

Profiling of Polycyclic Aromatic Hydrocarbon in vegetables grown on contaminated soils in a Sub-saharan tropical environment –Lagos, Nigeria.

Oluwatoyin T. Adetunde^{a}, Graham A. Mills^b, Temilola. O.Oluseyi^a, Aderonke. O.*

Oyeyiola^a, Kehinde O. Olayinka^a, and Babajide I. Alo^a,

^aDepartment of Chemistry, Faculty of Science, University of Lagos, Akoka, Yaba, Lagos, Nigeria

^bSchool of Pharmacy and Biomedical Science, University of Portsmouth, Portsmouth, PO1 2DT, United Kingdom

* E-mail address of the corresponding author: oadetunde@unilag.edu.ng

ABSTRACT

Diet has been established as a major source of exposure to PAHs for humans especially non-smokers. Therefore their presence in plants constitutes a major health concern. This research aims to determine the concentration and profile of sixteen US-EPA priority PAHs in tropical edible vegetables (*Corchorus olitorius* (Ewedu), *Celosia argentea* (Soko), *Amaranthus cruentus* L (Grain amaranthus/ Tete), *Telfairia occidentale* (Ugwu), *Basella alba* (Amunu tutu/White Spinash), *Lactuca Sativa* (Lettuce), *Allium ascalonicum* (Spring Onions/Alubasa elewe), *Talinum Triangulare* (Water leaf)), grown on potted contaminated soils. Vegetable grown on potted contaminated soils and contaminated soils were extracted using *n*-hexane/acetone mixture in ultrasonic bath. The extract was purified using a C₁₈ solid-phase extraction cartridge (5 mL). The resultant extract was separated and the PAHs quantified on an Agilent 6890 Gas chromatography/mass spectrometer (GC/MS). Total PAH concentration in contaminated soils and plants grown on them were 200 - 250,000 ng g⁻¹ and 100-5,000 ng g⁻¹, respectively. Concentration of PAHs in plant roots was generally higher than in the stems. PAH concentration in plant stems was also generally higher than in plant leaves. Two and three ringed PAHs which are the less toxic were dominant in most of the plant parts. One of the vegetable samples *Telfairia*

occidentale (Ugwu) consistently grew on all the soils samples which suggest it possess some potential for phyto remediation.

KEYWORDS: Vegetables, polycyclic aromatic hydrocarbons, soils, gas chromatography –mass spectrophotometer

INTRODUCTION

In tropical Africa, over a hundred vegetables species are cultivated for consumption. Specifically in Nigeria and other sub-Saharan African countries tropical vegetables has been part of the food systems for generations. With the increased awareness of the health protecting properties of vegetables immense attention has been drawn to the consumption of vegetables in Nigeria. Vegetables are now among the most important cultivated food crops (1).

Diet has been established as a major source for polycyclic aromatic hydrocarbons (PAHs) exposure to humans especially for non-smokers (2, 3), therefore their presence in plants constitutes a major health concern (4, 5). Accumulation of PAHs by vegetable may be an indirect exposure pathway to humans. Plants through their roots can take up PAHs from soil and water, bio- concentrate and translocate them to their storage organs which are usually eaten by man and other organisms (6-10). The amount of PAHs taken up by plants is a function of many factors, including initial soil concentrations, microbial population and plant species. Typical responses of plants to PAHs contamination are poor germination and growth (11).

PAHs are ubiquitous compounds known as carcinogens and mutagens. They have been found in petroleum and its products as well as in many contaminated sites (12). Contamination of soils by PAHs are usually due to anthropogenic activities such as cracking of crude petroleum, burning of

fossil fuels, oil spills, incineration of industrial and domestic waste among others. They are persistent, resistant to bio degradation and can be transferred to water bodies, soil and plant.

Cancer has become a major source of morbidity and mortality globally. A total of 1,660,290 new cancer cases and 580,350 cancer deaths were projected to occur in the United States in 2013 by Siegel *et al.* (13). Badmus *et al* (14) reported the hospital prevalence rate of prostate cancer as 182.5 per 100,000 male admissions in South Western Nigeria. Age standardised breast cancer incidence rate at the Ibadan and Abuja cancer based registries of Nigeria were found to be 52.0 per 100000 and 64.6 per 100000, respectively while cervical cancer incidence rate were 36.0 per 100000 and 30.3 per 100000, respectively (15). Human health, agricultural development and the ecosystems are all at risk unless water, land systems are properly monitored and regulated.

Soil and water are usually monitored but plant monitoring for contaminants has been totally neglected in all regulations (16-17). PAH concentration of *Spartina alterniflora* plants grown in potted contaminated sediment (900 $\mu\text{g g}^{-1}$ total PAHs) was 43 $\mu\text{g g}^{-1}$ and 0.2 $\mu\text{g g}^{-1}$ in root and leaf, respectively (18). Some studies on the uptake of PAHs by plants in Nigeria include those by Sojinua *et al.*(19) Ukiwe *et al* (20) and Ezekwe *et al* (21). They studied higher plants (none edible plants) which are not leafy vegetables. Studies on the uptake of PAHs by locally consumed leafy Nigerian vegetables from contaminated soils are not available.

Nigeria is faced with enormous environmental and agricultural challenges which threaten the livelihood of the tens of millions of its teeming population. One of the environmental challenges include contaminated lands as a result of oil (petroleum) spills (especially in the Niger Delta area of the South–Southern part country) spills of petroleum refined products during loading into tankers for distribution from the ports and tank farms in Lagos, South Western Nigeria, petroleum products

leakage from distribution tanks during accident or due to rust of tank and disposed lubricating oils in soils around automobile workshops among others (22-23).

Lagos, situated at the South-Western Coast of Nigeria is the fastest growing city in Africa. It is also densely populated. Approximately 60% of Nigeria's industrial and commercial activities are situated here (25). It is surrounded by water bodies and made up of many swampy areas. There is therefore a high demand for land. To meet the demand, land reclamation is the order of the day. Reclamation of swamps, former industrial sites, contaminated sites for use in transport, industrial/commercial, residential and allotment (refers to the provision of open space, commonly made by the local authority, for local people to grow fruit and vegetables for their own consumption and for sale to make a living) purposes have been ongoing. Some residents of residential areas from these reclaimed lands have private gardens. They are exposed to PAHs through consumption of food crops especially vegetables grown on them. Exposure risks in Nigeria are usually estimated without contribution from eating home grown vegetables. There is a dearth of information about PAHs in locally consumed vegetables from Nigeria. This research aims at determining the levels and profile of PAHs in locally consumed plants grown on potted contaminated soils from Nigeria.

METHODOLOGY

Chemicals and standards

A standard mixture of 16 USEPA PAHs and 2 alkylated PAHs (all 2,000 $\mu\text{g mL}^{-1}$) was obtained from Supelco (Bellefonte, PA, USA). The mixture contained naphthalene (NAP), 1-methylnaphthalene (1-MNAP), 2-methylnaphthalene (2-MNAP), acenaphthylene (ACY), acenaphthene (ACP), fluorene (FLR), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF),

benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcP), dibenzo[a,h]anthracene (DaH) and benzo[g,h,i]perylene (BgP). However, 1-methylnaphthalene (1-MNAP), 2-methylnaphthalene (2-MNAP) were not monitored. Since they are not part of the 16 priority PAHs. The deuterated internal standard solution mixture (all 2,000 $\mu\text{g mL}^{-1}$ in dichloromethane) contained d_{10} -acenaphthene, d_8 -naphthalene, d_{10} -phenanthrene, d_{12} -chrysene, d_{12} -perylene and d_4 -1,4-dichlorobenzene (Supelco). The certified reference materials, CRM 172-100G for USEPA PAHs used for method validation were from Supelco Analytical (Bellefonte, USA). All solvents were of HPLC grade or better and purchased from Fisher Scientific Ltd. (Loughborough, UK).

Soil Sampling

Contaminated composite surface soil samples were obtained from three locations in Lagos, Nigeria (A: N 06 X 30' 56.31", E 003 X 23' 58.5", B N 06 X 27' 31.0", E 003 X 21' 36.2", C N 06 X 26' 26.25", E 003 X 19' 49.5") and a control was also obtained from outside Lagos Nigeria (D: N 06 X 41' 30", E 003 X 51' 46"). Location A was a site used as depot and loading point for used for black oil Iganmu/Orile, Apapa, Lagos, B was a Premium motor spirit and Kerosene depot, Apapa, Lagos, C was a Premium motor spirit and Kerosene depot, Apapa Lagos and the D the control was a forest outside Lagos between January 2012 and March 2012. The samples were transported to the laboratory where a portion was air dried for 4 days in the dark at ambient room temperature ≤ 32 °C and sieved using 2 mm sized sieve and kept prior to analysis. Another portion was immediately prepared for planting and the remaining was kept for grain size analysis.

Physico-chemical analysis of soils

Particle size distribution of soils, were determined by the British Standard Method using wet sieving and sedimentation technique (25). Soil pH were determined in 0.01 mol L⁻¹ CaCl₂ (10 mL:5 g of soil). Total organic carbon (TOC) and Soil organic matter (SOM) were determined using the Walkley-Black titrimetric method (26). Oil and grease in soil samples were extracted in acetone: *n*-hexane (50:50 v/v), with an ultrasonic and quantified gravimetrically (27).

Extraction, clean-up and analysis of PAHs in soils

Between 0.5–5 g of each air dried soil samples (depending on the degree of contamination estimated by the oil and grease) were extracted for PAHs. Samples were spiked with deuterated internal standard (to evaluate the extraction efficiency) solution mixture which contained d₁₀-acenaphthene, d₈-naphthalene, d₁₀-phenanthrene, d₁₂-chrysene, d₁₂-perylene and d₄-1,4-dichlorobenzene solution (25 μL of 10 mg mL⁻¹) and extracted in an ultrasonic bath using three sequential extractions of acetone:*n*-hexane (1:1v/v). The combined extract (25 mL) was concentrated under nitrogen to about 500 μL. 200 mg C₁₈, Bond Elute, in 5 mL cartridge was used for clean-up under pressure. SPE cartridges were pre-conditioned with dichloromethane (DCM), methanol, methanol:water (1:1), water, (acetone : *n*-hexane: water (1:1 :1) and finally acetone: *n*-hexane (1:1) sequentially. The concentrated extract was then loaded and eluted with 5ml of DCM:*n*-hexane (1:1) at a flow rate of 1 mL min⁻¹. Eluates were evaporated to dryness under nitrogen and reconstituted in 1 mL of *n*-hexane. Care was taken to ensure the cartridge did not dry during the conditioning and loading of sample extract. For quality control, sample series were made to include a CRM extract, one standard that has been treated similarly to the samples (recovery determination), six standards of varying concentrations (0-5000 μg mL⁻¹) which contain each of the 16 PAHs (10, 24, 28-29). Working standard solutions were prepared in *n*-hexane. An

Agilent GC/MS (6890N GC) equipped with split/splitless injector, fitted with a HP-5MS UI capillary column (30 m, 0.25 mm i.d. x 0.25 mm film thickness) and connected to a mass selective detector (Agilent 5975) was used for PAH separation and quantification. Samples were injected (2 μ L) in splitless mode at an injection temperature of 290 $^{\circ}$ C. The column oven was held at 50 $^{\circ}$ C for 3.2 mins, raised to 150 $^{\circ}$ C at a rate of 30 $^{\circ}$ C min $^{-1}$. It was further raised to 238 $^{\circ}$ C at a rate of 2 $^{\circ}$ C min $^{-1}$. From 238 $^{\circ}$ C it was raised to 272 $^{\circ}$ C at a rate of 3 $^{\circ}$ C min $^{-1}$ and finally raised to 300 $^{\circ}$ C at a rate of 70 $^{\circ}$ C min $^{-1}$. At 300 $^{\circ}$ C it was held for 2.73 mins. Helium gas (the carrier gas) flowed at a constant flow rate of 1 mL min $^{-1}$. Mass spectrum were acquired using electron ionization (EI) at 70 eV. The injector and auxiliary temperatures were set at 290 $^{\circ}$ C and 300 $^{\circ}$ C, respectively. Ion source temperature was 250 $^{\circ}$ C. Identification and analysis of PAHs in soils were carried out by confirmation of retention time and abundance of quantification/confirmation ions compared to authentic standards. All the identified compounds were quantified using selective ion monitoring (SIM).

Soil Sample Preparation for Planting

The soil samples (A, B, C and D) were prepared for planting by removing large stones with the help of a farm sieve. Fertilizer (pink granular free flowing N.P.K 15-15-15) was added to the different soils in the ratio of 600 g to 40 kg and stored in the dark at room temperature for 4 days. Soils A, B, C, respectively were mixed with D the control in ratios of 1:9, 1:3, 1:1, 3:1 and 1:0 to obtain 10%, 25%, 50%, 75%, 100% contaminated soils of A, B, C. Control soil sample was also used for planting and tagged 100% D. 1.4 kg of each soil (including 100%D soil) was bagged in perforated black special planting nylons ready for planting in the green house. Each of these soil mixes were sampled and kept at -20 $^{\circ}$ C for analysis before planting commenced.

Seed sourcing and planting

Seeds of *Corchorus olitorius* (Ewedu), *Celosia argentea* (Soko), *Amaranthus cruentus* L (Grain amaranthus/ Tete) were sourced from National Horticultural Research Institute Nigeria (NIHORT) while *Basella alba* (Amunu tutu/White Spinash), *Lactuca sativa* (Lettuce), *Allium ascalonicum* (Spring Onions/Alubasa elewe), *Talinum triangulare* (Water leaf), *Telfairia occidentale* (Ugwu), were sourced from commercial farms in Lagos, Nigeria.

The seeds were pre-germinated and nursed using compost nursery in a green house at the botanical garden of the University of Lagos and were later identified in the Botany Laboratory of the University of Lagos at the 5 to 6 seed leaves stage (after two weeks from planting).

The seedlings were transplanted into bagged soils and their mixes in a green house at the Botanical garden of the University of Lagos, Nigeria to grow till maturation time. They were each planted for 7 weeks after which they were harvested and washed. Harvested plant samples were dried indoors at room temperature for a week and kept in double aluminium foil to protect them from sunlight. Packed samples were packed in labelled plastic bags and stored at 0 °C until analyses (30).

Extraction, clean-up and analysis of PAHs in Plants

All the harvested plants were divided into three parts namely the leaves, stems and roots but *Allium Ascalonicum* (Spring Onions/Alubasa elewe) and *Lactuca Sativa* (Lettuce) (which had only leaves and root) were divided into two parts. They were shredded with a domestic shredder and weighed for analyses. 0.5 – 5 g of plant materials were weighed into an amber glass bottles and extracted sequentially thrice in an ultrasonic bath using 5 mL of Hexane: acetone

(1:1,vol:vol). Extraction, clean up and analysis of PAHs were as in the analysis of soil above. The sum PAHs of the 16 priority USEPA PAHs were calculated based on dry weight of plants.

RESULTS AND DISCUSSION

Physico chemical properties of soil samples were determined and results are shown in Table 1. Particle size an important feature of soil, which affects soil physical and chemical properties such as structure, oxygen concentration and water content was determined (30-31). SOM for samples in this study were found to vary from 2.98 to 7.74%. Physical conditions of soil are impacted by SOM. Impacts of SOM include enhancing aeration, aggregation and water retention. SOM therefore provides suitable environments for plant growth (32). Soil samples in this study were predominantly sandy (49.71 to 84.73%). Clay fraction (<0.002 mm) of soil samples varied between 4.92 and 20.03% while silt fractions (0.05-0.002 mm) had a range of 0.06 to 29.01%. Oil and grease content for soil is a measure of soil pollution. Soil samples had 0.18 to 4.92 % oil and grease by weight. Analysis of the soil texture revealed a lack of systematic differences in grain size composition among the individual sites. Soil pH values measured in 0.01 molL⁻¹ CaCl₂ varied within the range of 6.8 to 8.0 for all the samples.

PAHs Concentration

To evaluate the extraction efficiency for the target compounds, recovery studies were carried out using 6 isotopically labelled PAHs, (d₁₀-acenaphthene, d₈-naphthalene, d₁₀-phenanthrene, d₁₂-chrysene, d₁₂-perylene and d₄-1,4-dichlorobenzene). The average surrogate recoveries were between 75 and 95 %. This demonstrates that there was no significant loss of analytes during sample preparation processes. Calibration curves were obtained using a series of varying

concentrations of a multi-component standard containing each of the 16 USEPA PAHs and the r^2 value of the calibration curves had a range of 0.994 to 0.999. Limit of detection (LOD) and limit of quantification (LOQ) were obtained as concentrations of target compounds in a sample that results in a peak with signal-to-noise (S/N) ratio of 3:1 and 10:1, respectively (33). The LOD and LOQ for the PAHs in this study had a range of 1.2 ng/ml to 60ng/ml and 3.8 ng/ml to 200 ng/ml, respectively for individual USEPA PAHs (Table 2). The LOD was used as method detection limit. Recovery for the individual PAHs in CRM 172-100G soil analyses were between 75 to 105 %.

PAH concentrations of the composite soil samples were analysed. Base on PAHs summations of the 16 priority PAHs concentration in samples, Soil B is a contaminated soil ($600-1000\mu\text{g g}^{-1}$) while soil A and C is a heavily contaminated ($> 1000\text{g g}^{-1}$) (34). Sum concentrations of the 16 priority USEPA PAHs for the contaminated soils were 104443, 701 and 253922 ng g^{-1} for soils A, B and C, respectively while for the control a value of 201 ng g^{-1} was obtained. Concentrations of PAHs in the soils mixes were also determined and their results are shown in Table 3.

Eight different commonly consumed vegetables in south western Nigeria (*Corchorus olitorius* (Ewedu), *Celosia argentea* (Soko), *Amaranthus cruentus* L (Grain amaranthus/ Tete), *Basella alba* (Amunu tutu/White Spinash), *Lactuca sativa* (Lettuce), *Allium ascalonicum* (Spring Onions/Alubosa elewe), *Talinum triangulare* (Water leaf), *Telfairia occidentale* (Ugwu)) were planted on the various soils (A, B, C, D) and their mixes. *Celosia argentea* (Soko) grew only on three mixes of soils (B25%, B50% and C10% and the control (D100%). *Amaranthus cruentus* L (Grain amaranthus/ Tete) and *Allium ascalonicum* (Spring onions/Alubosa elewe) both grew on soils A10%, A25%, B25%, B50%, B75%, C10% and on the control (D100%) while *Basella Alba*

(*Amunu tutu*/White Spinash) grew on soils A10%, A25%, B25%, C10% and D100%. *Talinum triangulare* (Water leaf) grew on soils A10%, B25%, B50%, C10% and D100%. *Corchorus olitorius* (*Ewedu*) grew on soils A10%, B25%, B50%, B75% and on D100%. *Lactuca sativa* (Lettuce) grew on only two soils namely B25% and D100%. All the plants in this study grew on the control soil (D).

Telfairia occidentale (*Ugwu*) consistently grew on all the soils and their mixes. This suggests *Telfairia occidentale* (*Ugwu*) has some special properties which enabled it grow even when planted heavily contaminated soils (A100% and C 100%) with high oil content of 4.92 % and 1.41 % where other plants failed to grow. This ability of *Telfairia occidentale* (*Ugwu*) makes it a potential crop in the phyto remediation of PAH contaminated sites. *Lactuca Sativa* (Lettuce) thrived only on two soils (B25 % and D100 %) and *CelosiaArgentea* (*Soko*) also grew on four soils (A25 %, A50 %, C10 % and 100 %). The soils and soils mixes on which *Lactuca Sativa* (Lettuce) and *CelosiaArgentea* (*Soko*) grew were the least contaminated soils. Their ability to grow on soils with low contamination makes them a potential bio indicator for polluted soils.

The 16 priority USEPA PAHs were analysed in the different plants parts and the results are shown in Table 3. PAH concentrations in plants grown on contaminated soils compared with the control soils were higher. The PAHs concentrations of roots were for most plants higher than in their stems and the PAHs concentrations of stems were higher for leaves (Table 3). This finding was similar to that of other researchers who worked on PAH(s) uptake by plant (30-32). Vácha *et al.*, (35) studied the influence of soil load with PAHs on their contents in selected plants (*Raphanus sativus* var and *Radiculaduo* variety and carrot (*Daucus carota*). The roots of tested plants were loaded with PAHs especially the lower molecular weight PAHs compared with the higher molecular weight PAHs predominant in soils. In another study by Zitka *et al.*, (36) the uptake of

fluoranthrene by plants was highest in roots exposed to contaminated soils compared to other parts. They attributed the high concentrations of fluoranthrene in root to the lipophilicity of PAH. Fluoranthrene (like other PAHs) because of its lipophilic property accumulates in the cellular compartments such as plasma membrane and membrane-based organelles known to contain lipids. When plants grow on PAH contaminated soils, PAHs initially adsorb to plant cell walls and they later gradually diffuse into subcellular fractions of tissues. Therefore, transpiration and the lipid content of root cell fractions are the main drivers of the subcellular partition of PAHs in roots and also determine accumulation of lipophilic compounds in plants. Concentration gradient from soil to plant also plays a major role in plant uptake of PAHs. Immobilisation and accumulation of PAHs in the roots compared to the leaves and stem may be because of chemical modification. PAHs interact with numerous hydroxyl groups in polysaccharides (such as cellulose, hemicelluloses and pectin) of plant cell (37). Un-Nisa and Rashid (38) in their study found that the Vetiver grass (*Vetiveria zizanioides*) effectively removes PAHs from soil and that the levels were significantly higher in root and shoot of contaminated soils compared to the levels in the control. In some plants, PAHs concentration were higher than the soil where it was planted. This is probably due to bioaccumulation of the PAHs by the plants.

PAH profiles in plants harvested and soils on which plants grew.

There were variations in the PAH profiles of soils samples (Figure 1a) and plant samples (Figures 1b, 1c, 2 and 3). Four to six-ring PAHs made up 25 % - 75 % of all the PAHs found in composite soil samples studied. No specific trend was observed in soil. Generally two and three-ring PAHs were higher in most of the plants compared with the higher membered rings. However, the PAH profiles in the various plant samples were not similar. Concentrations of two and three-ring PAHs were generally higher than the concentration of four, five and six-ring PAHs in plant samples. Similar observations has been previously described by Bakker *et al*, (39) and Sojinua *et al*, (20,

40) who proposed that it may have been as a result of wind drift and wash-off or the low absorption of the higher membered ringed PAHs from the leaves surfaces. This may also as a result of the lipohilicity of PAHs. The lipophilic property of PAHs increases with increase in ring size. Since plant is made up of predominantly water and less oils, more of the less lipohilic PAHs (2 and 3 rings) will move through the plant system by translocation from the root.

CONCLUSION

The levels of PAHs in plants grown on contaminated soils were higher than in plants grown on the control soils. Soils with higher PAHs concentrations also had higher levels of PAHs in plants grown on them. The amount in roots were generally higher than in leaves and stem in all the plants. *Telfairia occidentale* (Ugwu), consistently grew on all the soils studied (contaminated and non-contaminated soils). This ability of *Telfairia occidentale* (Ugwu) makes it a potential crop in phyto remediation of PAH contaminated sites. The soils and soils mixes on which *Lactuca Sativa* (Lettuce) and *CelosiaArgentea* (Soko) grew were the least contaminated soils. Their ability to grow on soils with low contamination makes them potential bio indicators for polluted soils.

Since the actual edible part for these vegetables are the leaves and not the root which had higher amounts of PAHs, less risk is associated with the consumption of these vegetable plants. However, data from this study will be used subsequently to access the actual risk associated with the consumption of contaminated vegetables.

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REFERENCES

- (1) Thompson, D., Agbugba, I. K. "Marketing of tropical vegetable in Aba area of Abia State" *Nigeria Journal of Agricultural Economics and Development* (2013): 2, 272- 279.
- (2) Wang, Y. C., Qiao, M., Liu, Y. X., Arp, H. P. H., Zhu, Y. G. "Comparison of polycyclic aromatic hydrocarbon uptake pathways and risk assessment of vegetables from waste-water irrigated areas in northern China" *Journal of Environmental Monitoring* (2011): 13, 433-439.
- (3) Wang, N., Lang, Y., Cheng, F., Wang, M. "Concentrations, Sources and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils of Liaohe Estuarine Wetland" *Bulletin of Environmental Contamination and Toxicology* (2011) : 87, 463-468.
- (4) Wang, P., Zhang, Q., Wang, Y., Wang, T., Li, X., Ding, L., Jiang, G. "Evaluation of Soxhlet extraction, accelerated solvent extraction and microwave-assisted extraction for the determination of polychlorinated biphenyls and polybrominated diphenyl ethers in soil and fish samples" *Analytica Chimica Acta* (2010), 663, 43-48.
- (5) Tao, S., Cui, Y. H., Xu, F. L., Li, B. G., Cao, J., Liu, W. X., Schmitt, G., Wang, X. J., Shen, W. R., Qing, B. P., Sun, R. "Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin" *Science of The Total Environment* (2004): 320, 11-24.
- (6) Essumang, D. K., Kowalski, K., Sogaard, E. G. "Levels, Distribution and Source Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) in Topsoils and Roadside Soils in Esbjerg, Denmark" *Bulletin of Environmental Contamination and Toxicology* (2011): 86, 438-443.
- (7) Kipopoulou, A. M.; Manoli, E.; Samara, C. Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area. *Environmental Pollution* 1999, 106, 369 - 380.
- (8) Meudec, A.; Dussauze, J.; Deslandes, E.; Poupart, N. Uptake of four PAHs Occuring into Aerial plant tissue Artificially Exposed to Heavy Fuel oil in Salicornia. *Chemosphere* 2005, 65, 474 - 481.
- (9) Ashraf, M. W.; Taqvi, S. I. H.; Solangi, A. R.; Qureshi, U. A. Distribution and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Vegetables Grown in Pakistan. *Journal of Chemistry* 2013, 2013, 5.
- (10) Marce, R. M.; Borrull, F. "Solid-phase extraction of polycyclic aromatic compounds" *Journal of Chromatography A*, (2000): 885, 273-290.
- (11) Sun, L., Liao, X., Yan, X., Zhu, G., Ma, D. "Evaluation of heavy metal and polycyclic aromatic hydrocarbons accumulation in plants from typical industrial sites: potential candidate in phytoremediation for co-contamination" *Environmental Science of Pollution Research* (2014): 11. 24-30.
- (12) Hong, S. H., Kang, B. H., Kang, M. H., Chung, J. W., Jun, W. J., Chung, J. I., Kim, M. C., Shim, S. I. "Responses of wild plant species to polycyclic aromatic hydrocarbons in soil" *Journal of Environmental Monitoring* (2009): 11, 1664-1672.
- (13) Li, P., Li, X., Stagnitti, F., Zhanga, H., Lin, X., Zang, S., Zhuoa, J., Xiong, X. Studies on the sources of benzo[a]pyrene in grain and aboveground tissues of rice plants. *Journal of Hazardous Materials* (2009): 162, 463-468.

- (14) Siegel, R., Naishadham, D., Jemal, A. "Cancer statistics" *A cancer Journal for Clinicians* (2013): 63, 11-30.
- (15) Badmus, T. A., Adesunkanmi, A. R., Yusuf, B. M. "Burden of prostate cancer in southwestern Nigeria" *Urology* (2010): 76, 412-416.
- (16) Jedy-Agba, E., Curado, M. P., Ogunbiyi, O., Oga, E., Fabowale, T., Igbinoba, F., Osubor, G., Otu, T., Kumai, H., Koechlin, A., Osinubi, P., Dakum, P., Blattner, W., Adebamowo, C. A. "Cancer incidence in Nigeria: a report from population-based cancer registries" *Cancer Epidemiology* (2012): 36, 271- 278.
- (17) Ashraf, M. W., Salam, A. Polycyclic Aromatic Hydrocarbons (PAHs) in Vegetables and Fruits Produced in Saudi Arabia. *Bulletin of Environmental Contamination and Toxicology* (2012): 88, 543-547.
- (18) Kaszubkiewicz, J., Kawalko, D., Perlak, Z. Concentration of polycyclic aromatic hydrocarbons in surface horizons of soils in immediate neighbourhood of illegal waste dumps *Polish Journal of Environmental Studies* (2010) 1, 73-82.
- (19) Watts, A. W., Ballester, T. P., Gardner, K. H. Uptake of polycyclic aromatic hydrocarbons (PAHs) in salt marsh plants *Spartina alterniflora* grown in contaminated sediments. *Chemosphere* (2006): 62, 1253-1260.
- (20) Sojinua, S. O., Sonibare, O. O., Ekundayo, O., Zeng, E. Y. Biomonitoring potentials of polycyclic aromatic hydrocarbons (PAHs) by higher plants from an oil exploration site, Nigeria *Journal of Hazardous Materials* (2010): 184, 759–764.
- (21) Ukiwe, L. N., Egereonu, U. U., Njoku, P. C., Nwoko, C. I. A. Degradation of Polycyclic Aromatic Hydrocarbons from Soil Leachate by Water Hyacinth (*Eichhornia crassipes*) *International Journal of Chemistry* (2012): 4, 55 - 61.
- (22) Ezekwe, I. C., Odu, N. N., Onyedikam, L. I. Heavy Metals and Polycyclic Aromatic Hydrocarbons in Water and Biota from a Drilling Waste Polluted Freshwater Swamp in the Mgbede Oil Fields of South-South Nigeria. *Bioremediation & Biodegradation* (2014) 258, doi:10.4172/2155-6199.1000258.
- (23) Anoliefo, G. O., Isikhuemhen, O. S., Ohimain, E. I. "Sensitivity Studies of the Common Bean (*Vigna unguiculata*) and Maize (*Zea mays*) to Different Soil Types from the Crude Oil Drilling Site at Kutchalli, Nigeria" *Journal of Soils and Sediments* (2006) : 6, 30 - 36.
- (24) Adetunde, O. T. Mills, G. A., Olayinka, K. O., Alo, B. I. "Assessment of occupational exposure to polycyclic aromatic hydrocarbons via involuntary ingestion of soil from contaminated soils in Lagos, Nigeria" *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* (2014): 49, 1661–1671.
- (25) DEFRA. *The Contaminated Land Exposure Assessment Model (CLEA): Technical basis and algorithms*: United Kingdom (2002).
- (26) Environment Agency. *Updated technical background to the CLEA model*: United Kingdom (2009).
- (27) Hong, L., Ghosh, U., Taniamahaj, A.N., Zare, R., Luthy, R. "PAH Sorption Mechanism and Partitioning Behavior in Lampblack-Impacted Soils from Former Oil-Gas Plant Sites" *Environmental Science and Technology* (2003): 32, 3267 - 3276.
- (28) Silva, B. O., Adetunde, O. T., Oluseyi, T. O., Olayinka, K. O., Alo, B. I. "Comparison of some extraction methods and clean-up procedures for the 16 priority US EPA PAHS" *Journal of Science Research and Development* (2011): 13, 129 – 143.
- (29) Oluseyi, T., Olayinka, K., Alo, B., Smith, R. M. "Improved analytical extraction and clean-up techniques for the determination of PAHs in contaminated soil samples" *International Journal of Environ Resource* (2011):5, 681- 690.
- (30) Nadal, M., Schuhmacher, M., Domingo, J. L. "Levels of PAHs in soil and vegetation samples from Tarragona County, Spain" *Environmental Pollution* (2004): 132, 1-11.

- (31) Huang, L., Dong, B. C., Xue, W., Peng, Y. K., Zhang, M. X. "Soil Particle Heterogeneity Affects the Growth of a Rhizomatous Wetland Plant" *PLoS ONE* (2013) : 8.213-223
- (32) Fallahzade, J., Hajabbasi, M. A." Soil Organic Matter Status Changes with Cultivation of Overgrazed Pastures in Semi-dry West Central Iran" *International Journal of Soil Science* (2011): 6, 114-123.
- (33) Inam, E., Ibanga, F., Essien, J." Bioaccumulation and cancer risk of polycyclic aromatic hydrocarbons in leafy vegetables grown in soils within automobile repair complex and environ in Uyo, Nigeria" *Environmental Monitoring and Assessment* (2016): 188, 681 -690.
- (34) Maliszewska-Kordybach, B."Dissipation of Polycyclic Aromatic Hydrocarbons in Freshly Contaminated Soils – The Effect of Soil Physicochemical Properties and Aging" *Water Air Soil Pollution* (2005) :168, 113-128.
- (35) Vácha, R., Čechmánková, J., Skála, J. Polycyclic aromatic hydrocarbons in soil and selected plants. *Plant Soil Environment* (2010):56, 434–443.
- (36) Zitka, O., Babula, P., Sochor, J., Kummerova, M., Krystofova, O., Adam, V., Havel, L., Beklova, M., Hubalek, J., Kizek, R. "Determination of Eight Polycyclic Aromatic Hydrocarbons and in Pea Plants (*Pisum sativum* L.) Extracts by High Performance Liquid Chromatography with Electrochemical Detection" *International Journal of Electrochemical Science* (2012): 7, 908 - 927.
- (37) Kang, F., Chen, D., Gao, Y., Zhang, Y. "Distribution of polycyclic aromatic hydrocarbons in subcellular root tissues of ryegrass (*Lolium multiflorum*Lam.)" *BMC Plant Biology* (2010): 10, 1-7.
- (38) Un-Nisa, W., Rashid, A. "Potential of *Vetiver* (*Vetiveria Zizanioides* L.) grass in removing selected PAHs from diesel contaminated soil " *Pakistan Journal of Botany* (2015): 47, 291-296.
- (39) Bakker, M. I., Casado, U. B., Koerselman, J. W., Tolls, J.,; Kolloffel, C. "Polycyclic aromatic hydrocarbons in soil and plant samples from the vicinity of an oil refinery" *The Science of the Total Environment* (2000):263, 91-100.
- (40) Sojinu, O. S., Sonibare, O. O., Zenga, E. Y. "Concentrations of polycyclic aromatic hydrocarbons in soils of a mangrove forest affected by forest fire" *Toxicological and Environmental Chemistry* (2011): 93, 450–461.

Table 1

Sample ID	Grain particles size analysis				Physico-chemical properties			
	Gravel (%)	Sand (%)	Clay (%)	Silt (%)	^a TOC (%)	^b SOM (%)	pH	Oil and grease (%)
A	28.52	66.50	4.92	0.06	1.73	2.98	8.0	4.92
B	13.79	74.67	11.54	6.37	2.23	3.84	7.3	1.41
C	4.99	84.73	10.20	0.08	2.40	4.13	7.1	3.96
D	1.25	49.71	20.03	29.01	4.50	7.74	6.8	0.18

a is Total organic carbon— TOC , b is Soil organic matter -SOM

Table 2

S/ N	Compound	MS target Ion for Quantitation (M ⁺)	Other target ions (abundant ions) used for SIM	Group based on Retention Time and ion	R ² Value	Calibration Range ng/ml	LOQ ng/ml	LOD ng/ml
1	NAP	128	126,127	Group 1(6mins)	0.995	0-5000	38.8	11.6
2	ACY	152	150, 76	Group 1 (6mins)	0.994	0- 5000	3.8	1.2
3	ACP	153*	154, 152	Group 2 (8mins)	0.995	0-4950	88.6	26.6
4	FLR	166	165,163	Group 2 (8mins)	0.995	0-4980	44.4	13.3
5	PHE	178	176, 152	Group 3 (12mins)	0.995	0-4990	12.0	3.6
6	ANT	178	176, 152	Group 3 (12mins)	0.996	0-5000	12.00	3.6
7	FLT	202	200, 201	Group 4 (22mins)	0.995	0-4970	90.0	27.0
8	PYR	202	200, 201	Group 4 (22mins)	0.999	0- 4950	90.0	27.0
9	BaA	228	226,113	Group5 (31.5mins)	0.996	0-4900	36.1	10.8
10	CHR	228	226,113	Group5 (31.5mins)	0.999	0-5000	16.3	4.9
11	BbF	252	126, 250	Group6 (40mins)	0.996	0-4890	141.2	42.4
12	BkF	252	126, 250	Group6 (40mins)	0.997	0-4800	120.0	36.0
13	BaP	252	126,250	Group6 (40mins)	0.995	0-4900	114.3	34.3
14	DaH	276	274,138	Group7 (50mins)	0.998	0-4890	200.0	60.0
15	BgP	278	276,139	Group7 (50mins)	0.998	0-4800	187.6	56.3
16	IcP	276	126, 250	Group7 (50mins)	0.997	0-4900	50.0	15.0

*Except for Acenaphthene whose M⁺ is 154

Table 3

Plant	Amount of sum 16 USEPA PAH plant parts and soil (ng g ⁻¹)				
Shoko	Soil type	Leaves	Stems	Roots	Soil
	A25%	440	400	187	330
	A50%	639	602	830	454
	C10%	1441	3743	2188	25578
	D100%	187	168	895	207
Tete	A10%	174	315	321	10630
	A10%	1336	1218	4240	26266
	B25%	1640	815	3192	330
	B50%	685	607	1678	454
	B75%	796	810	1877	578
	C10%	1224	666	1965	25578
	D100%	135	84	182	207
Spinach	A10%	735	651	82	10630
	A25%	3204	553	395	26266
	B25%	1409	2059	2021	330
	C10%	3217	298	1008	25578
	D100%	155	157	837	207
Orgwu	A10%	247	409	457	10630
	A25%	852	999	1357	26266
	A50%	718	1791	1986	52325
	A75%	842	812	1758	78384
	A100%	1346	1019	1971	104443
	B25%	832	855	1881	330
	B50%	1301	699	996	454
	B75%	952	259	572	578
	B100%	1279	832	129	701
	C10%	534	674	770	25578
	C25%	632	68	213	63636
	C50%	293	259	255	127064
	C75%	945	630	1143	190493
	C100%	914	1461	2832	253922
	D100%	161	484	495	207
Waterleaf	A10%	2855	7096	7490	10630
	B25%	1038	1648	1183	330
	B50%	3073	3448	5056	454
	C10%	3423	3168	3306	25578
	D100%	311	122	98	207
spring onions	A10%	1100		2342	10630
	B25%	979		1406	330
	B50%	1247		2068	454
	B75%	3061		5130	578
	C10%	423		1685	25578
	D100%	244		326	207
Lettuce	B25%	964		1512	330

Ewedu	D100%	916		1473	207
	A10%	1672	2362	2296	10630
	B25%	802	1881	4372	330
	B50%	1024	2963	3303	454
	B75%	1225	3001	3188	578
	D100%	802	1000	1891	207

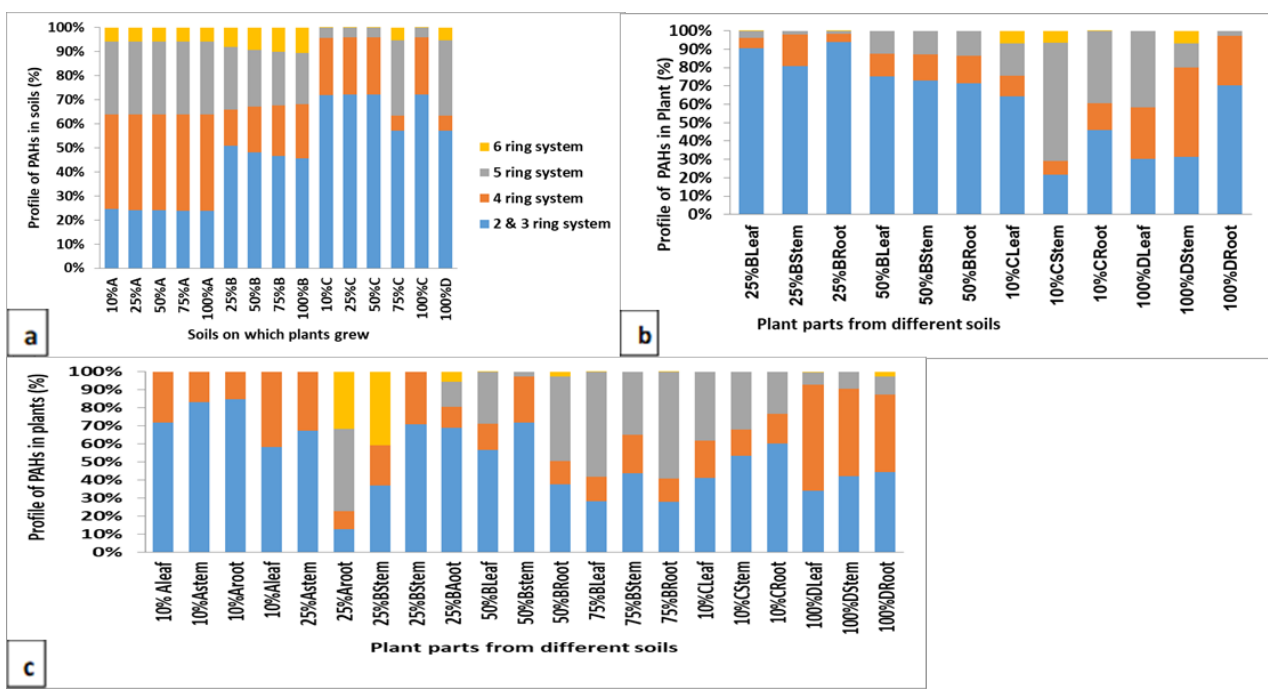


Figure 1: Soil,shok oand tete

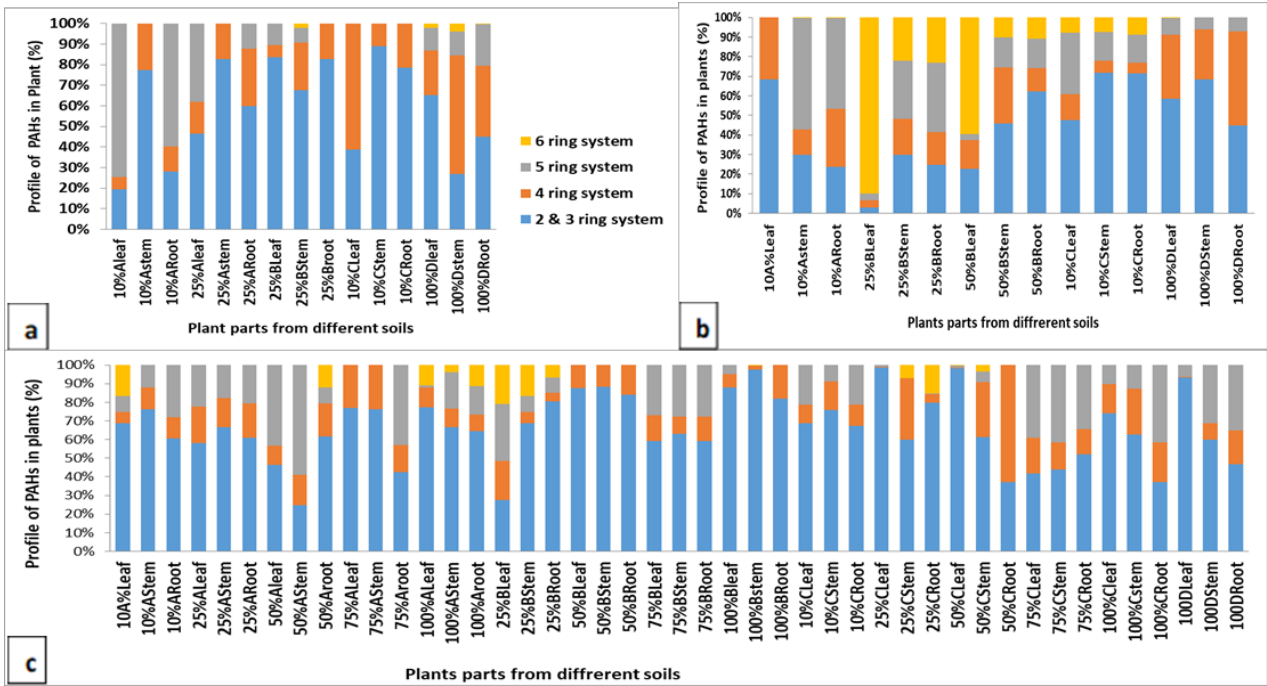


Figure 2: Spinach, water leaf and Ugwu

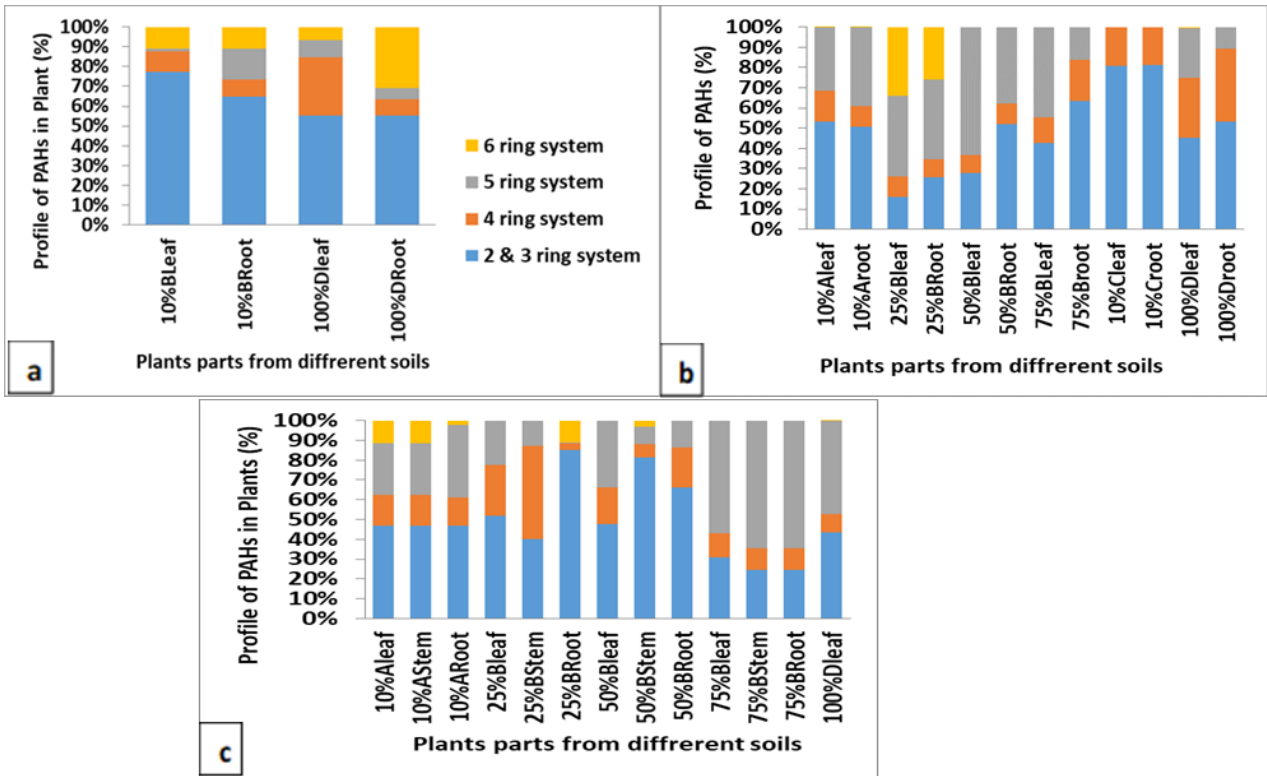


Figure 3: Lettuce, spring onions and ewedu