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Analysis and human health evaluation of trace metals and polycyclic aromatic hydrocarbons in *Ocimum basilicum* and *Vernonia amygdalina* cultivated close to industrial markets in Owerri, Imo State

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ABSTRACT

This study evaluated the presence of polycyclic aromatic hydrocarbons (PAHs) and trace metals in *Vernonia amygdalina* and *Ocimum basilicum* leaves grown near Ekeonunwa, Relief, and Toronto industrial markets in Owerri. High-performance liquid chromatography (HPLC) and Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES) were employed for analysis, with Cold Vapour Atomic Fluorescence Spectrophotometry (CV-AFS) specifically for mercury detection. PAH Concentrations (mg kg^{-1} PAHs): *V. amygdalina*: Ekeonunwa (5.56), Relief (8.99), Toronto (0.13) *O. basilicum*: Ekeonunwa (7.18), Relief (3.37), Toronto (0.17), while The average levels of metals in the soil samples ranked in descending order as follows: Fe > Mn > Zn > Cu > Al > Cd > Pb > Cr > Co > V > Li > Hg, while those in the vegetable samples followed the sequence: Fe > Mn > Zn > Cu > Al > Pb > Cd > Cr > V > Co > Li > Hg. Average metal concentrations were higher than FAO/WHO maximum permissible limits. Estimated Daily Intake (EDI) values for all metals were lower than their respective Reference Doses (RfD), Health Risk Index (HRI), Target Hazard Quotient (THQ), and Hazard Index (HI) values for both vegetables were significantly below 1, suggesting minimal risk from metal exposure. However, Target Cancer Risk (TCR) and Cumulative Target Cancer Risk (CTCR) assessments indicated a potential elevated cancer risk for individuals consuming these vegetables from areas where risk thresholds were surpassed. Preventative measures are recommended in these specific locations.

Introduction

It is paramount to emphasize the extent of contamination present in these food items, considering the crucial role of vegetables in the human dietary intake. As highlighted by Igwe and Echeme et al. (2013), Nigeria is abundantly blessed with a variety of edible and therapeutic flora. These botanical species serve as the primary reservoir of nourishment and healing agents (Igwe and Mgbemena, 2014). Understanding the levels of polycyclic aromatic hydrocarbon and trace metal contamination is crucial due to the utilization of these plants in the production of food and medicine, which includes *Vernonia amygdalina* and *Ocimum basilicum* (Borah and Deka, 2024). *V. amygdalina*, commonly known as bitter leaf, belongs to the Asteraceae botanical family. This perennial shrub can reach heights of up to 6 m and is predominantly distributed in tropical regions of Africa (Oyeyemi et al., 2018). Referred to locally as “onugbu,” it is a popular vegetable consumed and incorporated into various culinary delights in the Southeastern region of Nigeria. Moreover, *V. amygdalina* is frequently employed in traditional medicine for addressing conditions such as typhoid fever, yellow fever, diabetes, hypertension, stomach discomforts, seizures, abscesses, burns, and measles (Olorunfemi et al., 2012). Additionally, it is utilized for ailments like cancer, hiccups, urinary tract infections, menstrual cramps, anemia, skin inflammation, hemorrhoids, coughs, diarrhea, hepatitis, and cancer (Oyeyemi et al., 2018; Olorunfemi et al., 2012). *Ocimum basilicum*, commonly referred to as sweet basil, is a culinary and medicinal plant categorized under the *Lamiaceae* family (Dhama et al., 2021). Within

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Southeast Nigeria, it is identified by the local name "nchuanwu." Antimicrobial, antifungal, insecticidal, antiparasitic, antioxidant, anti-inflammatory, hepatoprotective, cardioprotective, neuroprotective, and anti-cancer properties are just a few of the health advantages associated with the plant (Dhama et al., 2021; Aminian et al., 2022).

Furthermore, it has been utilized in treating respiratory ailments. Polycyclic aromatic hydrocarbons (PAHs), typically solid and colorless, white, or light yellow in appearance, are pervasive organic contaminants (Abdel-Shafy and Mansour et al., 2016; Igwe et al., 2022; Igwe et al., 2022). These compounds are composed of multiple carbon and hydrogen atoms interconnected within aromatic rings. Studies suggest a carcinogenic nature of PAHs, indicating a potential link between PAH exposure and the rise in lung, skin, and bladder cancer incidents (Igwe et al., 2021). Human exposure to PAHs commonly transpires through the consumption of charred food, inhalation of polluted air, or ingestion of food tainted with PAH residues (Igwe et al., 2022; Igwe et al., 2022). Various sources of exposure include high-temperature cooking, combustion of organic substances, automotive emissions, and wildfires (Iwegbue et al., 2014). According to Ali and Khan (2018), trace metals are naturally occurring elements distinguished by their significant atomic mass and high density, which exceeds 5 g/cm^3. Certain trace metals, such as chromium, arsenic, cobalt, nickel, antimony, vanadium, and mercury, have been associated with endocrine disruption, cancer, mutagenesis, and teratogenic effects. Additionally, selenium, nickel, silver, copper, zinc, and other trace metals are also detected, with elements like cadmium and lead capable of damaging the central nervous system, affecting bone marrow, and leading to osteoporosis (Tchounwou et al., 2012; Koller and Saleh, 2018). Factors contributing to trace metal toxicity encompass paints, treated wood, mining tailings, industrial wastes, agricultural runoffs, occupational exposures, and mining activities (Igwe et al., 2021). The trophic transfer of trace metals in terrestrial and aquatic food chains and webs significantly impacts wildlife and public health. Once trace metals build up in agricultural soil, they create potential risks to the environment and also to the health of humans due to their not renewable and permanent nature (Muchuweti et al. 2006). In addition to the essential metals, vegetables can bioaccumulate additional metals in their edible and non-edible tissues, such as lead (Pb), chromium (Cr), copper (Cu), arsenic (As), cadmium (Cd), and nickel (Ni) (Singh et al. 2010).

In recent decades, the potential for harmful metals to bioaccumulate through polluted soil and water has made the contamination of ready-to-eat vegetables (RTE) by these metals a major worldwide concern (Khan et al. 2016). The rise in pollution has raised consumer concerns about safety worldwide, which has accelerated the need for safe food (Alam et al. 2018).

Industrial activities often release trace metals into the environment, leading to their accumulation in adjacent soil and water sources (Chouaieb et al., 2018; Gupta et al., 2018). Assessing their presence in plants helps evaluate the level of environmental contamination and monitoring their levels in edible plants is crucial for food safety (Guerrieri et al., 2024). Even at low quantities, elements like Cd, Hg, and Pb are extremely poisonous and non-essential; their buildup in the human body can cause serious health problems, including neurological and developmental diseases (Kim et al., 2012; Fasae and Abolaji, 2022; Wechselberger et al. 2023). A big information gap may result in bad policy decisions and undue consumer exposure (Golman and Loewenstein, 2018.). Therefore, a comprehensive risk evaluation is crucial to assess the hazardous metals present in these vegetables. The processes that lead to the accumulation of trace metals, especially mercury (Hg) and lithium (Li), and the associated health risks in samples of *Ocimum basilicum* and *Vernonia amygdalina* are poorly understood, despite the fact that plants are widely consumed in Africa. In Owerri, Imo state, in southeast Nigeria, two edible plants cultivated near polluted areas close to industrial markets were analysed for PAHs and trace metals. There exists a notable gap in information that could lead to suboptimal policy choices and unwarranted exposure of individuals. Consequently, our study was designed to explore the levels of trace metal and PAHs content and their potential effects on consumers of this vegetables in the top three densely populated industrial market cities, with the aim of bridging the aforementioned information deficit. This study's main goal was to quantify the levels of PAHs and trace metals (Al, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Pb, V, and Zn) in the soil sample and the two plants studied*,* *Vernonia amygdalina* and *Ocimum basilicum*. A variety of risk evaluation parameters, such as the bioaccumulation factor, estimated daily intake, contribution to provisional tolerated weekly intake, target hazard quotient, hazard index, and cancer risk, were calculated using the identified concentrations in order to address concerns regarding consumption safety. Additionally, the relationships between these components were also carefully examined.

Materials and methods

Study area

Geographically speaking, industrial/commercial markets is situated in Owerri, Owerri Municipal, Imo State in the southeastern part of Nigeria and is placed on latitude 05°25′30″N–05°27′20″N and longitude 07°01′00″E–07°03′00″E. Fig. 1 displays the study area and sampling locations. It is 120 acres in size and was established in 1981 for buying and selling of food produce. During the period from November to February, the prevailing weather conditions include Harmattan, characterized by dry coldness and dusty atmosphere (Abdullahi et al., 2009). From June to September, accompanied by sporadic extensions into October, the region experiences the rainy season. The average temperature in Owerri on a clear day ranges from a high of 31 °C (87 °F) to a low of 23 °C (71.8 °F), with an annual rainfall ranging from 17 mm (0.64 in) to 3200 mm (119.3 in) (Nnorom et al., 2020). Nighttime temperatures can drop to 20 °C (68 °F) while daytime temperatures can peak at 36 °C (96.8 °F). With an estimated population of approximately 1,160,000 (the current metropolitan area population in 2022) and covering an area of about 72 km^2 with an elevation of 205 m (673 ft), Owerri is situated in West Africa. The city is composed of three senatorial zones namely Owerri Municipal, Owerri North, and Owerri West. Owerri, in Imo State of Nigeria, is recognized as the largest urban centre and main commercial and industrial hub of south eastern Nigeria.

Sample collection

A total of 260 soil and two common vegetable species (*V. amygdalina* and *O. basilicum*) were collected randomly (in January-March 2023) from polluted areas near three industrial/commercial markets in the Owerri industrial zones of Imo state in South Eastern Nigeria (Fig. 1), employing standard sample techniques to evaluate the two leaves' PAH and Trace Metals concentrations (APHA, 2005). Furthermore, the sampling sites were closer to major highways. Vegetable samples were selected based on their availability for sampling, uniform distribution throughout the area, and their role in the locals' diet, seasonal vegetables were selected for sampling at different intervals and frequencies. A composite of vegetable samples, weighing one kilogramme each sample, was made from each sampling site. A taxonomist from Nnamdi Azikiwe University's Department of Botany in Awka recognised and verified the leaves. Following the vegetable's Voucher/Specimen number (NAU H. No. 132) for V. *amygdalina* and (NAU H. No. 188) for *O. basilicum*, the leaves were processed and delivered to the herbarium. As is customary during a typical cooking procedure, the samples were gathered and properly cleaned to remove any dust and air buildup using clean water. They underwent two more washing with distilled water after the inedible portions were disposed of and sliced into little pieces. The samples were ground with a sanitised mortar and pestle, homogenised, and allowed to air dry for fourteen (14) days in a hygienic setting to avoid additional contamination from the in-situ environment. Samples were then kept in sealed polythene bags at −21 °C for further analysis.

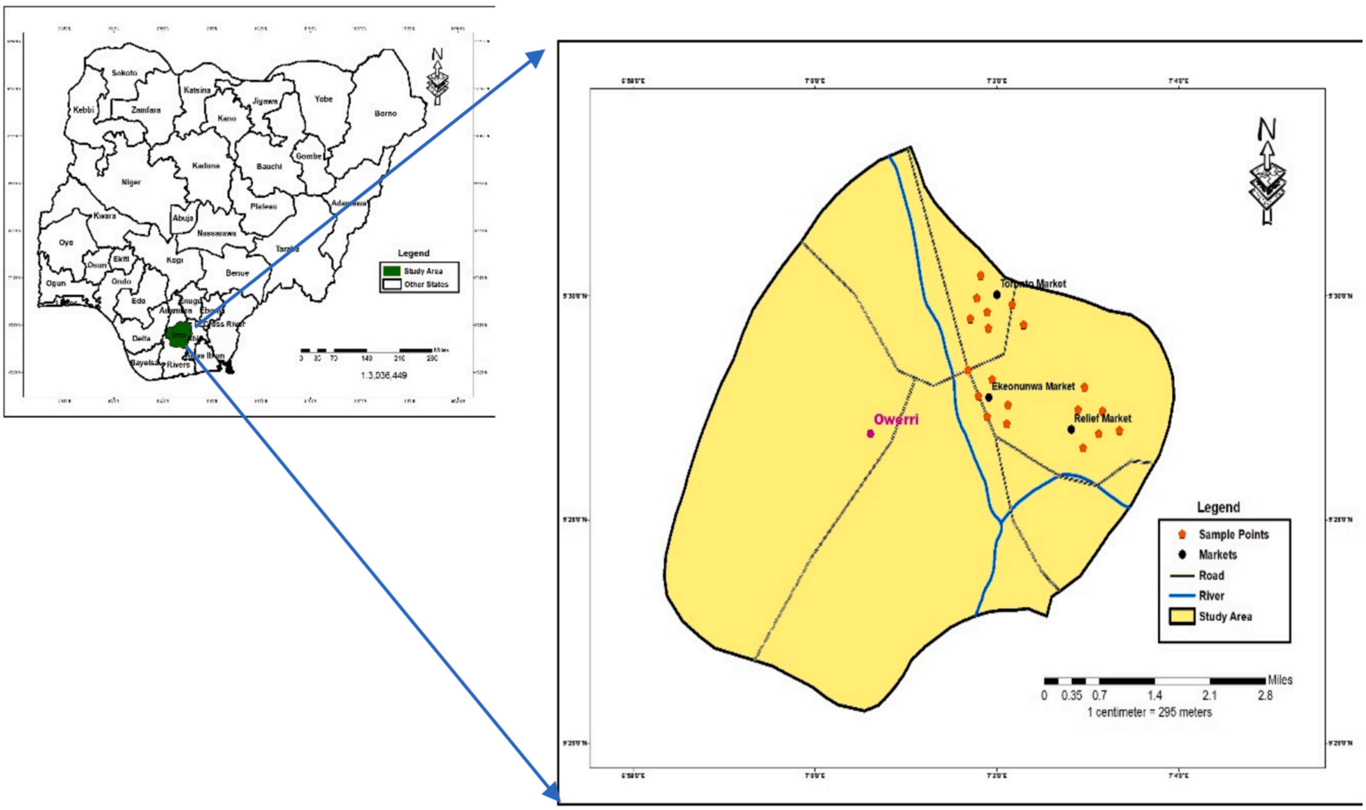

Fig. 1. Study region map displaying the sampling sites.

PAH extraction

Extraction of PAHs

The solid liquid extraction technique outlined by Al Nasir and Batarseh (2008) was used to prepare vegetable samples. In conclusion, a 500 mL Erlenmeyer flask was filled with 100 g of moist, homogenised vegetable samples. After adding 100 mL of acetone for the plants, the samples were left on a horizontal shaker overnight. Following an hour of shacking with 15 g of NaCl and 100 mL of cyclohexane, the liquid–liquid partitioning was completed. Before being put in a 250 mL Erlenmeyer flask, the analyte's organic layer was dried using 14 g of anhydrous sodium sulphate. After the extract was concentrated to 1 mL in a rotary evaporator, it was dried using a moderate N_2 gas stream. The residue was diluted in 3 mL of hexane, dried, and then redissolved in 5 mL of a 1:1 (v:v) ethyl acetate and cyclohexane combination. Lastly, a polytetrafluoroethylene (PTFE) microfiltration syringe was used to complete the cleanup. After the filtrate was concentrated to 1 mL, it was run over a 10 g deactivated alumina column that had been loaded with 3 g of anhydrous sodium sulphate. The substance was eluted with 50 mL of n-hexane and then reconcentrated to 4 mL with the help of a moderate nitrogen stream. In order to prepare for further HPLC analysis, the elute was subsequently divided into four portions and kept at −21 °C.

Instrumental analysis

An HPLC system (Waters, USA) was utilised to evaluate PAHs using a Waters PAH C18 column (4.8 mm × 250 mm, particle size 5 μm) and a fluorescence detector model DG90938259 (Khillare et al., 2012: Igwe et al., 2024). 50 % acetonitrile was kept for 7 min, 100 % acetonitrile was maintained until 29 min, and then there was a linear gradient to 50 % acetonitrile from 27 to 35 min. Acetonitrile and degassed water were supplied to the mobile phase in a gradient fashion (flux rate: 1.5 ml min–1). PAHs were quantified using the internal calibration approach, and they were identified by comparing their retention times to those of real standards. The sample injection volume was 20 μL, and the column oven was kept at a constant temperature of 36 °C. A blank sample was used to detect any contamination that might have happened throughout the course of the treatment. According to the following numbers, the fluorescence detector's excitation and emission wavelengths were supposed to be swapped at various frequencies: 256 and 260 nm for excitation, and 350, 430, and 480 nm for emission. Last but not least, the 18 PAH concentrations were arranged according to US-EPA priority using internal standards.

Quality assurance and quality control

Limit of detection (LOD), limit of quantitation (LOQ), blank, and standard spiked recoveries were used to verify the analytical procedure. Based on signal-to-noise ratios (S/N) of 4 and 10, respectively, Table 1 statistically assessed the resulting peak area, peak height, and retention length for both LOD and LOQ. A single standard solution was used to identify and quantify each chemical peak. A relative retention time method was used to make the identification. By comparing the peak regions of the samples with the standard solution, an external calibration approach was used to quantify the analyte. By using a statistical technique that took the analyte concentration in the sample into account, the LOD and LOQ of PAHs were determined.

Evaluation of the PAHs' risk

According to the USEPA (2007), risk assessment is the process of identifying the health hazards to people connected to exposures to pollutants through one or more exposure routes. This study evaluated the possible hazards that PAHs could present to human consumers of the vegetables using nutritional and carcinogenic methodologies.

Table 1
The analytical method's performance characteristics (n = 3).

Analyte	LOD (μg kg − 1 dry mass)	LOQ (μg kg − 1dry mass)	Average Recovery (%)	RSDr% range	Accreditation yes/no
TyB	0.1	0.4	104.2	0.2–10.1	no
NA	0.1	0.10	98.9	0.1–14.4	no
MyP	0.03	0.04	109.6	0.3–20.1	no
ACY	0.01	0.03	95.6	1.0–9.2	no
ACE	0.02	0.03	98.5	3.1–18.0	no
FL	0.04	0.08	99.4	0.1–8.1	no
PHEN	0.01	0.06	100.3	0.2–13.3	no
AN	0.04	0.6	100.4	0.2–9.1	no
FLUR	0.02	0.12	96.3	0.1–10.6	no
PY	0.1	0.03	103.3	0.3–9.5	no
BaA	0.01	0.4	94.7	0.2–8.7	no
Chry	0.02	0.04	100.1	0.1–11.4	no
Bbf	0.04	0.2	100.3	0.2–9.4	no
Bkf	0.02	0.6	98.5	0.2–10.3	no
BaP	0.1	0.08	88.4	0.4–18.4	no
dBAn	0.03	0.03	99.1	5.52–18.0	no
BPe	0.01	0.2	98.3	0.2–9.1	no
IcdP	0.1	0.3	100.2	0.5–6.4	no

Evaluation of dietary exposure

The general population's daily dietary exposure level to PAH4 was calculated using the formula in Eq. (1) (Wu et al., 2016).

$$E = C \times IR \quad (1)$$

Edogbo et al. (2020) determined that the daily intake rate of vegetables was 65 g/day. IR stands for daily intake rate of vegetables; E for daily dietary ΣPAH4 exposure level (ng/day); and C for PAH4 (the sum of benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, and chrysene) concentration in vegetables (ng/g).

Cancer risk assessment

The Margin of Exposure (MOE) method was used to evaluate the risk that exposure to PAHs, which can cause cancer or harm to genetic material, poses to humansIt is a ratio that evaluates the level of exposure to the target chemical and the dose at which a particular population first experiences a moderate but discernible negative effect (FSA, 2012).

$$MOE = \frac{BMDL_{10} \times BW}{E} \quad (2)$$

The lowest dose in Eq. (2) that is 95 % certain to result in no more than a 10 % incidence of cancer in animals is estimated by BMDL10 (benchmark dose lower confidence limit 10 %). For ΣPAH4, it was determined to be 0.34 mg/kg b.w./day (EFSA, 2008). The average body weight, or BW, for adults is 60.7 kg (Walpole et al., 2012). From a public health perspective, MOE > 10,000 is considered to be of low-risk concern (Rozentale et al., 2015).

Trace metals analysis

The samples were transported in plastic bags to the laboratory, where they were rinsed with distilled water after being cleaned with tap water and allowed to air dry at room temperature. After drying, the samples were homogenised, ground, and sealed in polyethylene zip bags for further analysis. All aqueous solutions were prepared using deionised water (19.1 MΩ cm^{-1}) from a Milli-Q system (Human Power 2 Plus, south Korea). They were all of the highest quality mineral acids and oxidants (HNO_3 and H_2O_2) (Wako Chemical Co, Japan).

Every piece of glassware and plastic was cleaned by rinsing it with deionised water after 15 h of soaking in a 15 % nitric acid solution. The Berghof speed wave, Germany, microwave closed system was employed for digesting. For total metal analysis, 0.2 g of the soil sample was treated with 1.7 mL 68 % HNO_3 (Kanto Chemical Co, Japan) and 4.7 mL 34 % HCl in a closed Teflon vessel and was digested in a Microwave Digestion System. For vegetable, 0.3 g of dried sample was digested with 5 mL 68 % HNO_3 and 2 mL 35 % H_2O_2 (Wako Chemical Co, Japan) in a Microwave Digestion System. After that, the digested soil and vegetable samples were put into a Teflon beaker, and Milli-Q water was added to get the volume up to 50 mL. The same procedure was used for a blank digest. The microwave system's digestion conditions were as follows: the temperature was raised to 180 °C in 8 min and maintained there for 6 min. Again, this procedure was carried out (Sarikurkcu et al., 2011).

Instrument optimization, performance evaluation and quality control

For trace metals, samples were analyzed using Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES) from PerkinElmer's ICP 7300DV and ICP 8300 except for the analysis of Hg which a Cold Vapour Atomic Fluorescence Spectrophotometer (CV-AFS) model PE-1000 (Nippon Instruments Corporation, Takatsuki Japan) was used. The optimized instrument parameters are presented in Supplementary Table S1. To check for efficiency in atomization, excitation and ionization processes in ICP, ionic (280.372 nm) to atomic (285.432 nm) lines intensity ratio of magnesium was used. The ratio obtained during the study was between 13.1 and 16.8. Method detection limit (MDL) was determined as described by EPA (1994) and presented in Supplementary Table 3S together with the corresponding wavelengths of detection. Each calibration used a minimum of four points over the concentration range of 0 – 500 and 0 – 5000 mg/L for trace elements. Calibration was linear and correlation coefficients for all elements were > 0.999. Samples and blanks were analysed, and each result reported (after auto blank subtraction) was an average of three replicate measurements. Oriental Basma Tobacco Leaves (INCT-OBTL-5), Certified Reference Material (CRM) provided by the Institute of Nuclear Chemistry and Technology in Poland, acted as quality control (QC) during the evaluation procedure as shown in Supplementary Table S2. Also, the accuracy of the equipment (ICP-OES 7300DV) was verified using validated Optima 8300 ICP-OES and spike recovery method. All these were done for quality control purposes. Result showed less than 5 % error for both equipment (Supplementary Table S3). Method precision was carried out by re-determining selected random replicate samples. The coefficient of variation was 1.79–4.37 %. The recoveries varied from 98 to 106 % (Supplementary Table S2).

Risk assessment parameters

In accordance with Ukaogo et al. (2024), the protocol included three groups of risk assessment parameters: intake estimation, non-cancer, and cancer risk parameter groups. The estimated daily intake (EDI), the contribution to the health risk index (HRI), and the provisional maximum tolerated daily intake (PMTDI) were all included in the first category (intake estimation risk assessment parameters). The second group consisted of the hazard index (HI) and target hazard quotient (THQ) (non-cancer risk assessment measures). In terms of cancer risk assessment metrics, target carcinogenic risk (TCR) is in the third category. The formulas utilised to determine the previously indicated values are included in the Appendix, together with a description of their overall importance (Wang et al., 2005; USEPA, 2007; USEPA, 2019; USEPA, 2010; USEPA, 2011; UNFPA, 2019; UNFPA, 2019).

Statistical analysis

Descriptive statistics were calculated using the data from every sample. Pearson's correlation coefficients were used to estimate the associations between the metal levels in the samples. To evaluate the variations in metal concentrations among samples, a one-way analysis of variance (ANOVA) was conducted with a significance level set at p <

0.05. All data analysis was conducted using Microsoft Office Professional Plus 2016 and the statistical software for social sciences (SPSS®) version 16 (SPSS Inc., USA). The sampling locations were identified using the Global Positioning System. It is important to note that only quantifiable values were used for statistical analysis, while values that were very low and below the MDL were labelled "zero.".

Results

PAHs concentrations in vegetables samples

PAH concentrations in leaves of *V. amygdalina* and *O. basilicum* that were collected from farmlands close to Ekeonunwa, the Relief, and Toronto industrial markets in Owerri city, respectively are shown in Tables 2. ΣPAH18 concentrations varied in leaves species of different farmlands. From highest to lowest, the Σ18 PAHs of vegetables (wet weight) were as follows: *V. amygdalina* close to Relief (8.99 mg/kg) > *O. Basilicum* close to Ekeonunwa (7.18 mg/kg) > *V. amygdalina* close to Ekeonunwa (5.56 mg/kg) > *O. Basilicum* close to Toronto (0.16 mg/kg). Some Σ18 PAHs of vegetables were below detection limit e.g 1,2,3-Trimethylbenzene, Naphthalene, 2-Methylnaphthalene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Acenaphthylene, Acenaphthene, Fluorene and Benzo[g,h,i]perylene in vegetable in close to Toronto market. Also, Pyrene and Benz[a]anthracene of *O. Basilicum* close to Ekeonunwa market were below detection limit. The mean concentrations of ΣPAHs ranged from 0.1 to 9.0 mg kg^{-1}, of which 0.16 mg kg-1 for *O. Basilicum* leaf samples from the Toronto market location was the lowest. The highest was 8 mg kg-1 for *V. amygdalina* leaf samples from the Relief market location. This result was consistent with some studies (Wu et al., 2016; Igwe et al., 2021). Table 4 shows the risk assessment for ΣPAH4 found in the vegetable samples. Levels of PAH4 exposure in the diet ranged from 3.25 to 165.75 ng/day.

Difference in the ratio of PAHs with various benzene rings

There were notable differences in the amounts of various benzene rings between the two leaves from distinct farming areas near industrial markets (Fig. 2). This proportion was comparable to earlier research (Tian et al., 2019; Dias et al., 2016).In overall, the material profiles were ruled by medium molecular- weight (MMW) PAHs, calculating for 71 %–89 %, and this portion was a lot higher than that of the stable high-molecular weight (HMW) PAHs, varying from 12 %-25 %; the low-molecular weight (LMW) PAHs content in the two vegetables of different farmlands close to industrial markets was very low. The physical and chemical characteristics of PAHs vary, perhaps because the compounds have varying vapour pressures (Tian et al., 2019). LMWPAHs are mostly found in gaseous form, although they are unstable and easily broken down (Ravindra et al., 2008).

Trace metal concentrations in soil

The trace element concentrations in the soil and vegetables (*V. amygdalina* and *O. basilicum* leaf) cultivated close to industrial markets are presented in Tables 5. The metal concentrations differed significantly between the vegetable species and geographical areas. The metal concentrations in soils are responsible for the variation in metal concentrations in vegetables. The concentration of total trace metals (Al, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Pb, V, Zn) in soil samples are presented in Tables 5. The order of average concentrations of trace metals in soils were of Fe > Mn > Zn > Cu > Al > Cd > Pb > Cr > Co > V > Li > Hg. Fe was found in the highest concentration among the study sites ranging from 440.600 ± 7.832 to 314.086 ± 4.045mg kg, while the lowest content was found for Hg ranging from 0.002 ± 0.001 to BDL over the study sites (Table 5). The average concentration of Al was twice of the Cu concentration. The content of Zn (0.133 ± 0.036 to 0.037 ± 0.002mg kg) was almost similar over the sampling sites except Ekeonunwa (*V. amygdalina*). The highest average Pb content was found in the Toronto (*V. amygdalina*) followed by Toronto (*O. basilicum)* and the lowest content was found in the Relief (*O. basilicum*). The average Cd content (0.167 ± 0.052mg kg) was varied over the study sites, while the range of Cd was from 0.433 ± 0.022 to 0.069 ± 0.001mg kg. The range of V and Li content in the study sites was 1.200 ± 0.002 to 0.061 ± 0.002mg kg and 0.007 ± 0.001 to 0.003 ± 0.001mg kg, respectively (Table 5). The highest mean Mn content was found in the Relief (*O. basilicum*) followed by Ekeonunwa (*V. amygdalina)* and the lowest concentration was found in the Ekeonunwa (*O. basilicum*).

Trace metal concentrations in vegetables

The mean concentrations of some trace metals in *V. amygdalina* and

Table 2
PAHs concentrations (mg kg^{-1}) in *V. amygdalina and O. Basilicum* leaf samples.

S/N	Contaminants	V. amygdalina			O. Basilicum		
		Ekeonunwa	Relief	Toronto	Ekeonunwa	Relief	Toronto
1	1,2,3-Trimethylbenzene	1.57 ± 0.06	0.87 ± 0.02	BDL	0.33 ± 0.04	0.02 ± 0.001	BDL
2	Naphthalene	BDL	0.63 ± 0.02	BDL	0.38 ± 0.02	0.03 ± 0.003	BDL
3	2-Methylnaphthalene	BDL	1.56 ± 0.01	BDL	0.59 ± 0.01	BDL	BDL
4	Acenaphthylene	BDL	0.56 ± 0.03	BDL	0.59 ± 0.03	0.10 ± 0.008	BDL
5	Acenaphthene	BDL	0.18 ± 0.02	BDL	0.86 ± 0.05	0.20 ± 0.009	BDL
6	Fluorene	BDL	0.16 ± 0.02	BDL	0.86 ± 0.01	0.20 ± 0.02	BDL
7	Anthracene	0.48 ± 0.01	0.25 ± 0.007	BDL	0.20 ± 0.02	BDL	BDL
8	Phenanthrene	0.58 ± 0.03	0.94 ± 0.01	BDL	0.37 ± 0.02	0.30 ± 0.01	BDL
9	Fluoranthene	0.83 ± 0.03	0.81 ± 0.03	BDL	0.51 ± 0.05	0.08 ± 0.002	BDL
10	Pyrene	0.05 ± 0.005	0.07 ± 0.0005	0.03 ± 0.002	BDL	0.40 ± 0.02	0.04 ± 0.001
11	Benz[a]anthracene	0.05 ± 0.008	1.79 ± 0.05	0.04 ± 0.002	BDL	0.05 ± 0.006	0.03 ± 0.004
12	Chrysene	0.84 ± 0.06	0.23 ± 0.008	0.01 ± 0.001	0.41 ± 0.03	0.20 ± 0.008	BDL
13	Benzo[b]fluoranthene	0.28 ± 0.007	0.25 ± 0.009	BDL	0.64 ± 0.01	0.70 ± 0.02	BDL
14	Benzo[k]fluoranthene	0.44 ± 0.01	0.39 ± 0.02	BDL	0.72 ± 0.02	0.06 ± 0.002	BDL
15	Benzo[a]pyrene	0.44 ± 0.03	0.28 ± 0.03	0.22 ± 0.01	0.72 ± 0.01	0.08 ± 0.007	0.05 ± 0.002
16	Diben[a,h]anthracene	BDL	0.04 ± 0.02	0.02 ± 0.001	0.03 ± 0.01	0.03 ± 0.004	0.02 ± 0.003
17	Indino[1,2,3-cd]pyrene	0.12 ± 0.001	0.14 ± 0.02	0.02 ± 0.001	0.6 ± 0.01	0.80 ± 0.01	0.02 ± 0.002
18	Benzo[g,h,i]perylene	BDL	BDL	0.01 ± 0.003	BDL	0.12 ± 0.01	ND
19	∑PAH4	1.61	2.55	0.05	1.77	1.03	0.08
20	∑PAH18	5.56	8.99	0.13	7.18	3.37	0.16

Values are means ± standard deviation of triplicate determinations. BDL means Below detection limit.

Table 4
Risk assessment of ΣPAH4 in the vegetable samples.

Risk Parameters	Ekeonunwa		Relief		Toronto	
	VA	OB	VA	OB	VA	OB
E (ng/day)	104.65	115.05	165.75	66.95	3.25	5.20
MOE	197,210	179,383	124,513	308,260	6,350,154	3,968,846

E = Dietary Exposure; MOE = Margin of Exposure, VA = *V. amygdalina*, OB = *O. basilicum*.

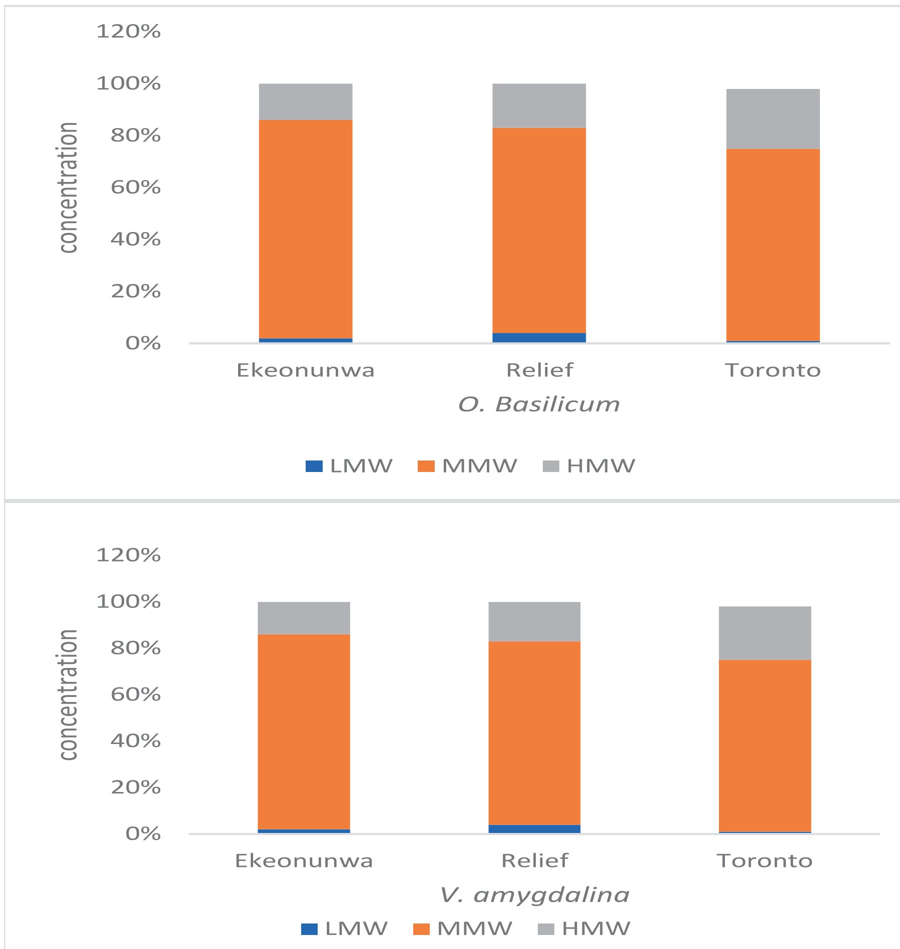

Fig. 2. Content ratios of different-ring PAHs in the leaves that were collected from farmlands close industrial markets in Owerri city.

O. basilicum leaf samples are presented in Tables 6. The results of the trace metals in the vegetable samples under the current study were compared with the guideline values of FAO/WHO and some other similar literature over the world. Fe was found in the highest concentration in the vegetables among the study sites ranging from 138.047 to 114.086mg kg-1. The content of Pb ranged from 3.920 to 0.123 mg kg −1, while the highest content of Pb was quantified in Toronto (*V. amygdalina*) and the lowest content was found in Ekeonunwa (*O. basilicum*). The content of Al, Cd, Co, and Mn were found in the range from 0.499 to 6.566, 0.147 to 0.633, 0.007 to 6.033, and 52.130 to 72.107 mg kg^{-1}. The *V. amygdalina* sample from Toronto market location recorded the highest Cd, Fe, Pb, V and Zn concentrations while Hg were BDL, the sample from Ekeonunwa recorded the highest Al, Cu and Mn concentrations while that of Relief location only recorded the highest mean concentration of Cr while Hg were BDL. On the other hand, *O. basilicum* sample from Toronto location also recorded the highest Cd, Co, Fe and Pb concentrations while Hg were BDL, that of Ekeonunwa location recorded the highest Cu, V and Zn concentrations while the sample from Relief location recorded the highest Al, Cr and Mn concentrations while Hg were BDL. Li and Hg recorded lowest values in all sites. Some of the vegetables under study had metal contents higher than the WHO-recommended thresholds (Table 6).

Bioaccumulation factor (BCF) of trace metals

A measure of a plant's capacity to take up metals from soil is called the bioaccumulation factor (BCF), which is the ratio of metals in the vegetable to metals in the soil which the plant grows on (Nnorom et al., 2020). Calculate the BCF coefficient of the trace metals using equation 3a in the supplementary material. Based on the analyses of the trace metals in the sampled *V. amygdalina* and *O. basilicum*, the greatest BCF values (1.00) for arsenic were found in Ekeonunwa, while the remaining elements accumulated in comparatively smaller ratios. The relevant outcomes are shown in Fig. 3. This demonstrates that arsenic, a non-essential metal with no apparent metabolic function, may be absorbed by vegetables (Kala, 2010). The results of our investigation align with

Table 5
Mean concentrations of trace metals (mg kg^{-1}) in soil samples.

Metals	*V. amygdalina*			*O. basilicum*			FAO/WHO,				
	Ekeonunwa	Relief	Toronto	Ekeonunwa	Relief	Toronto	2011 (mg/kg)	CCME	CEPA	(VROM, 2000[a])	(VROM, 2000[b])
Al	6.576 ± 0.354	6.399 ± 0.576	2.099 ± 0.052	5.599 ± 0.227	7.099 ± 0.329	2.413 ± 0.020	–	–	–	–	–
Cd	0.287 ± 0.032	0.267 ± 0.052	0.433 ± 0.022	0.269 ± 0.001	0.267 ± 0.077	0.419 ± 0.013	0.2	10	0.6	0.8	12
Co	0.011 ± 0.001	0.020 ± 0.001	6.011 ± 0.272	0.017 ± 0.001	0.022 ± 0.002	1.600 ± 0.090	50	50	–	9	240
Cr	0.099 ± 0.005	0.199 ± 0.021	0.148 ± 0.099	0.093 ± 0.002	0.133 ± 0.089	0.079 ± 0.002	1.3	64	200	100	380
Cu	67.597 ± 7.872	76.399 ± 3.212	45.973 ± 5.073	63.599 ± 0.446	74.367 ± 5.336	69.038 ± 3.020	73.3	63	200	36	190
Fe	314.086 ± 4.045	432.267 ± 5.775	440.600 ± 7.832	334.567 ± 1.945	412.267 ± 3.775	324.600 ± 3.802	425.5	–	–	–	–
Hg	0.005 ± 0.001	BDL	BDL	0.002 ± 0.001	BDL	BDL	–	2.0	–	–	–
Li	0.007 ± 0.001	0.005 ± 0.002	0.005 ± 0.002	0.003 ± 0.001	0.003 ± 0.002	0.005 ± 0.002	–	–	–	–	–
Mn	142.186 ± 3.034	162.147 ± 4.078	154.099 ± 3.001	137.027 ± 3.002	173.303 ± 4.039	183.033 ± 3.050	200	–	–	–	–
Pb	0.183 ± 0.055	0.340 ± 0.033	3.990 ± 0.009	0.127 ± 0.005	0.313 ± 0.073	0.990 ± 0.040	10	70	300	85	530
V	0.074 ± 0.007	0.061 ± 0.002	0.367 ± 0.002	1.200 ± 0.002	0.123 ± 0.005	1.067 ± 0.080	1.5	–	–		–
Zn	103.063 ± 5.001	112.076 ± 4.005	56.133 ± 0.036	108.073 ± 8.001	121.037 ± 4.002	73.068 ± 2.004	50	200	250	140	720

BDL = Below detection limit, Values are means ± standard deviation of triplicate determinations.
Chinese soil Guidelines (CEPA, 1995).
Canadian Environmental Quality Guidelines (CCME, 2003).
[a]Dutch soil quality standard (target value) (VROM, 2000).
[b]Dutch soil quality standard (intervention value) (VROM, 2000).

Table 6
Mean concentrations of trace metals (mg kg^{-1}) in vegetable samples.

Metals	*V. amygdalina*			*O. basilicum*			FAO/WHO, 2011(mg/kg)
	Ekeonunwa	Relief	Toronto	Ekeonunwa	Relief	Toronto	
Al	6.566 ± 0.23	6.319 ± 0.570	2.499 ± 0.050	4.509 ± 0.220	6.009 ± 0.320	1.413 ± 0.023	–
Cd	0.167 ± 0.013	0.147 ± 0.050	0.633 ± 0.020	0.159 ± 0.001	0.207 ± 0.070	0.319 ± 0.017	0.05
Co	0.007 ± 0.002	0.015 ± 0.001	6.033 ± 0.270	0.015 ± 0.001	0.027 ± 0.001	1.500 ± 0.090	–
Cr	0.079 ± 0.004	0.129 ± 0.020	0.133 ± 0.090	0.081 ± 0.002	0.130 ± 0.080	0.059 ± 0.005	2.3
Cu	21.567 ± 0.820	18.319 ± 0.210	32.933 ± 0.073	26.529 ± 0.406	21.360 ± 0.330	19.033 ± 0.028	40
Fe	110.086 ± 0.140	138.047 ± 0.075	130.600 ± 0.232	133.507 ± 0.905	132.067 ± 0.770	120.600 ± 0.832	425.5
Hg	0.003 ± 0.001	BDL	BDL	0.002 ± 0.001	BDL	BDL	–
Li	0.004 ± 0.001	0.003 ± 0.002	0.004 ± 0.002	0.003 ± 0.001	0.002 ± 0.001	0.003 ± 0.002	–
Mn	72.107 ± 0.030	65.107 ± 0.070	69.089 ± 0.001	70.026 ± 0.003	61.300 ± 0.030	52.130 ± 0.058	10
Pb	0.172 ± 0.050	0.311 ± 0.031	3.920 ± 0.089	0.123 ± 0.007	0.216 ± 0.070	0.950 ± 0.044	0.10
V	0.067 ± 0.006	0.047 ± 0.002	0.327 ± 0.032	1.000 ± 0.002	0.103 ± 0.003	1.057 ± 0.089	1.5
Zn	42.043 ± 4.001	31.013 ± 3.003	37.103 ± 3.086	46.083 ± 3.021	34.031 ± 4.002	43.066 ± 3.004	20

the mechanisms of metal bioaccumulation documented in the literature (Stihi et al., 2011; Turkekul et al., 2004; Radulescu et al., 2010; Gebrelibanos et al., 2016).

Health risks assessment of the trace metals

To find out how much of a health risk eating these trace metal-rich vegetables poses to the people of Owerri, the following variables were calculated: estimated daily intake (EDI), health risk index (HRI), target hazard quotient (THQ), hazard index (HI), and target carcinogenic risk (TCR) as shown in Supplementary material. The results of EDI of metals in the adult population are presented in Supplementary Table S4. Except for the EDI values of Pb in *V. amygdalina* from Toronto market location and that of V in *O. basilicum* from Ekeonunwa and Toronto market locations, all other EDI values of the metals in the vegetables from the different market locations are less than the reference oral dose (RfD) reported for the respective metals as shown in Supplementary Table S4 (USEPA, 2019). A reference dose is the US Environmental Protection Agency's maximum acceptable oral dose of a toxic substance (USEPA, 2007). The result of the EDI of metals for exposed population is presented in Table S4. The calculated EDI ranged between 0.0002 to 0.192 mg/kg with the highest EDI level recorded for Fe in *O. basilicum* close to Ekeonunwa market (0.192 mg/kg), while the lowest level of calculated EDI for Hg was recorded in *O. basilicum* (0.0002 mg/kg) close to Ekeonunwa market. The calculated EDI for Pb ranged between 0.000129 to 0.000357 mg/kg with the highest EDI level recorded in *O. basilicum* close to Toronto market (0.000357 mg/kg), while the lowest level of calculated EDI for Pb was recorded in *V. amygdalina* (0.000129 mg/kg) close to Relief market. The calculated EDI result for Al ranged between 0.0105 to 0.0000720 mg/kg with *O. basilicum* close Relief market. recording the highest level (0.0105 mg/kg), while the lowest level of calculated EDI for Co was recorded in *V. amygdalina* (0.000003 mg/kg)

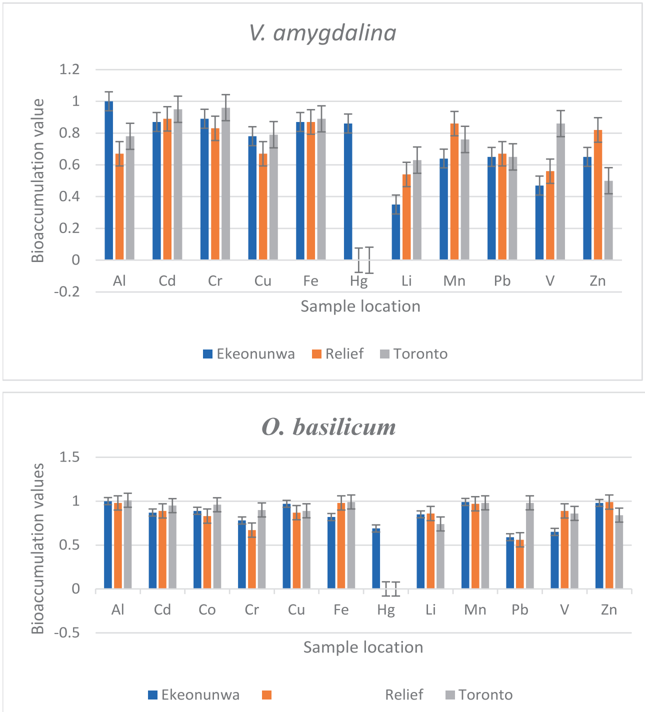

Fig. 3. Mean bio-concentration factors of trace metals.

close to Ekeonunwa market. The calculated EDI result for Li in the exposed population ranged from 0.000003 to 0.000006 mg/kg with the highest level recorded in *O. basilicum* (0.000006 mg/kg) close to Ekeonunwa market, while the lowest level of calculated EDI for Cu was recorded in *V. amygdalina* (0.00150 mg/kg) close to Ekeonunwa market. The calculated EDI result for Zn in the exposed populations ranged from 0.000054 to 0.000321 mg/kg with the highest recorded in *O. basilicum* close to Toronto market, while the lowest level of calculated EDI for Cr was recorded in *O. basilicum* (0.000035 mg/kg) close to Relief market. The result of the health risk index of metals in the vegetable samples is shown in Table S5. The HRI results for the metals detected in the *V. amygdalina* and *O. basilicum* samples are presented in Supplementary Table S5. The calculated HRI ranged between 0.0002 to 1.290 mg/kg with the highest HRI level recorded for V in *O. basilicum* close to Ekeonunwa market (1.290 mg/kg), while the lowest level of calculated HRI for Hg was recorded in *V. amygdalina* (0.0002 mg/kg) close to Relief market. The HRI values of the metals in the vegetables from the various market locations are all much lower than 1, with the exception of the Pb HRI values in *V. amygdalina* from the Toronto market location (1.220) and the V HRI values in O. basilicum from the Ekeonunwa (1.290) and Toronto market (1.143) locations. A population that is exposed to metals is considered safe if their HRI is less than 1, and unsafe if their HRI is greater than 1. Except for *V. amygdalina* from the Toronto location and *O. basilicum* from the Toronto and Ekeonunwa locations, where susceptibility to Pb and V poisoning is high, respectively, the exposed population surrounding the research region is therefore not at any danger of trace metal poisoning. The result of the THQ and HI is shown in Table S6. The THQ result of Pb in population ranged from 0.00008 to 0.89210 mg/kg with the highest level recorded in *O. basilicum* (0.225 mg/kg) close to Relief market while the lowest level was recorded in *V. amygdalina* (0.00008 mg/kg) close to Ekeonunwa market. Cadmium ranged from 0.82135 to 0.14244 mg/kg with *V. amygdalina* close to Ekeonunwa market recording the highest level, while the lowest level of Pb was recorded in *O. basilicum* (0.05600 mg/kg) close to Ekeonunwa market. Li ranged from 0.00012 to 0.00347 mg/kg with *V. amygdalina* close to Relief market recording the highest value, while the lowest level of Mn was recorded in *V. amygdalina* (0.0033 mg/kg) close to Toronto market. Cr ranged from 0.01178 to 0.08318 mg/kg with *O. basilicum* close to Toronto market recording the highest level, while the lowest level of Fe was recorded in *V. amygdalina* (0.00076 mg/kg) close to Ekeonunwa market. The summation of THQ is HI. Since the symptoms of diseases induced by many heavy metals may be similar, it is vital to account for the HI as well. Potential health issues are indicated by HI greater than 1, while potential health issues are indicated by HI less than 1. The result of the HI values ranged from 0.96872 to 2.01421 mg/kg with the highest HI value recorded in *V. amygdalina* (2.01421 mg/kg) while the lowest HI was recorded in *V. amygdalina* (0.96872 mg/kg) close to Relief market. The result of the HI shows that all the HI values were greater than one (>1) with the exception of *V. amygdalina* (0.96872 mg/kg) close to Relief market which recorded a value less than <1. Supplementary Table S7 lists the target carcinogenic risks (TCR) and cumulative target carcinogenic risks (CTCR) of Pd, Cd, and Cr resulting from vegetable diet. The vegetables' TCR values for Pb and Cd varied from 2.46-E07 in *O. basilicum* to 3.63-E05 in *V. amygdalina*, 4.03-E05 in *O. basilicum* to 6.80-E05 in *V. amygdalina*, and 5.30-E05 in both vegetables to 1.07-E04 in *V. amygdalina*, respectively.

Correlation analysis

A regression-based correlation analysis was performed in order to determine the likely sources of contamination for the vegetable samples under examination and to investigate the relationship between the trace metals. The correlation coefficient values between the levels of metals are shown in Table 7.

Al has good correlations with Fe, Zn, Cd, and Cu, as seen by their respective regression coefficients (r) of 0.70, 0.65, 0.40, and 0.33. With r values of 0.41 and 0.45 for Pb and Cd, respectively, Fe is demonstrating a strong association with these elements. Given that iron and aluminium are the most common crustal elements, it is likely that the contamination of these elements (Al, Fe, Zn, Cu, and Cd) in these samples comes from the crust of the earth. Additionally, Mn exhibits a strong association with Cu, Co, and Cr; Zn with Cu; Cu with Mn, V, and Zn; Zn with Co; Cr with Hg; and Li with Pb. This implies that there are numerous sources of contamination for these metals, such as crustal pollution, the use of contaminated water for farming, the use of pesticides and fertilisers, air particulate matter, industrial emissions, waste disposal, human activities, etc.

Discussion

PAHs concentrations in vegetables

According to these findings, the highest PAHs were found in the V. *amygdalina* sample from the Relief market location, which was followed by the Ekeonunwa and Toronto market locations. The highest PAHs were found in the *O. basilicum* sample from the Ekeonunwa market location, which was followed by the Relief and Toronto market locations. Because there are more automobile activities and traffic around Ekeonunwa and Relief market areas, there may be more PAHs in *V. amygdalina* and *O. basilicum* from those locations. Notably, the Toronto market location was purposefully selected as a study area to more or less act as a background because it is the most remote. Therefore, it should come as no surprise that the samples taken from there contained the fewest PAHs. Higher levels of PAH18 were found in a *Talinum triangulare* leaf sample collected from the Good-morning, Afule, and Ahiaohuru marketplaces in the city of Aba, according to Igwe et al. (2021). According to Igwe et al., (2022); Igwe et al., (2022), the leaf sample of Piper guineense from Orieugba market ranged from 96.85 to 289.25 ng/day, while that of Isigate market in Umuahia, Abia State, Nigeria, ranged from 14.30 to 507.65 ng/day. All of the samples containing PAH4 had MOE values greater than 10,000 when the EFSA-established BMDL10 value of 0.34 mg/kgbw/day, a daily vegetable diet of 65 g per person, and an adult body weight of 60.7 kg were used.

Table 7
Correlation metrix trace metal concentrations of the plant and soil samples.

	Al	Cd	Co	Cr	Cu	Fe	Hg	Li	Mn	Pb	V	Zn
Al	1											
Cd	0.40	1										
Co	0.24	0.10	1									
Cr	0.25	0.25	0.22	1								
Cu	0.33	0.20	0.22	−0.08	1							
Fe	0.70	0.45	0.30	0.25	0.10	1						
Hg	0.31	0.30	0.18	0.33	0.25	0.24	1					
Li	0.32	0.24	0.31	0.26	0.10	0.25	0.24	1				
Mn	0.60	−0.20	0.51	0.40	0.46	0.09	0.25	0.24	1			
Pb	0.21	0.31	0.34	−0.01	0.31	0.41	−0.01	0.32	0.24	1		
V	0.27	0.25	0.21	−0.05	0.42	0.31	0.26	−0.12	0.25	−0.03	1	
Zn	0.65	0.40	0.27	0.21	0.60	0.32	0.31	0.26	0.30	0.25	−0.09	1

This indicates that there was little health concerns connected to vegetable samples from the farms close to the industrial markets. According to Igwe et al. (2021), daily dietary exposure levels for *Talinum triangulare* and *Piper guineense* derived from farms close to marketplaces in the city of Aba varied from 0.00 to 259.35 ng/day. The MOE values in the majority of the categories were less than 10,000, suggesting a certain cancer risk with regard to PAH4, according to the paper by Wu et al. (2016), which examined PAH concentrations in vegetables across age groups.

Trace metal concentrations in soil

The prominent industrial activity noted at the sites of industrial markets was tanning facilities, lead melting, battery repairs and charging, metal processing, automobile workshops etc. The results of the trace metals in soil under the current study were compared with the guideline values of FAO/WHO, the Canadian Environmental Quality Guidelines, Dutch soil quality standard and Chinese soil quality (Table 5) (FAO/WHO, 2011; CCME, 2003; VROM, 2000; CEPA, 1995) as well as the various experimental outcomes from previous studies (Wiseman et al., 2013; Tiwari, et al., 2011; Ding et al., 2019; Bahrami et al., 2019; Ahammed et al., 2024; Igwe et al., 2024). However, the metal content in the studied agricultural soil close to industrial markets was found higher than most of the recommended values provided by FAO/WHO except Pb and Cd content (Table 5) (FAO/WHO, 2011). For instance, all of the locations had Pb contents that were higher than the FAO/WHO limit, which is deemed detrimental to organisms, but lower than the Canadian Environmental Quality Guidelines (CCME, 2003) and Chinese soil guidelines (Grade II) (CEPA, 1995). However, the average Pb value was regarded as mildly to moderately contaminated agricultural soil near industrial markets (VROM, 2000). All of the research soils contents that were lower than the Chinese soil guideline (Grade II) (CEPA, 1995), Dutch soil quality standard (VROM, 2000), Canadian Environmental Quality standard (CCME, 2003), and FAO/WHO, (2011) as shown in Table 5. Compared to other sites, the Pb value at the Ekeonunwa site was lower, suggesting that industrial waste had no effect on the farm that grew vegetables. The dumping of garbage from several battery manufacturers in Owerri city may be connected to the lead pollution in the agricultural soil under investigation near industrial marketplaces (Proshad et al., 2019). Following the breakdown of industrial waste that contains Pb and Cd, a significant amount of these metals may be released. The content of Al, Fe, Hg, Li, Mn, V, Co, Cr, and Zn did not exceed the standard limit established by various quality assurance agencies worldwide (Table 5), suggesting that these metals did not have any detrimental effects on humans (CCME (Canadian Council of Ministers of the Environment), 2003; CEPA, 1995; VROM, 2000. The lower content of these metals in the farm soil may be linked to the lack of heavy industrial activities, which can release a significant portion of these metal-containing garbage, in the Owerri industrial areas (Proshad et al., 2019). The Cu concentration of the sampling point of Ekeonunwa, Relief, and Toronto was more than the guideline value, indicating a risk to the organisms; the remaining sites were classified as mildly to moderately contaminated. The Zn concentration in the Ekeonunwa and Relief sites was lower than the other organisational norm but greater above the standard established values of (FAO/WHO, 2011). Although the higher Zn concentrations in the soils from all sites indicated mild to moderate contamination, the biological system was not yet harmed by these levels (VROM, 2000). When compared to agricultural soils, the values of every metal under study were significantly lower at the Toronto site. Because of the big highway road between them, the reduced trace metal content suggests that industrial activities had little effect on the vegetables' growing farm. The current study results have been compared with the past investigation on agricultural soil over the world (Toronto, Canada; Gujarat, India; Tongling, China; Ahvaz, Iran; Khulna, Bangladesh; Aba, Nigeria) (Wiseman et al., 2013; Tiwari, et al., 2011; Ding et al., 2019; Bahrami et al., 2019; Ahammed et al., 2024; Igwe et al., 2024). The average concentration of Cd in our study was 0.419mg kg, which was lower than the cultivated soil values of Toronto of Canada (0.51 mg kg), Tongling of China (0.48 mg kg), Gujarat of India (19.25 mg kg), Aba of Nigeria (0.433 mg kg) (Wiseman et al., 2013; Tiwari, et al., 2011; Ding et al., 2019; Igwe et al., 2024). The Pb concentration in our study (0.340mg kg) was lower than Toronto of Canada (13 mg kg), Tongling of China (85.1 mg kg), Gujarat of India (13.12 mg kg), Ahvaz of Iran. (8.31 mg kg). Aba of Nigeria (1.120 mg kg) (Wiseman et al., 2013; Tiwari, et al., 2011; Ding et al., 2019; Bahrami et al., 2019; Igwe et al., 2024). The Zn concentration in our study (121.037mg kg) was higher than Gujarat of India (85.36 mg kg), Ahvaz of Iran. (109.3 mg kg). Aba of Nigeria (4.033 mg kg) (Tiwari, et al., 2011; Bahrami et al., 2019; Igwe et al., 2024). On the other hand, other trace metals content was lower than the agricultural soil of Toronto, Canada; Gujarat, India; Tongling, China; Ahvaz, Iran; Khulna, Bangladesh and Aba, Nigeria (Wiseman et al., 2013; Tiwari, et al., 2011; Ding et al., 2019; Bahrami et al., 2019; Ahammed et al., 2024; Igwe et al., 2024).

Trace metal concentrations in vegetables

Our present research on metal levels in plants also found that these levels were higher than the trace metal content found in other regions of the world (Echem and Kabari, 2012; Kntapo et al., 2018; Ashraf et al., 2021; Wang et al., 2005; Singh et al., 2010; Kalagbor et al., 2014; Islam et al., 2016; Wu et al., 2016; Ding et al., 2018; Igwe et al., 2024). Kalagbor et al. (2014) reported trace metals concentrations (mg/kg) in *V. amygdalina* obtained from a cottage farm in Port Harcourt, Rivers State, Nigeria, as follows: Cr = 2.25, Mn = 37.25, Co = 2.25, Cu = 8.00, Cd = 1.5, Zn = 90.50 and Pb = 6.25. These values are very high compared to the values obtained in this study except for Mn. Also, Echem and Kabari, (2012) reported mean concentrations of Fe, Pb, Cr and Zn in *V. amygdalina* grown along Aba-Port Harcourt Road in eastern Nigeria as 2.960, 0.220, 0.030 and 0.890 mg kg^{-1} respectively, except for the value of Fe which is much lower than what is reported herein, other values are somewhat similar to what is reported in this study. Furthermore, Kntapo et al. (2018) reported the concentrations of Fe and

Zn in *O. basilicum* obtained from Kaduna State in Nigeria as 0.577 and 0.034 mg kg^{-1} respectively which is lower than present study. Furthermore, these industrial markets' activities release significant amounts of trace metals from these wastes, which then build up in the soil and raise the concentration of heavy metals in the vegetables that are grown (Proshad et al., 2018). Lastly, the results of this study provide a strong message to the local population: the foods grown near industrial markets are unsafe for human consumption. Igwe et al. (2024) discovered that growing urbanization and industrialisation was the cause of the elevated levels of Al, Fe, Pb, Cd, Mn, and Zn in polluted areas near three commercial markets in Aba industrial districts, Abia state, in southeast Nigeria. The recovery rates for Oriental Basma tobacco leaves varied from 98 % to 106 %. Three triplicate CRM sample results were used to evaluate the precision, which is displayed in Supplementary Table S2.

Health risks assessment of the trace metals

To find out how much of a health risk eating these trace metal-rich vegetables poses to the people of Owerri, the following variables were calculated: estimated daily intake (EDI), health risk index (HRI), target hazard quotient (THQ), hazard index (HI), and target carcinogenic risk (TCR). The results of EDI of metals in the adult population are presented in Supplementary Table S4. Except for the EDI values of Pb in *V. amygdalina* from Toronto market location and that of V in *O. basilicum* from Ekeonunwa and Toronto market locations, all other EDI values of the metals in the vegetables from the different market locations are less than the reference oral dose (RfD) reported for the respective metals as shown in Supplementary Table S4 (USEPA, 2019). A reference dose is the US Environmental Protection Agency's maximum acceptable oral dose of a toxic substance (USEPA, 2007). This indicates that the adult population is not at risk of the adverse effects of these metals except in *V. amygdalina* from Toronto market location where the population is susceptible to Pb poisoning and also in *O. basilicum* from Ekenunwa and Toronto market locations where the population is susceptible to V poisoning. Mitigation measures are therefore required in these areas. In a prior study, Zafarzadeh et al., (2018) found that the HRI values for Zn, Cd, Pb, and Cu in vegetables from Iran's Golestan Province were less than 1. Supplementary Table S6, provides the THQ values that were acquired throughout this investigation. The exposed population is unlikely to suffer negative health consequences if the THQ is less than 1, and vice versa (USEPA, 2010). All other THQ values of the metals in the vegetables from the various market locations are less than 1, with the exception of Pb in V. *amygdalina* from the Toronto market location (1.221) and V in *O. basilicum* from the Ekeonunwa (1.284) and Toronto market (1.143) locations. The combined metals' non-carcinogenic danger potential is assessed using the HI. The exposed population may have negative health impacts if the HI value is higher than 1, in which case mitigation actions are necessary (Wang et al., 2005). Both the *V. amygdalina* sample from the Toronto market location and the *O. basilicum* sample from the Ekeonunwa and Toronto market locations have HI values greater than 1. Therefore, when these veggies are consumed, the population in these areas is exposed to the cumulative danger effects of these trace metals. Pb, Cd and Cr have been reported as known carcinogenic agents (USEPA, 2010). According to Al Amin et al., (2020), the TCR is the likelihood that a person would get cancer during their lifetime as a result of being exposed to carcinogens. A TCR value of between 10^{-6} and 10^{-4} indicates an increased risk of developing cancer. A value above 10^{-4} which is the upper limit of the range indicates lifetime cancer risk to population who consumed contaminated foods (Al Amin et al., 2020). The TCR values of Pb in the studied vegetables are below the upper limit (10^{-4}) which implies a no-lifetime-cancer-risk due to Pd poisoning to the population around the study areas. Except for the TCR values of Cd in *V. amygdalina* from Toronto market location (1.76-E04) and in *O. basilicum* from Relief (1.09-E04) and Toronto (1.71-E04) market locations, all other TCR values for Cd are below the upper limit (10^{-4}). For Cr, only the TCR value in *V. amygdalina* from Relief market location insignificantly exceeded the upper limit (1.07-E04). Furthermore, it was believed that the total of the individual trace metal risks would represent the cumulative cancer risk resulting from consuming a specific type of vegetable that exposes one to many carcinogenic trace metals (Sultana et al., 2017). While the CTCR values of Cd and Cr in the investigated vegetables and places are all above the threshold cancer risk level, the CTCR values of Pb in the investigated vegetables and locations are below it. According to the TCR and CTCR of the vegetables under study, there may be a carcinogenic risk to the local population at the locations where the threshold risk limit was surpassed; as a result, mitigation measures are needed there.

Conclusion

From the results of this study, we gained better knowledge regarding accumulation and potential health risks of trace metals and polycyclic aromatic hydrocarbons in soils and vegetables cultivated close to industrial markets in Owerri. There are no health hazards for the people who consume *V. amygdalina* and *O. basilicum* in the research locations based on the samples' PAHs level. This study also showed that the soils from the farms were polluted with Cd and Pb but the other metals were within their respective safe limits for agro soils; Pb and Cd concentrations in vegetables exceeded the respective FAO/WHO. The population living close to locations where the threshold risk limit was surpassed may be at risk for cancer based on the TCR and CTCR of the examined vegetables. Overall, the results of this study indicate a definite impact of industrial emissions on vegetables grown in the vicinity and the associated health risks. Data from this study support the potential contribution of urban plants to reducing industrial waste and vehicle emissions, two issues that remain very concerning. Seasonal variation, might be sampled in the future, and analysis and correlations are drawn.

CRediT authorship contribution statement

Prince O. Ukaogo: Writing – review & editing, Writing – original draft, Supervision, Investigation, Data curation. **Okenwa U. Igwe:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization. **Ogechi C. Nwankwo:** Validation, Software, Resources, Project administration, Formal analysis. **Chisom Friday:** Visualization, Software, Investigation, Data curation. **Eluu H. Oko:** Validation, Resources, Funding acquisition, Formal analysis, Conceptualization. **Oluebube F. Ezenwafor:** Writing – review & editing, Writing – original draft, Methodology, Investigation.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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