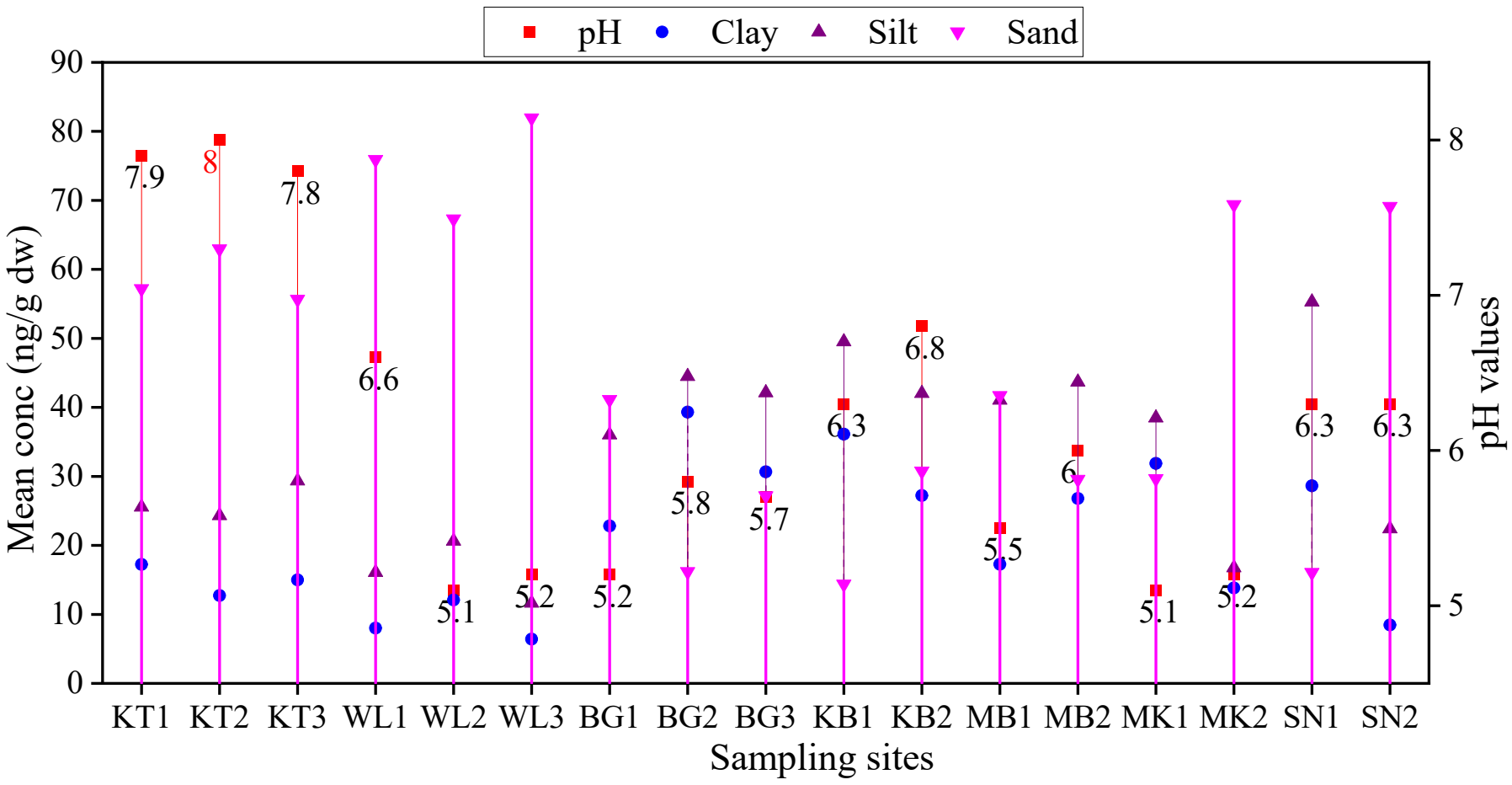


**Figure S5** Soil pH and particle-sizes distribution in the soil profile

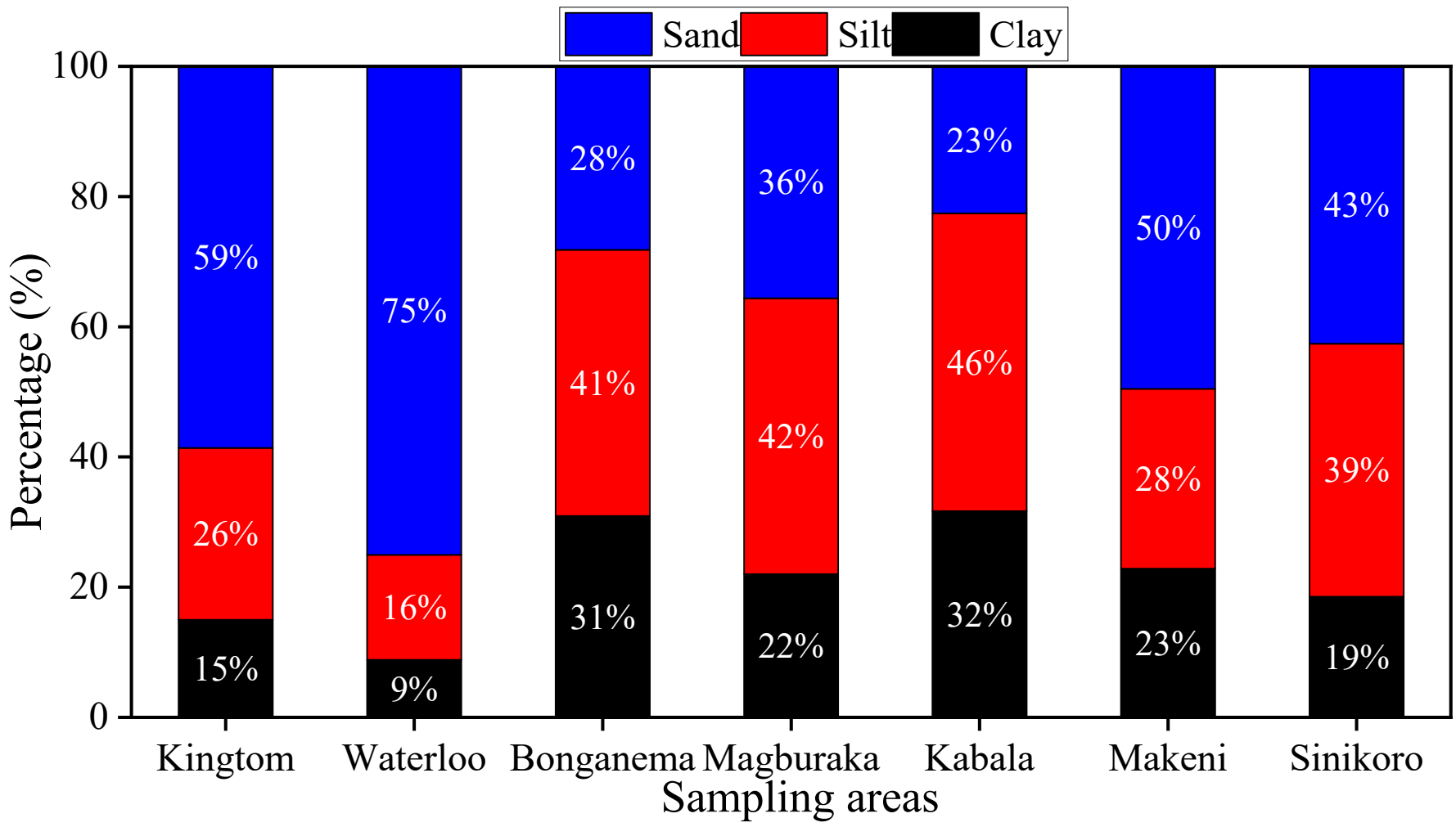


**Figure S6** Soil particle-sizes percentage composition and distribution in the soil profile