Investigation of Hydrocarbon Marker (PAHs) Resulting from Anthropogenic Inputs of Some Selected Vegetables in Saudi Arabia

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ABSTRACT

This study investigated Polycyclic Aromatic Hydrocarbons (PAHs) contamination in fresh and processed vegetables from three Saudi Arabian cities: Hail, Qassim, and Kharj. Local market vegetable samples were analyzed using solid phase and Soxhlet extraction methods, followed by GC-MS analysis. Total PAH concentrations ranged from 5.85 to 23.66 ng g^{-1} dw, with the highest concentration found in Qassim potato peels (23.66 ng g^{-1} dw) and the lowest in Kharj cabbage (5.85 ng g^{-1} dw). The predominant PAH species identified were FI, DBA, BbF, and BaP. PAH ratios indicated that combustion-derived PAHs were dominant across all samples, suggesting high levels of carcinogenic compounds. The findings highlight potential health risks for local populations and organisms in these regions. The study emphasizes the importance of environmental monitoring and recommends implementing regular assessment protocols for these contaminants throughout Saudi Arabia to address public health concerns and mitigate potential risks to human health and the broader ecosystem environment.

Keywords: PAHs, Vegetables, Anthropogenic inputs, Carcinogenic, Diagnostic ratios, Saudi Arabia.

INTRODUCTION

The assessment of environmental hazards associated to different food items is an important research topic for human health. Due to their nutritional value, vegetables are one of the foods

that people eat, and their contamination could pose a threat to a significant portion of the population (Sharma and Nagpal, 2020; Pavlíková *et al.,* 2023). The three most dangerous types of pollutants that may affect vegetables are pesticides, heavy metals, and PAHs (Tusher *et al.,* 2021).

Inefficient burning of garbage and fossil fuels produces the persistent organic pollutants, or PAHs. Although they have both anthropogenic and natural origins, much of their development may be attributed to the latter. They are abundant in the soil, water, and air and can persist for decades. Benzo (a) anthracene (BaA), dibenzo (ah) anthracene (DBA), benzo (k) fluoranthene (BkF), benzo (b) fluoranthene (BbF), and benzo (a) pyrene (BaP) are among the PAHs that have been the subject of extensive research on its carcinogenic chemical class (Hu *et al.,* 2018). PAHs are pollutants found in a variety of foods.

Environmental contamination and food processing are the main sources of PAHs in food. It is widely known that dietary exposure to PAHs can result in elevated levels of DNA adduct, mutations, and genetic alterations, in addition to a variety of cancers (Nie *et al.,* 2014; Ewa and Danuta, 2017; Sampaio *et al.,* 2021).

Since eating vegetables is the main way that individuals in Saudi Arabia are exposed to PAHs, experts and local officials have raised serious concerns about PAH contamination in vegetables grown in rural areas. Saudi Arabia produces a wide range of fruits and vegetables for both local consumption and export to neighboring nations (Ashraf and Salam, 2012).

The potential for agricultural output in Saudi Arabia is limited, nevertheless, due to a lack of arable land and renewable water. As the Gulf's biggest oil producer, Saudi Arabia is constantly involved in petrochemical production, refining, and exploration. It appears that the main reason for the high levels of PAHs in the environment is the widespread usage of fossil fuels in all facets of life. Haider *et al.,* (2020) and Kim *et al.,* (2013). Yet to date, Saudi Arabia has not taken any concrete steps to determine the levels of PAHs in vegetables cultivated in agricultural fields. The potential damage that oil exports may cause to individuals as well as the environment is one of the most concerning issues (Ashraf *et al.,* 2013).

In light of the prevalence of risks of PAHs to the environmental and human health, the current study intends to evaluate and highlight the current understanding regarding the traits, consequences, and hazards related with the presence of these pollutants in the local vegetables.

MATERIALS AND METHODOLOGY

Sampling

The five types of vegetables including potatoes, carrots, lettuce, cabbage, and mint were chosen from the markets in Hail, Al-Qassim, and Al-Kharj in Saudi Arabia. Ten vegetable samples were collected, and the sampling description is displayed in Table 1. To determine the recent PAH inputs, fresh vegetable samples were acquired from non-commercial requests; extra attention was taken to collect the samples in the Hail, Al-Qassim, and Al-Kharj regions. The vegetables are weighed to obtain their initial weight (wet weight). The vegetable samples are then dried in an oven at a specific temperature, often around 95°C, typically 30 h, to ensure complete water removal. This temperature is chosen to evaporate water without damaging the organic components of the sample. Prior to being homogenized in a blender mill, the samples were cleaned, peeled, and then chopped into small pieces.

Prior to being analyzed using a gas chromatography with a mass spectrometer detector (GCMS), the samples were carefully labeled and allowed to air dry before being placed in freezer-safe bags at 4°C (Zakaria *et al.,* 2006; Masood *et al.,* 2021; Alkhadher *et al.,* 2023 a,b,c; Magam *et al.,* 2024).

Table 1: The description of vegetables utilized in this study

Sample	Types	Part 1	Part 2	Description of site	DMC (%)
PPH	Potato	-	Peels	Hail	2.8
PCH	Potato	Cores	-	Hail	21.6
PPQ	Potato	-	Peels	Qassim	3.0
PCQ	Potato	Cores	-	Qassim	21.9
CPH	Carrot	-	Peels	Hail	1.2
CCH	Carrot	Cores	-	Hail	5.2
CPK	Carrot	-	Peels	Kharj	1.1
CCK	Carrot	Cores	-	Kharj	4.9
LTH	Lettuce	Total	-	Hail	7.4
LTQ	Lettuce	Total	-	Qassim	7.2
CTH	Cabbage	Total	-	Hail	6.1
CTK	Cabbage	Total	-	Kharj	6.2
MTH	Mint	Total	-	Hail	2.9
MTQ	Mint	Total	-	Qassim	2.7

DMC: Dry Matter Content

Chemicals Analyses

Hexane, dichloromethane (DCM), acetone, methanol (MeOH), ethanol, cyclohexane, isooctane (HPLC grade), and sodium sulphate were all supplied by E. Merck. Deionized, twice-distilled water was used during the experiment. To eliminate water, weighted sodium sulphate (Na_2SO_4) was baked for four hours at 400°C in a muffle furnace. It was then cooled in a desiccator and kept for later use in an oven set at 120°C. To eliminate water, 60-200 mesh size silica gel (SIL-A-200) was baked for 6 h at 400°C and subsequently for 4 h at 200°C. Before being kept in a desiccator for use in the two-step column chromatography, the dried silica gel was allowed to cool (Takada and Ishiwatari, 1992; Alkhadher *et al.,* 2020 a,b).

An aluminum container was filled with vegetable samples and anhydrous sodium sulphate (Na_2SO_4) to dry them. The dried material has been well mixed and is now prepared for use in the subsequent Soxhlet extraction stage. 50 g of congenial vegetal material was mixed with 250 mLof a 3:1 v/v dichloromethane (DCM): n-hexane and 100–150 g of hot anhydrous sodium sulfate. After that, the mixture was put in cellulose thimbles that had been cleaned beforehand and left in a Soxhlet extraction for eight to ten hours (Magam *et al.,* 2016; Ghasemi and Keshavarzifard, 2022).

Teflon is used to seal the attachment portions of the device to stop leaks. To keep the target compound from sunlight, the device is wrapped in aluminum foil once the attachment portion has been sealed. Once the Soxhlet extraction process is finished, it is let to cool at room temperature for ten minutes. The extract volume is reduced to 1 mL using a rotary evaporator before being moved to the pear-shaped flask for fractionation analysis.

According to Alkhadher *et al.,* 2022; Hartmann *et al.,* (2000), Zakaria *et al.,* (2000), Zakaria *et al.,* (2001), Boonyatumanond *et al.,* (2006), Qi *et al.,* (2014), and Sharifi *et al.,* (2022), the concentrated extract was purified using column chromatography on silica gel. In short, silica gel and anhydrous sodium sulfate were completely packed inside a 1.5 cm glass column (7.5 cm by 2 cm) in the uppermost section of the column.

To elute the PAH extraction, 75 milliliters of methylene chloride were utilized. The clean extract was diluted in 2 mL of n-hexane after being evaporated using a moderate nitrogen flow. Finally, the samples are assessed using GC-MS. The extracted PAH chemicals were measured by GC-MS in a GC (7890A) interfaced with an HP-5MS fused-silica capillary column of 30-m length, 0.25-mm internal diameter, and 0.25-m film thickness, and a C5975 quantum-selective quadrupole detector (SIM mode) with split/splitless injector. The carrier gas (He) was high-purity helium at a steady pressure of 100 kg cm^{-2}.

A 1 μL aliquot of each purified sample extract was added to the GC-MS using an injector. After two minutes at 70°C, the GC-MS temperature program ramped up at a rate of 30°C per minute until it reached 150°C. After 15 min, the temperature was raised to 310°C at a rate of 4°C per minute.

Prior to the samples were analyzed, a PAHs standard combination consisting of 11 compounds and the internal injection standard were injected into a GC-MS. PAHs compounds were identified by comparing their retention durations in the samples to those of the compounds in the reference mixture. The 5 mg/L standard solution used for GC-MS calibration is represented by the chromatogram.

Dibenzo (a, h) anthracene (DBA), Fluorene (Fl), Pyrene (Py), Benzo (a) anthracene (BaA), Chrysene (Chr), Phenanthrene (Phe), Anthracene (Ant), Benzo (b) fluoranthene (BbF), Benzo (k) fluoranthene (BkF), Benzo (a) pyrene (BaP), and Acenaphthylene (Acy) were the eleven PAH congeners that were analyzed in each sample. The documented carcinogenicity of five of these PAH congeners and the availability of standards were the basis for their selection (Orif *et al.,* 2023).

Using this technique, the recoveries of PAHs from vegetables were examined by analyzing vegetable samples that had been spiked at the level of five-time limitations. The samples were spiked with the PAH standards after the homogenization step. Peak IDs were confirmed by running samples and standards under identical conditions (Zhong & Wang, 2002).

Statistical analysis

The mean values and outcomes from all parameters (Cronbach's Alpha) and Mean separation were compared using SPSS® 2018 in combination with a descriptive statistical analysis technique. The least significant difference (L.S.D.) value was used to split means at ($P<0.05$) and

determine whether there was a significant difference between means using the SPSS program version 18.

RESULTS AND DISCUSSION

PAHs Distribution and Concentration in the Vegetables

The samples utilized in this investigation were meticulously selected to encompass a broad spectrum of hydrocarbon sources, specifically polycyclic aromatic hydrocarbons (PAHs), within the Hail, Qassim, and Kharj municipalities in Saudi Arabia. The quantification of individual PAH concentrations in the aforementioned cities is delineated in Table 2. The findings indicate that the highest PAH concentration is observed in the vegetable sample of Potato peel from Qassim (PPQ), while the lowest total PAH concentration is recorded in the Cabbage from Kharj (CTK) at 23.66 ng g^{-1} and 5.85 ng g^{-1}, respectively. This disparity can be attributed to the clearly influence of anthropogenic activities in the predominantly urbanized region of Qassim, coupled with the spatial dynamics of urban development; conversely, the lower PAH concentration in the vegetable sample is sourced from a locale distanced from human-induced emissions.

The overall PAH content, as illustrated in Table 2, reveals that peel vegetables such as potato and carrot exhibit the highest concentrations, whereas cabbage and lettuce demonstrate relatively diminished levels, indicating that the peels are subject to greater contamination than their respective cores. Lise *et al.,* (2002) have documented elevated benzo(a)pyrene (BaP) concentrations in Danish potato, lettuce, and carrot with their peels. Leafy vegetables, including mint, lettuce, and cabbage, were subjected to analysis, with mint exhibiting the highest PAH concentrations at 20.97 ng g^{-1}, surpassing all vegetable cores. Similarly, cabbage presented comparable values at 20.84 ng g^{-1}. These observations suggest that the accumulation of airborne PAHs is markedly enhanced due to the extensive surface area of mint and cabbage leaves. According to the Food and Agriculture Organization/World Health Organization (FAO/WHO), airborne PAHs are deposited on crops, particularly those characterized by broad foliage (JECFA, 2005).

Benzo(a)pyrene (BaP) exhibited superior concentrations relative to other PAH congeners across all vegetable samples, as evidenced in Table 2. As delineated in Table 2, the highest concentration of BaP was identified in mint at 16.08 ng g^{-1} dry weight (dw) from the Qassim region, followed by carrot peel from Kharj at 12.69 ng g^{-1} dw, and lettuce from Hail at 11.20 ng g^{-1} dw, with the lowest BaP concentration detected in lettuce from Qassim at 2.90 ng g^{-1} dw. Regarding Fluorene (Fl), the data indicated that the highest concentration was present in potato peel from Hail at 10.8 ng g^{-1}, followed by potato peel from Qassim at 1.18 ng g^{-1} dw and mint at 1.05 ng g^{-1} dw, while the lowest levels were recorded in lettuce from both Hail and Qassim areas at 0.03 ng g^{-1} dw (Table 2). In terms of Phenanthrene (Phe), the results indicated that the highest concentration was found in carrot core from Hail at 0.64 ng g^{-1} dw, followed by potato core from Hail at 0.45 ng g^{-1} dw and mint from Qassim at 0.32 ng g^{-1} dw, whereas the minimum concentrations of Phe were observed in carrot peel, cabbage, and lettuce from Kharj and Qassim regions, respectively, at 0.01 ng g^{-1} dw. For Anthanthrene, the high outcomes showed that the highest level was found in carrots peel in Kharj with 0.26 ng g^{-1} dw, while there were no concentrations found of Ant was located in potato core in Qassim area (Table 2).

As for Pyrene (Py), the results showed that the highest value of Pyrene was located in mint in Hail area with 3.52 ng g^{-1} dw, followed by potato core in Qassim area with 2.72 ng g^{-1} dw. While 0.06 ng g^{-1} dw of Py, the lowest level, was discovered in potato cores in the Hail area. As for Benzo[a]anthracene (BaA), the results showed that the highest value of BaA was located in potato peel in Qassim area with 8.47 ng g^{-1} dw followed by carrots peel in Hail area with 1.02 ng g^{-1} dw, while the minimum level of BaA was found in cabbage in Kharj area with 0.09 ng g^{-1} dw (Table 2). For Anthanthrene, the elevated results indicated that the peak concentration was identified in carrot peels from Kharj, measuring at 0.26 ng g^{-1} dw, whereas no detectable concentrations of Anthanthrene were observed in the core of potatoes within the Qassim region (Table 2).

Regarding Pyrene (Py), the findings revealed that the maximal concentration of Pyrene was detected in mint from the Hail region, quantified at 3.52 ng g^{-1} dw, succeeded by the potato core in the Qassim area, which presented a concentration of 2.72 ng g^{-1} dw. Conversely, the lowest concentration of Pyrene, measured at 0.06 ng g^{-1} dw, was identified in potato cores within the Hail area. Concerning

Benzo[a]anthracene (BaA), the data indicated that the highest concentration was recorded in potato peels from the Qassim area at 8.47 ng g^{-1} dw, followed by carrot peels in the Hail region with a concentration of 1.02 ng g^{-1} dw, while the minimum concentration of BaA was found in cabbage within the Kharj area, measured at 0.09 ng g^{-1} dw (Table 2).

For Chrysene (Chr), the results indicated that the highest concentration was detected in mint from the Hail area, quantifying at 4.84 ng g^{-1} dw, followed by cabbage in the Hail area with 1.46 ng g^{-1} dw, while no measurable concentration was found in carrot peels within the Hail area. The findings further indicated that Benzo[b]fluoranthene (BbF) exhibited its highest

concentration in carrot peels from the Hail area at 8.94 ng g^{-1} dw, while lowest concentration was noted in mint from the Hail area, recorded at 0.39 ng g^{-1} dw.

It was also demonstrated that Benzo(k) fluoranthene (BkF) reached its highest concentration in cabbage from the Hail area at 0.11 ng g^{-1} dw, whereas its lowest concentration was observed in carrot cores from Kharj, potato cores from Hail, and mint from Hail, all at 0.01 ng g^{-1} dw. Additionally, the concentration of Dibenzo(a,h)anthracene (DBA) was observed at its highest level in carrot peels from the Hail area, recorded at 3.34 ng g^{-1} dw, with its lowest concentrations found in lettuce from the Al Qassim area at 0.21 ng g^{-1} dw (Table 2 and Figure 1).

Table 2: Average PAH values in samples from the vegetable (ng g^{-1})

Samples	Acy	Fl	Phe	Ant	Py	BaA	Chr	BbF	BkF	BaP	DBA	∑PAHs	∑LMW PAHs	∑HMW PAHs	LMW/ HMW[1]	STD[2]
PPH	0.11	10.8	0.02	0.06	0.07	0.99	1.2	0.95	0.04	6.36	1.55	22.16	11.06	11.1	1	3.439
PCH	0.03	0.56	0.45	0.29	0.06	0.21	0.78	2.33	0.01	3.87	2.89	11.49	1.39	10.1	0.14	1.343
PPQ	0.51	1.18	0.07	0.04	0.86	8.47	0.91	1.03	0.06	9.45	1.07	23.66	2.67	20.99	0.13	3.4
PCQ	0.09	0.19	0.05	ND	2.72	0.28	0.11	0.79	0.02	3.8	0.28	8.35	3.06	5.28	0.58	1.279
CPH	1.02	0.04	0.05	0.07	0.08	1.02	ND	8.94	0.1	7.72	3.34	22.38	1.26	21.12	0.06	3.275
CCH	0.07	0.58	0.64	0.16	2.39	0.21	0.72	1.02	0.08	7.31	0.86	14.06	3.85	10.21	0.38	2.106
CPK	0.12	0.08	0.01	0.26	0.22	0.23	0.97	0.84	0.05	12.69	1.25	16.72	0.68	16.03	0.04	3.729
CCK	0.03	0.06	0.02	0.03	0.11	0.23	0.63	0.62	0.01	6.57	0.62	8.93	0.26	8.67	0.03	1.927
LTH	0.45	0.03	0.31	0.11	0.13	0.56	0.4	3.38	0.06	11.2	0.52	17.15	1.03	16.11	0.06	3.335
LTQ	0.09	0.03	0.01	0.02	0.82	0.12	0.14	1.78	0.03	2.9	0.21	6.15	0.97	5.19	0.19	0.943
CTH	0.17	0.09	0.05	0.08	0.06	0.82	1.46	5	0.11	10.86	2.15	20.84	0.44	20.39	0.02	3.33
CTK	0.06	0.14	0.01	0.01	0.44	0.09	0.24	0.82	0.03	3.53	0.49	5.85	0.65	5.2	0.13	1.026
MTH	0.23	1.05	0.2	0.02	3.52	0.16	4.84	0.39	0.01	7.18	0.63	18.21	5.01	13.21	0.38	2.427
MTQ	0.11	0.66	0.32	0.03	1.49	ND	0.26	0.44	0.02	16.08	1.54	20.97	2.61	18.35	0.14	4.734

[a]Abbreviations for PAH compounds in this study: Acenaphthylene (Acy), Fluorene (Fl), Phenanthrene (Phe), Anthracene (Ant), Pyrene (Py), Benzo (a) anthracene (BaA), Chrysene (Chr), Benzo (b) fluoranthene (BbF), Benzo (k) fluoranthene (BkF), Benzo (a) pyrene (BaP) and Dibenzo (a, h) anthracene (DBA).
[1]LMW/HMW = Ratio of ∑ of the concentrations of PAHs (from Acy to Py) divided by ∑ of the concentrations of PAHs (from BaA to DBA).
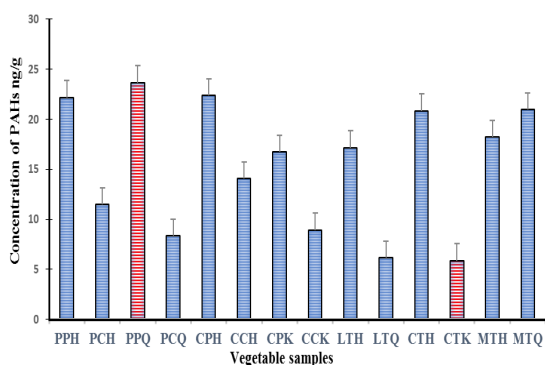[2]STD = Standard Deviation, ND: not detected

Fig. 1. The average concentrations of PAHs in a certain area's produce

Source of PAHs in Vegetables

Anthropogenic sources represent a significant origin of polycyclic aromatic hydrocarbons (PAHs). These anthropogenic sources can be fundamentally categorized into two distinct classifications: petrogenic PAHs and pyrogenic PAHs. Numerous methodologies exist to distinguish between pyrogenic and petrogenic PAHs, including the categorization based on low- and high-molecular-weight classifications (Yang, 2000; Guinan *et al.,* 2001; Zakaria *et al.,* 2003; Masood *et al.,* 2016; Masood *et al.,* 2018; Asfaram *et al.,* 2020). In the present investigation, we employed the

low/high (L/H) molecular weight ratio to ascertain the origins of PAHs.

A plethora of studies have demonstrated that the ratio of low molecular weight (LMW) to high molecular weight (HMW) PAHs can serve as a reliable indicator for determining the origins of anthropogenic PAHs, predicated on their structural characteristics and spatial distribution. (Zakaria *et al.,* 2002; Sakari *et al.,* 2010; Mirsadeghi *et al.,* 2013; Nozar *et al.,* 2014; Karyab *et al.,* 2014; Asfaram *et al.,* 2020). Whereas non-combustion sources, such as crude oil and fuel oil, predominantly comprise LMW PAHs, specifically 2-ring and 3-ring PAH compounds, petrogenic PAHs, pyrogenic PAHs, or pyrolytic PAH substances are primarily characterized by the presence of HMW PAHs, including 4-, 5-, and 6-ring PAH compounds. (Mai *et al.,* 2002; Zakaria *et al.,* 2002; Bouloubassi *et al.,* 2012). Generally, an LMW to HMW PAH ratio exceeding 1.0 indicates petrogenic contamination, whereas a ratio falling below 1.0 signifies a pyrogenic PAH source (Magi *et al.,* 2002; Qiao *et al.,* 2006; Chen and Chen, 2011; Masood *et al.,* 2016; Masood *et al.,* 2018; Asfaram *et al.,* 2020).

In the current study, the values of the LMW/HMW PAHs within a sample of vegetables varied from 0.02 to 1.00 (refer to Table 2). Furthermore, the results indicate that all vegetable samples contained PAHs originating from combustion processes. The LMW/HMW PAH ratios across all vegetable samples collected from different sites in Saudi Arabia (Hail, Qassim, and Kharj) were found to be ≤ 1.0 (see Fig. 2). These results underscore the predominance of HMW PAHs and illustrate that the combustion-derived PAHs identified in urban air particulate matter, which exhibited a high concentration of HMW PAHs, exerted a considerable adverse effect on the vegetable samples (namely, 4-, 5-, and 6-ring PAHs). It is plausible that the prevailing winds in these cities may have transported pyrogenic PAHs from air particles enriched in HMW PAHs to the vegetable stores and agricultural fields; however, additional research is essential to substantiate this hypothesis.
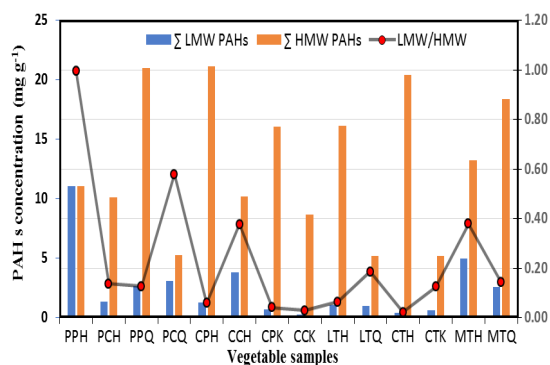

Fig. 2. Comparison between the concentrations of the LMW and the HMW PAHs in the vegetable samples of in selected cities in north-western Saudi Arabia (Hail, Qassim and kharj)

Evaluation of the Diagnostic Ratio for PAHs

Utilizing indicators that calculate precise ratios of specific concentrations of polycyclic aromatic hydrocarbons (PAHs) within the samples, it becomes feasible to identify the probable causes of PAH emissions into the atmosphere (Tsymbalyuk *et al.,* 2002; Yunker *et al.,* 2002; Soclo *et al.,* 2002; Masood *et al.,* 2016; Masood *et al.,* 2018). The researchers employed various PAH ratios to accurately delineate the origins and sources of PAHs in the course of this study. Empirical evidence supports the assertion that petrogenic and pyrogenic sources of PAHs can be effectively differentiated through the analysis of parent PAH ratios as well as alkylated PAH ratios, which are predicated upon the relative abundance of distinct PAHs or PAH groupings (Zakaria *et al.,* 2002; Yunker *et al.,* 2002; Mirsadeghi *et al.,* 2013; Keshavarzifard *et al.,* 2014; Keshavarzifard *et al.,* 2015; Masood *et al.,* 2018; Asfaram *et al.,* 2020). In order to assess the environmental risks associated with PAHs, it is imperative to ascertain their origins and potential sources within the environment. The anthropogenic release of PAHs can be elucidated through the understanding of both petrogenic and pyrogenic origins.

In the present study, the researchers discerned that the ratios depicted in the cross plots for the low molecular weight (LMW) to high molecular weight (HMW) and the toxic equivalent of PAH carcinogenicity (TEQ PAHcarc) in the vegetable samples were consistently lower than or equal to 1. Regarding the correlation of LMW/HMW in relation to TEQ PAHcarc being less than or equal to 1, the researchers concluded that the PAHs observed in all vegetable samples were primarily derived from

pyrogenic sources (Fig. 3). The LMW/HMW ratios, ranging from 0.02 to 1.00, corroborate this finding (Table 2), thereby revealing the predominance of HMW (combustion-derived PAHs) over LMW PAHs in the majority of the vegetable samples.
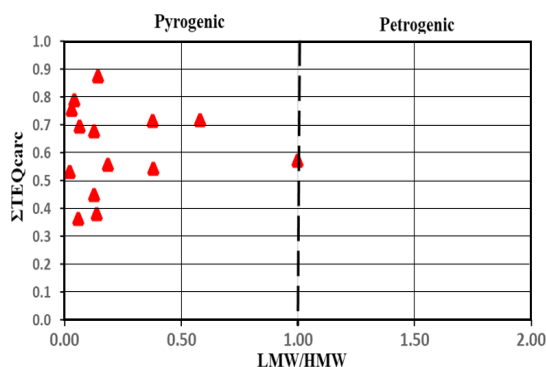

Fig. 3. PAH cross plots for the ratios of LMW/HMW vs. TEQ PAHcarc

The principal origins of PAHs in food are attributed to food processing activities and environmental contamination. PAHs predominantly accumulate in plants due to the deposition of airborne particles onto exposed surfaces. Given that gaseous deposition is considered the primary mechanism through which PAHs are introduced, low concentrations of PAHs can adhere to the surfaces of fruits and vegetables via surface adsorption, with these PAHs, which precipitate from the atmosphere, posing a risk of surface contamination. The levels and characteristics of PAHs present in surrounding fruits and vegetables have been shown to be influenced by emissions resulting from fossil fuel combustion (Zhong and Wang, 2002; Paris *et al.,* 2018).

Nevertheless, there have been specific instances in which a correlation between concentrations of polycyclic hydrocarbons in soil and plants has been identified, indicating a plausible pathway for soil contamination to reach plant roots. Vegetables constitute the primary component of the Saudi diet, and as such, it is posited that food serves as the principal route through which individuals are exposed to PAHs (Ashraf *et al.,* 2013).

The primary factor contributing to the escalation of polycyclic aromatic hydrocarbons (PAHs) in adjacent ecosystems appears to be the pervasive utilization of fossil fuels across numerous aspects of daily existence. Root vegetables, including Solanum tuberosum (potatoes) and Daucus carota (carrots), exhibited elevated concentrations of these toxic compounds, whereas Brassica oleracea (cabbage) and Lactuca sativa (lettuce) demonstrated comparatively lower levels. It was observed that all vegetable peels were found to harbor greater contamination than the edible inner portions. The intake of these hazardous substances can be mitigated through the removal of the outer layers of root vegetables and leafy greens. Certain studies have indicated that due to the substantial surface area of the leaves of lettuce and cabbage, the uptake of the aforementioned hydrocarbons from the atmosphere was significantly augmented (Zhong and Wang, 2002).

One contributing factor to the proliferation of these compounds is the processes of cooking, heating, and cigarette smoking conducted in outdoor environments. Additionally, vehicular emissions represent another source of PAHs present in indoor dust within the Kingdom of Saudi Arabia. The policy decision by the Saudi Arabian government to reduce reliance on coal as a principal energy source for electricity generation further exacerbates the prevalence of these compounds. The practice of burning coal and straw for culinary purposes is prevalent in rural locales, leading to elevated PAH concentrations in rural dust. Previous research has established that cigarette smoking is a predominant contributor to indoor PAH levels. (Ashraf *et al.,* 2013; Alamri *et al.,* 2021).

The predominant source of PAHs identified within domestic dust may be attributed to the natural gas utilized for cooking purposes. Various factors contributing to the rising levels of PAHs in Saudi Arabia include oil spills in aquatic environments, extensive use of fossil fuels, incomplete combustion of fossil fuels, wood and coal combustion, automobile emissions, energy generation, refuse incineration, climatic changes (notably heavy rainfall), industrial wastewater discharge (with industrial sources of PAHs encompassing oil refineries, establishments employing solid and liquid hydrocarbon feedstocks for the production of chemical by-products, plastic manufacturing industries, and high-temperature furnaces), domestic sewage, and runoff from roadway surfaces (Ashraf *et al.,* 2013; Alamri *et al.,* 2021; Masood *et al.,* 2021).

Factors contributing to the reduction of PAHs in Saudi Arabia encompass photodegradation (photo-oxidation). Moreover, various methodologies have been implemented to eliminate PAHs from aquatic environments, including chemical oxidation, microbial degradation, and volatilization. The presence of hydrophobic pollutants in aquatic systems is moderated through their sorption to naturally occurring particulates, with solubility emerging as a critical characteristic influencing the reduction of PAHs, as their solubility exceeds that of alkanes of comparable molecular weight. Additionally, temperature variations can influence the aqueous solubility of PAHs. The molecular weight of these substances is among the primary determinants for their reduction. It is noteworthy that not all PAH compounds present in petroleum are amenable to degradation, as certain compounds exhibit considerable resistance to degradation processes (Saeed *et al.,* 2011).

The city of Hail is characterized by a notably weak dispersal factor, attributable to insufficient precipitation, the spatial planning of buildings over extensive areas, and the expansion of thoroughfares. Over the past century, urbanization and industrialization have precipitated a swift escalation in emissions, resulting in heightened atmospheric pollution within Hail. A significant local pollution load, including PAHs, has been caused by the region's low wind speed, high emission rate, and frequent reversals. Consequently, one of Saudi Arabia's most polluted megacities is Hail. It would seem reasonable to assume that urban environments have higher levels of particulate matter than rural ones, given that the majority of PAH sources are found in or around metropolitan regions. PAHs can be discharged into the atmosphere in two different states: a solid phase where they bind to particulate matter and a vapor phase. (2016) Abdel-Shafy and Mansour.

Toxicity Equivalents of PAHs in the Vegetables

Benzo(a)pyrene represents a significant constituent of polycyclic aromatic hydrocarbons (PAHs) that arise as a consequence of the incomplete combustion of fossil fuels or organic materials. This compound exhibits both carcinogenic and mutagenic properties, with human exposure to benzo(a)pyrene occurring through various mediums such as smoke, air, water, and food sources.

The overall concentration of benzo(a)pyrene in vegetables serves as an indicator of their potential toxicity (Norramit *et al.,* 2005).

Benzo(a)pyrene was employed as a reference point for the assessment of PAHs in food items, particularly concerning carcinogenic PAHs. In accordance with the guidelines established by the European Commission's Health and Consumer Protection Directorate-General in 2002, the ratios of the concentrations of [PAH]/[B(a)pyrene] in food products are observed to range from 0.5 to 1.10. The comparative quantities of both carcinogenic PAHs and the total PAHs are depicted in Figure 4.
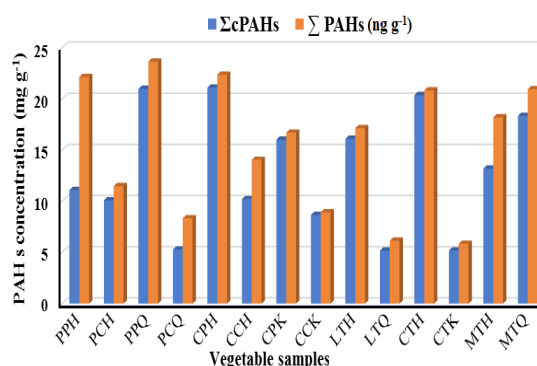

Fig. 4. Comparison levels between total PAHs and carcinogenic PAHs in vegetable samples

In this investigation, the potential carcinogenicity of the analyzed vegetable samples was assessed based on the aggregate concentration of polycyclic aromatic hydrocarbons (PAHs) with recognized cancer-causing properties (cPAHs), specifically identified by the United States Environmental Protection Agency (US EPA) as including dibenzo[a,h]anthracene (DBA), benzo(a)pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (IcdP), and chrysene (CHR) (Bojes and Pope, 2009). The findings derived from the current study indicate that the carcinogenic compounds such as BaP (2.90-16.08 ng g^{-1}), BbF (0.39-8.94 ng g^{-1}), and DBA (0.21- 3.34 ng g^{-1}) are the predominant constituents across all vegetable samples, as detailed in Table 3.

As demonstrated in Fig. 5 and 6, it is feasible to ascertain the proportional contribution of each individual PAH towards the carcinogenic activity within each vegetable sample, based

on the calculated benzo(a)pyrene equivalent (BaPeq) values for each specific carcinogenic PAH. According to Table 3, the samples of Qassim mint, Kharj carrot, and Hail cabbage and lettuce exhibit notably elevated [PAH]/[B(a)pyrene] ratios of 16.08, 12.69, 10.86, and 11.20 respectively, signifying that these samples are predominantly influenced by benzo(a)pyrene. The dominance of benzo(a)pyrene in these samples raises concerns regarding potential human health risks, as this compound possesses a significant cancer-causing potential upon consumption of the vegetables. Conversely, the samples of Qassim lettuce, Kharj cabbage, as well as Qassim and Hail potatoes, manifest lower values for the [PAH]/[B(a)pyrene] ratio, indicating that the PAH concentrations are more pronounced in these samples and are thereby governed by the overall PAH concentration. In contrast to the aforementioned higher [PAH]/[B(a)pyrene] ratio values, these samples appear to be less affected by benzo(a)pyrene, which may suggest a correlation with other PAH compounds (Norramit *et al.,* 2005).
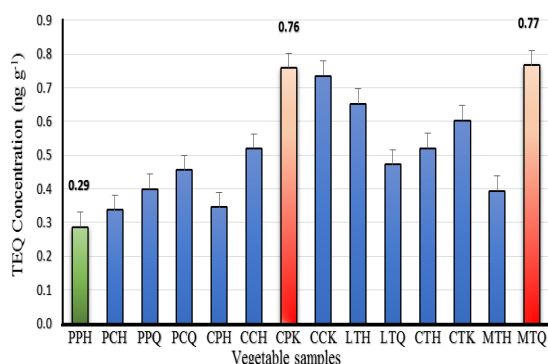

Fig. 5. The TEQs of total toxic BaP equivalent for all 11 PAH compounds

To evaluate the carcinogenic potential of polycyclic aromatic hydrocarbons (PAHs) present in the vegetable samples, their toxicity equivalency quotient (TEQ) in relation to benzo[a]anthracene (BaA) was calculated. The assessment of the potential toxicological impact of PAHs in sediment matrices has been effectively accomplished utilizing the toxic equivalence factor (TEF) methodology, initially articulated by Nisbet and LaGoy (1992), wherein toxicity is expressed with reference to the standard benzo[a]pyrene (BaP) (Sprovieri *et al.,* 2007).

All specimens examined in this investigation had their PAH TEQs and carcinogenic PAH TEQs (TEQcarc) computed, with the results delineated in Table 4 and Fig. 5 and 6. As illustrated in Fig. 5 and 6, the TEQ values for the PAHs exhibited variability throughout the sampling period, ranging from 0.29 to 0.77 ng TEQ/g. The highest TEQ values were recorded for Qassim mint (0.77 ng TEQ/g) and Kharj carrot (0.76 ng TEQ/g), both of which were collected from the regions of Qassim and Kharj. These samples signify a substantial influence from petrogenic and combustion-related sources, attributed to urbanization and vehicular emissions in proximity to agricultural areas in Qassim and Kharj. Conversely, the minimum TEQ value (0.29 ng TEQ/g) was detected in Hail potato peel, situated in an urban zone adjacent to farming regions characterized by minimal pollution levels.
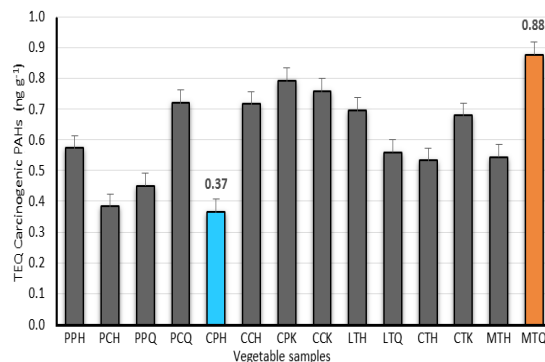

Fig. 6. The TEQs of total toxic BaP equivalent for potential carcinogenic PAHs

The cumulative toxicity equivalency quotients of the carcinogenic PAHs (TEQcarc) ranged from 0.37 to 0.88 ng TEQ/g, thereby constituting over 90% of the total PAH TEQ. The peak TEQcarc values (0.88 ng TEQ/g) were identified in Qassim mint, whereas the TEQcarc values for the Kharj carrot samples were recorded at 0.79 ng TEQ/g. When juxtaposed with findings from pertinent prior studies, the TEQcarc values derived from this research are generally lower than those reported in samples collected from dust-affected areas in Riyadh (0.02-129.52 ng TEQ/g) (EL-Saeid *et al.,* 2023). According to Alghamdi *et al.,* (2022), the concentrations of PAH compounds reported are reflective of the rapid industrialization, urbanization, and elevated dust levels in Riyadh

City, which may ultimately pose health risks to inhabitants of the northern and various regions of the city.

Concerning the individual ∑PAHs presented in Table 4, the predominant ∑PAH compounds identified include BaP (16.08 ng TEQ/g) in Qassim mint, BaP in Kharj carrot peel (12.69 ng TEQ/g), BaA (8.47 ng TEQ/g) in Qassim potato peel, CHR (4.84 ng TEQ/g) in Hail mint, B(b)F (8.94 ng TEQ/g) in Hail carrot peel, B(k)F (0.11 ng TEQ/g) in Hail cabbage, and D(a,h)A (3.34 ng TEQ/g) in Hail carrot peel. In terms of their individual contributions to the TEQcarc, these values indicate a significant concentration of carcinogenic PAH compounds in the selected vegetable samples sourced from Hail, Qassim, and Kharj municipalities. These results suggest that the aquatic species are likely to suffer negative health impacts. However, our findings are consistent with those of EL-Saeid *et al.,* (2023), who found that BaP B(b)F and B(a)A in Riyadh Street dust contributed significantly to TEQ.

As a whole, the TEQ values of the PAHs in the vegetable samples varied greatly between urban and industrial areas, and, with the exception of a few samples, the findings indicate that the PAH levels measured in the vegetables would not likely cause any immediate toxic effects to aquatic species in Hail, Qassim, and Kharj cities. The results revealed inconsistencies in the PAHs, making it difficult to compare the conclusions of dietary analyses undertaken by different investigators. The researched BaA, which virtually always present in any writing, could be utilized as a marker for PAH in foods. The ratio of the highest to the lowest [PAH]/[BaP] for any specific PAH is used to calculate the maximum observed variability of [PAH]/[BaP] across different meals. We investigated the distribution (profiles) of PAHs in relation to benzo[a]pyrene in a range of meals. Specifically, the hazards of using benzo[a] as a marker for a specific group of PAHs (such as carcinogenic PAH) or a class of PAH compounds (Sampaio *et al.,* 2021).

Table 3: Carcinogenic PAHs concentrations at the vegetable samples

Samples	BaA	Chr	BbF	BkF	BaP	DBA
PPH	0.99	1.20	0.95	0.04	6.36	1.55
PCH	0.21	0.78	2.33	0.01	3.87	2.89
PPQ	8.47	0.91	1.03	0.06	9.45	1.07
PCQ	0.28	0.11	0.79	0.02	3.80	0.28
CPH	1.02	0.00	8.94	0.10	7.72	3.34
CCH	0.21	0.72	1.02	0.08	7.31	0.86
CPK	0.23	0.97	0.84	0.05	12.69	1.25
CCK	0.23	0.63	0.62	0.01	6.57	0.62
LTH	0.56	0.40	3.38	0.06	11.20	0.52
LTQ	0.12	0.14	1.78	0.03	2.90	0.21
CTH	0.82	1.46	5.00	0.11	10.86	2.15
CTK	0.09	0.24	0.82	0.03	3.53	0.49
MTH	0.16	4.84	0.39	0.01	7.18	0.63
MTQ	0.00	0.26	0.44	0.02	16.08	1.54
∑cPAHs	13.40	12.67	28.34	0.64	109.52	17.38

Table 4: Concentrations of the total and the carcinogenic PAHs and their corresponding toxicity equivalency quotients (TEQs) in the vegetables

Samples	∑ PAHs (ng g⁻¹)	∑ cPAHs[a]	TEQ[b]	TEQcarc[c]
PPH	22.16	11.10	0.29	0.57
PCH	11.49	10.10	0.34	0.38
PPQ	23.66	20.99	0.40	0.45
PCQ	8.35	5.28	0.46	0.72
CPH	22.38	21.12	0.34	0.37
CCH	14.06	10.21	0.52	0.72
CPK	16.72	16.03	0.76	0.79
CCK	8.93	8.67	0.74	0.76
LTH	17.15	16.11	0.65	0.69
LTQ	6.15	5.19	0.47	0.56
CTH	20.84	20.39	0.52	0.53
CTK	5.85	5.20	0.60	0.68
MTH	18.21	13.21	0.39	0.54
MTQ	20.97	18.35	0.77	0.88

[a]Sum of concentrations of the potential carcinogenic PAHs (BaA, Chr, BaP, BbF, BkF and DBA).
[b]The total toxic BaP equivalent for all 11 PAH compounds.
[c]The total toxic BaP equivalent for potential carcinogenic PAHs.

Statistical analysis

Cronbach's Alpha is used to assess reliability. Its value generally fluctuates between 0 and 1, however there is no lower limit to the co-efficient. The closer Cronbach's Alpha co-efficient is to 1.00, the more reliable the items on the scale. Data demonstrate that PAH levels in the sample collections vary greatly among vegetable samples. The analysis of variance revealed significant differences ($P \leq 0.005$) in PAH levels between sample collections (Table 5).

The above tables demonstrate the reliability test using Cronbach's Alpha for each sample in the compound. We discover that the reliability coefficients are high (>0.75), which implies that the samples are reliable. The previous table showed that the mean PPH in the study sample was 2.01, with a standard deviation of 3.439. The mean CPK in the study sample was 1.52, with a standard deviation of 3.729. Furthermore, the average LTQ in the study population was 0.56, with a standard deviation of 3.335. Furthermore, the mean MTQ in the study sample was 1.90, with a standard deviation of 4.734.

Table 5: Reliability statistics of correlation coefficients (r) among the concentrations of individual PAHs in vegetable samples with characteristics

Cronbach's Alpha	Reliability Statistics Cronbach's Alpha Based on Standardized Items	N of Items
.951	.973	14

CONCLUSION

Specific PAHs had mean values of 0.22, 1.11, 0.16, 0.08, 0.93, 0.96, 0.91, 2.02, 0.05, 7.82, and 1.24 ng g^{-1} dw, respectively. The PAH values in the 14 vegetable samples ranged from 5.85 to 23.66 ng g^{-1} dry weight. Cabbage total Kharj had a low total concentration of 5.85 ng g^{-1} dw, whereas potato peel Qassim (PPQ), carrot peel Hail, and potato peel Hail had the highest values of 23.66, 22.38, and 22.16 ng g^{-1}, respectively. According to multiple author studies, the combustion of PAHs is one of the primary indoor pollutants since it contains PAHs, which are considered the most polluting compounds. The PAHs infecting vegetable samples appear to be pyrogenic, based on the diagnostic ratios. TEQBaP values were higher for high molecular weight PAHs (HMW) and PAHs with more benzene rings than for low molecular weight PAHs (LMW), as calculated by the total equivalency factor based on BaP. It is vital to discover the spatial-temporal control drivers influencing PAH levels in vegetable samples in the future. Emphasizing the close relationship between vegetable consumption and human health problems is very critical, especially in highly populated areas. This monitoring method should stimulate more hydrocarbon research in Saudi Arabia, contributing to the body of information on hydrocarbon residues in various samples.

Conflict of interest

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

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