Title	Occurrence, distribution, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in surface soils from the Kumasi Metropolis, Ghana
Author(s)	Bortey-Sam, Nesta; Ikenaka, Yoshinori; Nakayama, Shouta M. M.; Akoto, Osei; Yohannes, Yared Beyene; Baidoo, Elvis; Mizukawa, Hazuki; Ishizuka, Mayumi
Citation	Science of The Total Environment, 496, 471-478 https://doi.org/10.1016/j.scitotenv.2014.07.071
Issue Date	2014-10-15
Doc URL	http://hdl.handle.net/2115/57346
Type	article (author version)
File Information	Sci Total Env v.496 p.471-478.pdf

[Instructions for use](#)

Occurrence, distribution, sources and toxic potential of polycyclic aromatic hydrocarbons (PAHs) in surface soils from the Kumasi metropolis, Ghana

Nesta Bortey-Sam ^a, Yoshinori Ikenaka ^a, Shouta M.M. Nakayama ^a, Osei Akoto ^b, Yared Beyene Yohannes ^a, Elvis Baidoo ^b, Hazuki Mizukawa ^a, Mayumi Ishizuka ^{a*}

^aLaboratory of Toxicology, Department of Environmental Veterinary Sciences, Graduate School of Veterinary Medicine, Hokkaido University, Kita 18, Nishi 9, Kita-ku, Sapporo 060-0818, Japan

^bDepartment of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

* Corresponding author: Mayumi ISHIZUKA, e-mail: ishizum@vetmed.hokudai.ac.jp

Laboratory of Toxicology, Department of Environmental Veterinary Sciences, Graduate School of Veterinary Medicine, Hokkaido University, N18, W9, Kita-ku, Sapporo 060-0818, Japan

Tel: +81-11-706-6949; Fax: +81-11-706-5105

Abstract

As a developing country, the economic and population growth rates in Ghana over the past few years have seen tremendous increase. The growing rate of industrialization is gradually leading to contamination and deterioration of the environment and pollution is likely to reach disturbing levels. Surface soil samples were collected randomly from 36 communities in the Kumasi metropolis, Ghana, to determine the concentrations, distribution, sources and toxic potential of emission of polycyclic aromatic hydrocarbons (PAHs) since no such comprehensive study has been conducted. The mean concentration of total PAHs in the surface soils in each community ranged from 14.78 at Ahinsan to 2084 ng/g dry weight at Adum with an average of 442.5 ± 527.2 ng/g dry weight. Diagnostic ratios and chemical mass balance models of the results showed that PAHs in surface soil samples from the study area were mainly from fuel combustion. Carcinogenic potency of PAHs load from the city centre was approximately 150 times higher as compared to a pristine site, Kwame Nkrumah University of Science and Technology's Botanical Garden. BaP, a human carcinogen, contributed 70% of the total PAHs toxicity level from the city centre of Kumasi.

Keywords: Surface soil; Kumasi; PAHs; Chemical Mass Balance; Diagnostic ratio

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants and produced primarily as a result of oil spillage and/or incomplete combustion of organic materials including wood, fossil fuels and petroleum products (Ravindra et al., 2008). Many PAHs are mutagenic and some are carcinogenic and these raise concerns over their occurrence in the environment (Flowers et al., 2002; Thorsen et al., 2004; Cornelissen et al., 2006). Due to their high hydrophobic properties, PAHs can be sorbed on atmospheric particles and thus transported over a long distance, being a source of diffuse pollution (Wilcke, 2007; Ravindra et al., 2008). Point sources of pollution are usually derived from industrial activities, transport, industrial waste waters, road run offs and accidental fuel spills (Johnsen and Karlson, 2007).

Soil system is considered the most important long-term repository for PAHs and is also considered to be a steady indicator of the environmental pollution state (Nam et al., 2003; Mueller and Shann, 2006). PAHs in soils may further accumulate in vegetables and other biota via food chains (Li et al., 2008). This accumulation leads to direct or indirect exposure to humans. Moreover, leaching of PAHs from soils are possible sources of groundwater contamination (Bispo et al., 1999; Cousins et al., 1999). Therefore, knowledge of soil contamination with PAHs is needed to avoid any food production risk and to restrict the deleterious effect of these contaminants. Many studies have been conducted on the concentrations and distributions of PAHs in soils in some countries (Wilcke, 2000; Wang et al., 2010; Essumang et al., 2011; Marusenko et al., 2011). However, no comprehensive work has been done to address the accumulation and distribution of PAHs in surface soils in the Kumasi metropolis, Ghana.

As a developing country, the economic and population growth rates in Ghana over the past few years have seen tremendous increase. Currently, the Gross Domestic Product (GDP) and annual population growth rates of Ghana stand at 6.1% and 2.5% respectively (Ghana Statistical Service, 2013). The growing rate of industrialization is gradually leading to contamination and deterioration of the environment and pollution is likely to reach disturbing levels. Studies have shown that industrialization and pollution are positively correlated (Walsh, 2000; Olaifa et al, 2004).

Kumasi (a metropolis of Ghana) is one of the most industrialized and economically significant cities and has been subjected to heavy anthropogenic influences as a result of the rapid economic development and urbanization. The human population has drastically increased, number of cars has doubled during the past decade and many gas stations are located in this region leading to greater fuel combustion rate. These could lead to more fuel leakages, smoke production from exhaust of automobiles and high levels of PAHs in the environment. In addition garbage, paper, cloth, wood are burnt in open environment in the Kumasi metropolis and all these are potential sources of contamination with PAHs (Ravindra et al., 2008). Domestic emissions of PAHs are from the use of traditional fuels such as charcoal (i.e. using coke ovens to convert wood into charcoal) and crop residues for cooking, water heating etc.

The objectives of the study were therefore: to determine the concentrations of 22 PAHs including the 16 that are listed by the United States Environmental Protection Agency (USEPA) as priority pollutants in surface soil samples from the Kumasi Metropolis; to identify the possible sources of PAHs in surface soils from the Kumasi metropolis; to develop distribution maps of PAHs throughout the city using Geographic Information System (GIS) and; to evaluate the extent of pollution and toxic potential of PAHs in soils from Kumasi.

2. Methodology

2.1. Sample collection

Soil samples were randomly collected from 36 communities in the Kumasi metropolis in May 2011. Global positioning system (GPS) was used to locate the sampling positions. Soil samples were also collected from a pristine site, i.e. Kwame Nkrumah University of Science & Technology (KNUST) Botanical Gardens and was used for comparison Fig. 1. A total of 129 soil samples (0–10 cm top layer) were collected using a stainless steel scoop and stored in labeled corning tubes (Corning Incorporated, New York, USA). The soil samples obtained were stored at –20 °C in the Department of Chemistry, KNUST, Ghana and later transported to the Laboratory of Toxicology, Graduate School of Veterinary Medicine, Hokkaido University, Japan where they were stored at –30 °C before analysis. A map showing the sampling area is presented in Fig. 1.

Prior to chemical analysis, soil samples were air dried at room temperature and passed through a 2 mm sieve to remove the coarse soil fraction. Soil organic carbon is an important controlling factor for adsorption of PAHs to soil (Wang et al., 2013). As soil organic carbon indicator a gravimetric method by ignition loss was estimated. Loss on ignition (LOI) was determined at oven temperature of 600 °C for 5 h, and data is shown in Table 1.

2.2. Sample extraction and clean-up

For PAHs analysis, 10 g of soil sample were weighed into extraction thimble and covered completely with glass wool after spiking with of 25 µL of 1 mg/L PAH surrogate standards

(acenaphthene_ d_{10} , phenanthrene_ d_{10} , chrysene_ d_{12} , and perylene_ d_{12}). Extraction of PAHs from soil samples was done by soxhlet extractor (Soxtherm Gerhardt Variostat; Soxtherm V7.5, Germany) using 170 mL acetone/hexane (1:2; v/v) for 6 h. The extracts were dehydrated by filtering through anhydrous sodium sulphate (Kanto Chemical Co., Inc, Tokyo, Japan). The dehydrated extracts were collected into a round bottom flask. It was then concentrated to approximately 1.5 mL on a rotary evaporator and transferred into a test tube. The dehydrated extract in the test tube was further concentrated to 0.3 mL under a gentle N₂ stream. The extracts were cleaned-up to remove other contaminants such as lipids and pigments that may have been extracted with PAHs. Clean-up was done using column (40 cm) packed with 5% water content silica gel (Kanto Chemical Co., Inc, Tokyo, Japan). It was then eluted with 100 mL of diethyl ether/hexane mixture (1:4; v/v). The eluate was further concentrated to 2 mL using a rotary evaporator. 300 μ L of n-decane was added to the extract and further concentrated to 0.3 mL using a gentle N₂ stream. All solvents used (Kanto Chemical Co., Inc, Tokyo, Japan) were of analytical grade.

2.3. PAHs analysis

PAHs analyses were carried out using Auto Sampler 3000 Gas Chromatograph (Focus GC) coupled with a Thermo scientific Mass Selective Detector (DSQ II MS, Kanagawa, Japan) operating in the electron impact mode (GC-MS). The selective ion monitoring mode was used for quantification. A FactorFour capillary column, VF-Xms, 30 m, 0.25 mm inner diameter, 0.25 μ m film thickness (Varian Inc., Lake Forest, CA, USA) was used for separation. Helium gas was used as the carrier gas at a constant flow rate of 1.2 mL/min. Injector and mass transfer line temperatures were 260 °C and 280 °C, respectively. Temperature programming for the column was as follows, initial temperature of 90 °C held for 1 min, ramped to 280 °C at 10 °C/min and

finally to 320 °C at a ramp rate of 5 °C/min and held for 10 min. 1 µL sample was injected in the splitless mode for analysis. Concentrations of total PAHs and that of 22 individual PAHs (AccuStandard, New Haven, USA) including 16 USEPA priority pollutants (naphthalene (Nap), acenaphthylene (Acl) acenaphthene (Ace), , fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DBahA), benzo[g,h,i]perylene (BghiP), perylene (Peryl), benzo[e]pyrene (BeP), triphenylene (Tri), methylene phenanthrene (Methy-Phe), 1-methyl phenanthrene (Me-Phe) and retene (Ret)) were measured in each sample. Difficulties were often associated with the GC separation of Chr and Tri; BbF and BkF, for this reason, the sum of these isomers was used as an abbreviation, Chr and BbF + BkF respectively. All results were expressed in dry weight (dw) basis.

2.4. Quality control

Quantitation was performed using internal standard calibration method (five-point calibration; 10, 50, 100, 200 and 400 µg/L), and correlation coefficients (r^2) for the calibration curves were all greater than 0.995. Analytical methods were checked for precision and accuracy. Limits of detection (LODs) were calculated based on $3SD/S$ (SD is the standard deviation of the response of seven replicate standard solution measurements and S is the slope of the calibration graph). LODs of PAHs were in the range of 0.04–0.54 ng/g dw. Four surrogate standards were added to soil samples to quantify procedural recoveries. Surrogate recoveries (acenaphthene_ d_{10} , phenanthrene_ d_{10} , chrysene_ d_{12} , and perylene_ d_{12}) in spiked soil samples ranged from 86–99%. The final PAH concentrations were not corrected from the recoveries of the surrogate standards. For each batch of 10 samples, a method blank (solvent), a spiked blank (surrogate standards

spiked into solvent), a matrix spike (surrogate standards spiked into pre-extracted soil), and duplicate sample were analyzed. The average recoveries in ten spiked blanks and matrix spikes varied from 85–102% for PAHs (22 components). Blanks that were run periodically contained no detectable amount of target analyte. The coefficients of variation of PAHs concentration in duplicates were less than 15%.

2.5. Data analysis

Data analysis was performed using IBM SPSS v 20 for windows (SPSS Inc., Illinois, USA). Kurtosis, skewness (Z value = skewness/standard error) and Kolmogorov–Smirnov (K–S) tests were used to determine the normality of data and were considered statistically significant if p value was less than 0.05 and Z value was greater than 1.96. Spearman and Pearson's correlations were also used to evaluate the relationships between LOI, individual and total PAHs concentrations, and was considered statistically significant if p value was less than 0.05. The source diagnostic indices were calculated from the PAHs concentration ratios. Diagnostic ratio plots were done using JMP 9 (SAS Institute, Cary, NC, USA). Spatial distribution of PAHs in soil was performed by using Arc–GIS 9.3 software (ESRI, New York).

3. Results and discussion

3.1. Concentrations of total PAHs in surface soils from the Kumasi Metropolis

The mean concentrations of total PAHs in soil samples from 36 communities in the Kumasi metropolis ranged from 14.78 at Ahinsan to 2084 ng/g dw at Adum (Table 1), with mean value 442.5 ± 527.2 ng/g dw. Kurtosis, skewness and K–S tests for normality showed a significant variation in the concentrations of PAHs in surface soils from the communities for all the

measured analytes (Z value > 1.96 ; $p < 0.0001$). Table 1 shows the mean concentrations of total PAHs from the sampling communities in Kumasi.

The component of PAHs which is typically of greatest interest in terms of potential cancer hazard is BaP. This compound had been known to exhibit a high carcinogenic activity in animals and has been listed as a proven human carcinogen (WHO, 2000). BaP concentration in the soils recorded a percentage abundance of 8% and it was the 6th most abundant PAH determined in surface soils from the study area (Table 1). The mean concentrations of BaP in soil samples from the communities ranged from 0.5939 ± 0.3284 (Ahinsan) to 259.5 ± 38.37 ng/g dw (Adum) (Table 1). However, the mean value of BaP throughout the 36 communities was 32.59 ± 51.90 ng/g dw. Kurtosis and K–S normality tests indicated a significant variation in the distribution of BaP through the communities ($p < 0.0001$). Table 1 shows the mean concentrations of BaP in surface soils from the communities in Kumasi.

In this study, the LOI contents among 129 soil samples ranged from 1.584–22.59%, with a mean value of $4.826 \pm 2.810\%$. The results of correlation tests before and after log transformation among individual, total PAHs and LOI showed that all individual and total PAHs were not significantly correlated with LOI ($p > 0.05$), (data not shown). This could be due to the result of non–equilibrium adsorption between LOI and PAHs. Another likely reason for lack of correlation between LOI and PAHs may be that urban soils have different sources of PAHs and soil pH values (Wang et al., 2013).

3.2. Distribution maps for carcinogenic PAH and sum of 16 USEPA PAHs in surface soil of the Kumasi metropolis

PAHs concentrations spread throughout the communities with the highest concentrations exhibited from the city centre. GIS coordinates and concentrations of PAHs in surface soils

obtained from Kumasi were used to create the distribution maps. The distribution maps in Fig. 2, showed higher levels of BaP and sum of 16 USEPA priority pollutants from the city centre of Kumasi, and this could be due to the high or heavy vehicular load, congestion and combustion rate within the region. The distributions maps of some carcinogenic PAHs (BaA, BbF, BkF, DBahA, Chr and IcdP) (IARC, 2006) in surface soils are shown in Fig. 2. In the surface soils from Kumasi, Flu recorded the highest PAH concentration followed by its isomeric Pyr, interestingly these two showed the same distribution pattern ($p < 0.0001$) with extremely high concentrations at Suame, Mbrom, Adum, Suntreso, Romanhill and Sofoline. From Table 1, Suame exhibited the highest for both Flu and Pyr at concentrations of 381.3 ± 54.57 and 355.1 ± 49.42 ng/g dw respectively. The distribution map for BaA is not too different from the 2 mentioned above, since very high concentrations were also recorded at the same sampling communities as Flu and Pyr (Table 1). The distributions of BbF + BkF, BeP and BaP with same molecular weight were nearly identical and higher concentrations were recorded in Romanhill and Adum. This trend is observed for all PAH of similar molecular weight, and critical observation has shown that PAHs of the same molecular weight have similar distributions (Venkataraman and Friedlander, 1994).

3.3. Source identification

3.3.1. Diagnostic ratio charts

Diagnostic ratio is a widely used technique to apportion the origin of PAHs presented in different environmental media (Yunker et al., 2002; Bucheli et al., 2004). The ratios of different PAHs are expected to vary with sources most likely due to various routes of PAH formation under different combustion conditions. This method is probably more pronounced at extreme locations such as urban areas close to the point sources (Christensen and Bzdusek, 2005).

Diagnostic ratios of PAHs, such as ratios of BaP/BghiP, IcdP/(IcdP + BghiP), and Ant/(Phe + Ant), Flu/(Flu + Pyr), can be applied to identify the possible sources of PAHs (Yunker et al., 2002). Although the use of diagnostic ratios has been criticized by a variety of authors and notwithstanding the known uncertainties, it was used in this paper only as an indicative way to give insight about sources (Katsoyiannis et al., 2007; Galerneau, 2008; Katsoyiannis et al., 2011; Katsoyiannis and Breivik, 2014).

IcdP/(IcdP + BghiP) ratios ranged from 0.01 to 1.00 in surface soil samples from the Kumasi metropolis. Accordingly to literature (Mark et al., 2002), IcdP/(IcdP + BghiP) ratios between 0.20 and 0.50 imply fuel combustion sources (vehicle and crude oil). The results from this study suggested that most of the PAHs identified in surface soil in the study area originated from fuel combustion processes and in particular from vehicular traffic and non-traffic (Fig. 3a). Vehicles as the major source of PAHs found confirmation with BaP/BghiP ratios which was significantly over 0.6 suggesting traffic origins for those contaminants, which originated from fuel combustion. Fig. 3a indicated that 74% of PAHs identified in surface soils from the Kumasi metropolis by the IcdP/(IcdP + BghiP) ratios were between 0.20 and 0.50 and were therefore coming from fuel combustion. IcdP/(IcdP + BghiP) ratios greater than 0.50 representing 23% were coming from coal, wood or grass combustion and 3% (that is IcdP/(IcdP + BghiP) ratios less than 0.20) were from petroleum sources.

The ratio of Ant/(Ant + Phe) ranged from 0.00–1.00, Flu/(Flu + Pyr) from 0.01–0.64 (Fig. 3b). The Ant/(Ant + Phe) ratios between 0.00 and 0.10 imply petroleum sources, on the other hand if the ratio is between 0.1 and 2.5, then the source is known to be from combustion (Yunker et al., 2002). From Fig. 3b, Ant/(Ant + Phe) showed that more than 90% of PAHs in surface soils from the Kumasi metropolis were from combustion sources with about 66% originating from fuel

combustion and 30% from coal/wood or grass combustion, Fig. 3b, Flu/(Flu + Pyr). This observation is consistent with the conclusion drawn from the assessment of BaP/BghiP and IcdP/(IcdP + BghiP) given above.

3.3.2. Chemical mass balance (CMB) model

CMB model (version 8) was also applied for source identification per each (sampled) community and the source profiles used were classified as either coal related (power plant, residential or coke oven) or traffic related (gasoline engine, diesel engine or traffic tunnel). CMB is one of the widely used techniques for the determination of PAHs sources. The basic idea of the CMB model is that the measured chemical pollutants in a sample are the sums of the contributions from several sources (Li et al., 2001; Wang et al., 2010). However, only relative compound concentrations in a source or a sample profile (e.g., normalized with BeP, or any other PAH compound) are important (Christensen et al., 1999). Difficulties were often associated with the GC separation of BbF and BkF. For this reason, the sum of these two isomers was used with an abbreviation BbF + BkF. Fig. 4 shows the source profiles used in this study. In general, the contributions appeared similar in most cases. Fuel contributions from diesel and gasoline engines were dominant from the most polluted sites in the Kumasi metropolis of Ghana. In Adum, the largest apportioned contributor was gasoline engine recording 42%, 25% from diesel engines and 33% of the total PAHs sources was from coke oven. From Romanhill, the CMB data showed that 81% of the PAHs sources were from fuel combustion, and gasoline engines accounted for 39% of the total and the rest was from diesel engines (42%). Also in Mbrom, the source of PAHs was attributed to fuel combustion. This accounted for 72% of the sources and diesel engines was

dominant with 46% of the total. From Fig. 4, 70% of PAHs in the surface soils from Suame was from diesel (36%) and gasoline (34%) engines. There was no difference in source contributions from Suntreso as 84% of the total contribution was attributed to gasoline engines. The overall CMB results clearly showed that gasoline and diesel engines were the two major sources of PAHs in soil samples from the most contaminated communities in the Kumasi metropolis. These results are in agreement with the known PAH sources at this location. That is, PAHs input in the Kumasi metropolis was significantly influenced by fuel combustion (diesel and gasoline engines) as was also indicated by the diagnostic ratio methods.

3.4. Kumasi Soil Toxicity Assessment

Maliszewska–Kordybach (1996) has classified pollution levels of PAHs in soils into 4 categories based on the 16 USEPA priority pollutants, namely unpolluted (< 200 ng/g), weakly polluted (200–600 ng/g), polluted (600–1000 ng/g) and severely polluted (> 1000 ng/g). By this classification, 51% of soil samples from the communities in this study were considered unpolluted with PAHs (< 200 ng/g). The least polluted community was Ahinsan. About 30% of the communities had their soils weakly polluted with PAHs while 5% of the communities in the study area were polluted with PAHs. The severely polluted communities representing 14% of the communities were Adum, Mbrom, Suame, Romanhill and Suntreso (Table 1). The mean concentrations of total PAHs (16 USEPA PAHs) recorded from the severely polluted communities were 1708 (Adum), 1441 (Mbrom), 1435 (Suame), 1379 (Romanhill) and 1045 ng/g dw (Suntreso) respectively. The high levels of PAHs in soil samples from these communities (Table 2; Fig. 4) could come from the high vehicular traffic and the high human population who may use firewood or charcoal for domestic heating. The high concentrations of total PAHs in the surface soils from these severely polluted communities could pose high

environmental and human health risks (Ping et al., 2007). The study indicated that in these communities (Adum, Romanhill, Mbrom, Suame and Suntreso), PAHs compounds including the human carcinogenic compounds (BaA, BbF, BkF, BaP, DBahA, Chr and IcdP) (IARC, 2006) were high (Table. 2).

Health risk assessment of carcinogenic PAHs cannot be related only to overall concentration. Rather, each PAH has a different carcinogenic potential. Health risk assessment associated with PAHs uptake is often estimated on the basis of the BaP concentrations. BaP is the highest carcinogenic contributor in almost every study (Halek et al., 2008). The development and establishment of a toxicity equivalency factors (TEFs) are used in the assessment of mixtures containing PAHs. The TEFs were used to quantify the carcinogenic potential of other PAHs relative to BaP and to estimate benzo[a]pyrene–equivalent concentration (BaPeq) (Nadal et al., 2004). The list of TEFs (Table 3) compiled by Tsai et al. (2004) was adopted to calculate BaPeq. Therefore, the carcinogenic potencies of individual PAHs has to be considered by multiplying their concentration with the appropriate TEF.

The Toxicity Equivalent Concentrations (TEQ's) which are the sum of average BaPeq concentration in soil, $TEQ = \sum(C \times TEF)$, from KNUST Botanical Gardens and 5 most polluted communities were 1.245 BaPeq ng/g and 188.2 BaPeq ng/g respectively (Table 3). This implies that carcinogenic potency of PAHs load in these 5 severely polluted communities were higher (approximately 150 times higher than from KNUST Botanical Garden) and BaP contributed 70% of the total toxicity level.

4. Conclusions

The concentrations of total PAHs in surface soils from 36 communities in the Kumasi metropolis ranged from 14.87–2084 ng/g dw, and levels found in the city centre were higher than

those in the other sampling points. The most abundant PAHs in surface soils were Flu (61.70 ± 86.85 ng/g dw), followed by its isomeric Pyr (57.94 ± 78.68 ng/g dw). The highest concentration of BaP (Group 1 carcinogen) in surface soils from the Kumasi metropolis was recorded in Adum (259.5 ± 38.37 ng/g dw). CMB and diagnostic ratio methods were used to identify the sources of PAHs in soil samples and results demonstrated that 74% of PAHs identified in surface soils in the Kumasi metropolis were from fuel combustion processes. Distribution maps indicated that PAHs spread throughout the Kumasi metropolis and the city centre was the most polluted. The carcinogenic potency of PAHs load in the 5 severely polluted communities was approximately 150 times higher than from KNUST Botanical Garden and BaP contributed 70% of the total toxicity level.

Acknowledgements

This study was supported by Grants-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan awarded to M. Ishizuka and Y. Ikenaka as well as the Research Fellowship from the Japan Society for the Promotion of Science grant-in-aid awarded to S. Nakayama, and the foundation of JSPS Core to Core Program (AA Science Platforms).

References

- Bispo A, Jourdain MJ, Jauzein M. Toxicity and genotoxicity of industrial soils polluted by polycyclic aromatic hydrocarbons (PAHs). *Org Geochem* 1999;30:947–52.
- Bostrom CE, Gerde P, Hanberg A, Jernstrom B, Johanson C, Kyrklund T, et al., Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ Health Perspect* 2002;110:451–89.
- Bucheli TD, Blum F, Desaulles A, Gustafsson O. Polycyclic Aromatic Hydrocarbons, black carbon and molecular markers in soils of Switzerland. *Chemosphere* 2004;56:1061–76.
- Christensen ER, Bzdusek PA. PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis. *Water Res* 2005;39:511–24.
- Christensen ER, Rachdawong P, Karls JF, Van Camp RP. PAHs in sediments: Unmixing and CMB modeling of sources. *J Environ Eng* 1999;125:1022–32.
- Cornelissen G, Breedveld GD, Kalaitzidis S, Christanis K, Kibsgaard A, Oen AMP. Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. *Environ Sci Technol* 2006;40:1197–1203.
- Cousins IT, Beck AJ, Jones KC. A review of the processes involved in the exchange of semi-volatile organic compounds (SVOC) across the air–soil interface. *Sci Total Environ* 1999;228:5–24.
- Essumang DK, Kowalski K, Sogaard EG. Levels, distribution and source characterization of polycyclic aromatic hydrocarbons (PAHs) in topsoils and roadside soils in Esbjerg, Denmark. *Bull Environ Contam Toxicol* 2011;86:438–43.
- Flowers L, Rieth SH, Coglian VJ, Foureman GL, Hertzberg R, Hofmann EL, Murphy DL, Nesnow S, Schoeny RS. Health assessment of polycyclic aromatic hydrocarbon mixture: current practices and future directions. *Polycycl Aromat Compd* 2002;22:811–21.
- Galerneau E. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. *Atmos Environ* 2008;42:8139–49.
- Ghana Statistical Service, 2013.
http://www.statsghana.gov.gh/docfiles/2010phc/National_Analytical_Report.pdf
http://www.statsghana.gov.gh/docfiles/GDP/2nd_quarter_gdp_2013_newsletter.pdf
[assessed in November 2013].
- Halek F, Nabi G, Kavousi A. Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Teheran, Iran. *Environ Monit Assess* 2008;143:303–11.

- IARC. Monograph on the Evaluation of Cancer Risks to Humans. Volume 92. Polycyclic aromatic hydrocarbons. Lyon, France: IARC Press; 2006.
- Johnsen A, Karlson U. Diffuse PAH contamination of surface soils: environmental occurrence, bioavailability and microbial degradation. *Appl Microbiol Biot* 2007;76:533–43.
- Katsoyiannis A, Breivik K. Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. *Environ Pollut* 2014;184:488–94.
- Katsoyiannis A, Sweetman AJ, Jones KC. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ Sci Technol* 2011;45:8897–906.
- Katsoyiannis A, Terzi E, Cai Q-Y. On the use of PAH molecular diagnostic ratios in sewage sludge for understanding of PAH sources. Is this use appropriate? *Chemosphere* 2007;69:1337–9.
- Li K, Christensen ER, Van Camp RP, Imamoglu I. PAHs in dated sediments of Ashtabula River, Ohio, USA. *Environ Sci Technol* 2001;35:2896–902.
- Li YT, Li FB, Chen JJ, Yang GY, Wan HF, Zhang TB, Zeng XD, Liu JM. The concentrations, distribution and sources of PAHs in agricultural soils and vegetables from Shunde, Guangdong, China. *Environ Monit Assess* 2008;139:61–76.
- Maliszewska-Kordybach B. Polycyclic aromatic hydrocarbons in agricultural soil in Poland, preliminary proposals for criteria to evaluate the level of soil contamination. *Appl Geochem* 1996;11:121–7.
- Mark BY, Robie WM, Roxanne V, Reginald HM, Darcy G, Stephanie S. PAHs in the Fraser river basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 2002;33:489–515.
- Marusenko Y, Herckes P, Hall SJ. Distribution of polycyclic aromatic hydrocarbons in soils of an arid urban ecosystem. *Water Air Soil Pollut* 2011;219:473–87.
- Mueller KE and Shann JR. Polycyclic aromatic hydrocarbons in spiked soil: impacts of bioavailability, microbial activity and trees. *Chemosphere* 2006;64:1006–14.
- Nadal M, Schuhmacher M, Domingo JL. Levels of PAHs in soil and vegetation samples from Tarragona Country, Spain. *Environ Pollut* 2004;132:1–11.
- Nam JJ, Song BH, Eom KC, Lee SH, Smith A. Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea. *Chemosphere* 2003;50:1281–9.
- Olaifa FG, Olaifa AK, Onwude TE. Lethal and Sub lethal effects of copper to the African cat fish (*Clarias gariepinus*). *African J Biomed Res* 2004;7: 65–70.
- Ping LF, Luo YM, Zhang HB, Li QB, Wu LH. Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environ Pollut* 2007;147:358–65.
- Ravindra K, Sokhi R, Van Grieken R. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 2008;42:2895–921.
- Straif K, Baan R, Grosse Y, Secretan B, El Ghissassi F, Coglianò V. WHO International Agency for Research on Cancer Monograph Working Group, Carcinogenicity of polycyclic aromatic hydrocarbons. *Lancet Oncol* 2005;6:931–2.
- Thorsen WA, Cope WG, Shea D. Bioavailability of PAHs: effects of soot carbon and PAH source. *Environ Sci Technol* 2004;38:2029–37.

- Tsai PJ, Shih TS, Chen HL, Lee WJ, Lai CH, Liou SH. Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmos Environ* 2004;38:333–43.
- Venkataraman C, Friedlander SK. Source resolution of fine particulate polycyclic aromatic hydrocarbons in a receptor model modified for reactivity. *Environ Sci Technol* 1994;28:563–72.
- Walsh CJ. Urban Impacts on the ecology of receiving water: a frame work for assessment, Conservation and restoration. *Hydrobiologia* 2000;431:107–11.
- Wang WT, Simonich SM, Xue M, Zhao JY, Zhang N, Wang R, et al. Concentrations, sources and spatial distribution of polycyclic aromatic hydrocarbons in soils from Beijing, Tianjin and surrounding areas, North China. *Environ Pollut* 2010;158:1245–51.
- Wang XT, Miao Y, Zhang Y, Li YC, Wu MH, Yu G. Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: occurrence, source apportionment and potential human health risk. *Sci Total Environ* 2013;447:80–9.
- Wang Z, Chen JW, Tian FL, Yang P, Qiao XL, Yao ZW. Application of factor analysis with nonnegative constraints for source apportionment of soil polycyclic aromatic hydrocarbons (PAHs) in Liaoning, China. *Environ Forensics* 2010;11:161–7.
- WHO, Regional Office for Europe Air Quality Guidelines for Europe (Second Edition): Polycyclic aromatic hydrocarbons. Copenhagen, WHO Regional Publications. European Series 2000;91:92–6.
- Wilcke W. Global patterns of polycyclic aromatic hydro carbons (PAHs) in Soil. *Geoderma* 2007;141:157–66.
- Wilcke W. Polycyclic aromatic hydrocarbons (PAHs) in soil-a review. *J Plant Nutr Soil Sci* 2000;163:229–48.
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. PAH in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition *Org Geochem* 2002;33:489–515.

Figure caption:

Fig. 1. Map showing the sampling areas within the Kumasi sub-metro.

Fig. 2. Distribution of IARC carcinogenic PAHs and $\sum_{16}$ USEPA PAHs in surface soil from the Kumasi metropolis.

Fig. 3a. Diagnostic ratio charts for BaP/BghiP and IcdP/(IcdP + BghiP) in soil samples.

Fig. 3b. Diagnostic ratio charts for Ant/(Phe + Ant) and Flu/(Flu + Pyr) in soil samples.

Fig. 4. Chemical mass balance model for sources of PAHs in surface soils from the severely polluted communities in the Kumasi metropolis.

14 **Table 1**

15 Mean concentration of PAHs in surface soils from the sampling communities in Kumasi (ng/g dw).

sample site	LOI	Nap	Acl	Ace	Fle	Phe	Ant	Methy -Phe	Me-Phe	Flu	Pyr	Retene	BaA	Chr	BbF +BkF	BeP	BaP	Peryl	DBahA	IcdP	BghiP	Σ_{22} PAH
Ayigya	4.1	nd	0.19	nd	0.34	2.0	0.27	0.27	0.10	3.4	2.7	0.78	1.3	0.93	1.7	1.5	1.2	0.40	0.38	1.0	1.0	19
Bomso	3.1	1.4	0.41	0.10	0.35	2.1	0.45	0.25	0.72	1.6	1.6	0.76	0.61	0.89	1.2	2.1	0.83	0.38	0.61	1.4	3.8	21
Susuanso	2.8	5.3	1.5	0.13	0.95	7.8	1.9	0.65	0.95	5.3	6.1	2.0	2.7	2.9	3.2	7.4	3.7	1.2	1.6	6.1	13	75
Oforikrom	7.4	7.9	2.7	0.35	1.5	24	5.4	3.2	2.1	35	30	2.8	12	8.2	10	9.4	7.9	1.8	0.66	7.5	7.8	182
Afunkwanta	3.2	6.4	1.9	0.10	0.86	7.1	1.1	1.1	1.0	15	16	2.8	7.7	5.8	10	12	8.9	3.2	1.4	12	16	133
Amakom	3.4	6.3	4.2	0.14	1.2	12	2.1	0.92	0.88	36	27	2.6	7.7	6.9	9.9	12	8.2	2.5	0.88	9.5	16	169
Asafo	3.3	10	2.3	0.39	1.2	15	4.5	5.7	3.8	58	48	3.2	14	5.3	20	17	17	5.1	1.8	19	26	280
Romanhill	5.5	13	9.7	3.9	5.5	95	15	15	10	188	179	25	148	80	161	159	156	57	16	148	156	1647
Central market	5.9	15	2.5	0.44	2.5	14	3.1	4.5	2.3	31	22	32	18	9.3	19	21	15	5.8	2.8	17	28	271
Kejetia	7.8	nd	2.5	0.80	2.1	17	4.6	4.6	2.2	56	45	19	34	19	42	46	39	14	6.1	55	52	465
Adum	7.5	16	21	1.5	3.1	55	25	9.0	4.1	230	212	4.9	102	60	298	276	259	81	18	188	214	2084
Asawasi	3.9	3.9	3.7	0.68	2.0	22	4.2	4.2	2.2	73	56	5.1	43	24	51	45	45	15	4.9	39	42	491
Manhyia	4.1	3.9	5.1	1.2	1.5	25	6.8	6.8	2.1	90	70	4.3	66	34	71	61	71	24	8.9	56	55	668
Ashtown	5.5	5.1	3.4	0.39	1.0	14	4.3	2.8	1.7	57	51	3.1	46	22	50	46	51	18	6.6	43	45	476
Mbrom	4.3	5.4	12	25	11	143	39	35	13	280	250	7.2	206	100	91	85	102	37	10	80	80	1620
Racecourse	6.2	1.9	2.8	1.7	8.8	63	10	25	25	38	75	26	10	10	10	12	7.0	2.8	1.8	17	30	384
Bantama	3.2	nd	0.87	0.10	1.1	5.9	1.0	0.89	0.76	10	8.9	2.0	4.0	3.1	5.4	6.4	3.9	1.3	0.74	5.6	6.8	69
Aboabo	5.3	4.0	1.4	0.17	1.2	11	4.7	1.3	3.0	10	21	20	3.7	5.0	4.2	8.0	2.8	1.1	0.14	4.0	4.5	114
Dichemso	4.1	8.1	0.66	0.10	0.87	4.9	0.63	0.64	0.71	6.7	6.3	2.2	3.1	2.3	5.2	5.9	4.6	1.7	0.68	5.3	7.2	68
Yennyawoso	4.3	nd	0.39	0.10	0.92	5.1	1.0	1.2	1.2	5.6	6.8	2.2	2.1	1.6	3.2	4.2	2.4	0.8	0.30	3.3	5.8	48
Krofrom	5.2	12	2.2	0.96	2.5	20	5.8	3.8	5.0	30	30	8.7	12	8.9	16	16	14	4.5	1.1	13	16	227
Suame	4.6	9.3	7.1	7.1	5.6	208	25	10	9.3	381	355	10	107	62	57	51	52	13	9.6	48	82	1515
Anomangye	2.7	6.6	1.5	0.21	2.8	19	1.5	1.5	5.6	30	34	11	5.6	9.4	9.7	15	4.4	3.6	1.1	7.0	23	195
New Suame	4.5	2.1	0.47	0.10	0.78	4.5	0.62	0.64	0.53	5.9	4.6	3.9	2.5	2.1	3.9	3.6	2.5	0.93	0.35	1.9	0.20	42
Tafo	4.4	11	1.1	0.30	1.8	16	3.1	2.2	3.1	31	31	18	7.6	6.8	4.6	5.7	5.8	2.4	0.84	7.7	17	180

Tafo Nhyiaeso	5.5	7.0	1.7	0.24	1.6	12.9	3.7	6.8	8.9	11	37	11	6.8	6.2	8.0	9.2	5.6	0.66	0.31	3.7	5.6	149
Ahinsan	4.8	0.74	0.22	0.10	0.25	0.90	0.29	0.11	0.10	3.1	3.0	0.25	0.60	0.49	0.92	0.95	0.59	0.24	0.27	0.56	1.1	14
Atonsuo	3.9	nd	0.83	0.10	0.57	3.7	0.52	0.52	0.37	3.9	3.6	2.2	1.2	1.2	2.0	1.9	1.3	0.36	0.18	1.2	1.5	27
Kaasi	4.4	9.6	2.2	0.43	0.92	9.6	2.5	0.86	0.70	13	15	1.0	4.5	4.0	7.3	9.3	5.2	1.8	0.46	7.2	18	115
Ahodwo	3.3	0.38	0.79	0.10	0.64	3.3	0.43	0.49	0.37	5.2	6.8	1.8	1.9	2.9	3.4	5.4	2.1	1.0	1.6	4.6	6.6	50
Asokwa	8.2	12	12	0.26	2.4	20	4.3	2.7	1.9	31	31	5.3	7.3	7.7	10	13	8.8	2.8	1.1	13	30	221
Suntreso	3.9	1.6	11	2.1	2.5	59	17	8.7	6.4	209	176	5.2	109	51	94	76	90	28	12	99	106	1170
Patasi	4.7	9.2	3.0	0.48	1.2	15	3.7	3.7	1.7	53	52	3.7	37	20	45	46	45	16	5.5	54	67	488
Sofoline	5.1	nd	2.8	0.81	1.0	33	9.2	9.2	3.1	106	95	1.8	79	39	65	65	67	25	9.3	64	62	743
Danyame	5.6	3.8	2.2	0.69	1.1	19	3.7	3.7	2.1	73	68	4.1	37	22	44	43	44	15	5.2	42	52	490
Dakodwom	6.5	2.1	2.5	0.36	0.98	11	3.3	2.3	1.6	57	54	4.8	35	19	49	43	44	16	4.4	36	45	437
KNUST	4.1	1.0	0.12	nd	0.23	1.3	0.18	0.11	0.22	1.0	1.4	1.5	0.33	0.42	1.5	1.3	0.85	0.83	0.10	0.68	0.62	13

16 nd: not detected; LOI: Loss on ignition; KNUST: KNUST Botanical Gardens

17

18

19

20 **Table 2**

21 Concentrations (ng/g dw) of PAHs in surface soils from 5 most polluted communities.

PAHs compound	No. of rings	Min	Max	Mean	SD	% abundance
Nap	2	1.7	17	9.2	6.0	0.58
Acl	3	7.1	21	13	5.3	0.78
Ace	3	1.6	25	7.9	9.8	0.50
Fle	3	2.6	11	5.6	3.3	0.35
Phe	3	56	208	112	64	7.0
Ant	3	15	39	24	9.6	1.5
Methy-Phe	3	8.8	35	16	11	0.98
Me-Phe	3	4.2	13	8.8	3.6	0.55
Flu	4	188	381	258	77	16
Pyr	4	177	355	235	73	14
Retene	3	4.9	25	11	8.4	0.66
BaA	4	102	207	134	44	8.4
Chr	4	51	101	71	19	4.4
BbF+BkF	5 + 5	57	298	140	95	8.8
BeP	5	51	277	129	91	8.1
BaP	5	52	259	132	80	8.2
Peryl	5	13	81	43	26	2.7
DBahA	5	9.7	19	13	4.1	0.85
IcdP	6	48	189	113	55	7.0
BghiP	6	80	214	128	57	7.9
$\sum_{22}$ PAH		933	2777	1607	746	
$\sum_{16}$ PAH		850	2345	1398	605	
$\sum_{car}$ PAH		321	1072	605	299	

22 $\sum_{car}$ PAH: BaA, BbF, BkF, BaP, Chr, DahA and IDP according to IARC (2006).

23 bold indicates 16 USEPA PAHs

24

25

26

27 **Table 3**

28 List of TEF and total Benzo(a)Pyrene–equivalent concentration (BaP_{eq}).

PAHs	TEF values	BaP _{eq} ng/g	
		KNUST mean ± SD	5 polluted communities mean ± SD
BaP	1	0.85 ± 0.82	132 ± 80
DBahA	1	0.10 ± 0.12	13 ± 4.1
BbF+BkF	0.1	1.5 ± 1.3	141 ± 96
BaA	0.1	0.33 ± 0.09	135 ± 44
IcdP	0.1	0.68 ± 0.43	113 ± 55
Chr	0.01	0.42 ± 0.22	71 ± 19

29 List of TEF values was compiled by Tsai et al. (2004)

30

31

32

Nap	0.001	1.0 ± 0.28	9.2 ± 6.0	0.0010	0.0092
Ace	0.001	0.02 ± 0.01	7.9 ± 9.8	0.000020	0.0079
BghiP	0.01	0.62 ± 0.94	128 ± 57	0.0062	1.3
BeP	0.01	1.3 ± 1.1	129 ± 91	0.013	1.3
Pyr	0.001	1.4 ± 0.46	235 ± 74	0.0014	0.24
Flu	0.001	1.1 ± 0.43	258 ± 77	0.0011	0.26
Ant	0.01	0.18 ± 0.14	24 ± 9.6	0.0018	0.24
Phe	0.001	1.4 ± 0.24	112 ± 64	0.0014	0.11
Peryl	0.001	0.83 ± 0.65	44 ± 26	0.00083	0.040
Fle	0.001	0.23 ± 0.04	5.6 ± 3.4	0.00023	0.0056
Acl	0.001	0.12 ± 0.03	12 ± 5.3	0.00012	0.012
Sum				1.2	188

33

34

35

36

37

38

Fig. 1.

Fig. 2.

50
51
52
53

Fig. 3a.

Fig. 3b.

Adum

Romanhill

Mbrom

Suame

Suntreso

Contribution of the sources

Fig. 4.