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Polycyclic Aromatic Hydrocarbons (PAHs) in Vegetables and Fruits Produced in Saudi Arabia

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Abstract Popular varieties of vegetables were collected from major cities of Saudi Arabia and analyzed for polycyclic aromatic hydrocarbons (PAH) contents. Eight important PAH congeners were analyzed. Total PAH contents of the root vegetables like potato and carrot showed higher values (11 μg kg^{-1}), whereas turnip showed relatively lower contents at 9.26 μg kg^{-1}. For the fruit vegetables, all the peels were found to be more contaminated than cores. For leafy veg etables, maximum PAH level was shown by cabbage (8.34 μg kg^{-1}), which turned out to be more than any of the cores of fruit vegetables. Among individual PAH congeners, anthracene showed higher levels in all vegetables. For benzo(a)anthracene, maximum concentration (2.21 ± 1.75 μg kg^{-1}) was encountered in turnip cores. Highest benzo(e)-pyrene concentration was found in potato (2.90 ± 1.10 μg kg^{-1}) followed by turnip (2.10 ± 1.09 μg kg^{-1}). Benzo (b)fluoranthene and benzo(k)fluoranthene showed relatively lower levels in all samples studied. Human exposure to PAH by consumption of these vegetables is estimated, by using typical Saudi intake rates. The study revealed that cumulative dietary exposure of Saudi population to PAHs ranges from 0.20 to 0.85 μg p^{-1} d^{-1}.

Keywords PAH · Vegetables · Risk assessment · Human exposure

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Polycyclic aromatic hydrocarbons (PAHs) are group of fused aromatic ring compounds formed during incomplete combustion of fossil fuels and garbage. PAHs are originated from both natural and anthropogenic sources, the later providing, by far, the major contribution. These compounds are found throughout the environment in the air, water and soil, and can remain in the environment for months or years. PAHs are recognized class of carcinogenic compounds and many studies have been carried out to identify the human exposure sources. There is sufficient evidence about carcinogenicity of PAHs like benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(ah)anthracene (IARC 1983). Recently, the Joint FAO/WHO Expert Committee on Food Additives have declared that, B(a)A, B(b)F, B(k)F, B(a)P and D(ah)A are clearly carcinogenic and genotoxic (JECFA 2005).

The sources of PAHs in food are predominantly from environmental pollution and food processing steps. There are many studies showing uptake of PAHs by plants (Kipopulou et al. 1999; Vousta and Samara 1998) and contamination of PAHs was often found in various food categories including vegetables (Tao et al. 2004; Camargo and Toledo 2003; Zhong and Wang 2002). In plants, PAHs are present mainly due to deposition of airborne particulates on their exposed surfaces. The waxy surface of vegetables and fruits is able to concentrate low molecular mass PAHs through surface adsorption and particle-bound high molecular mass PAHs can contaminate the surface due to atmospheric fall-out (EFSA 2008). Moreover, despite of poor solubility in water, PAHs, they can be taken up and bio-accumulated by plants (Meudec et al. 2006). Since the gaseous deposition is the main pathway for the accumulation of PAHs in vegetables, the emissions from the fossil fuels combustion was shown to influence the PAHs levels and profiles in vegetables and fruits grown nearby. In some cases, however, direct relationship between soil and plant PAH concentrations were also observed suggesting a possible pathway from contaminated soil and to plant roots (Meudec et al. 2006).

Since diet is believed to be the major source of human exposure to PAHs (Philips 1999), and vegetables happen to be the basic food in Saudi diet, it is a major concern of local authorities that how and to what extent PAHs are accumulated in the vegetables grown in agricultural areas. The Kingdom of Saudi Arabia produces a variety of vegetables and fruits for local consumption and export to neighboring states. More than half of the Kingdom's cultivated area (57%) is in the central regions. In the south of the country, Jizan, Al Baha and Najran combined rank second with nineteen percent of the cultivated land, while Al Jouf, Tabouk and Hayel in the north rank third with thirteen percent. The Eastern and Western Regions together account for eleven percent of the cultivated land. Vegetables grown in these areas supply the local as well as neighboring markets. Saudi Arabia is the biggest oil producing country in the Gulf region and widespread activities regarding exploration, refining and petrochemicals production continue throughout the year. Extensive use of fossil fuels in all walks of life appears to be the most important reason for the prevalence of PAHs in the environment. However, so far, no viable efforts have been made in Saudi Arabia to determine levels of PAHs in vegetables produced in major agricultural farms. This paper presents the results obtained from a study on selected vegetable crops cultivated in various parts of Saudi Arabia. Nine important vegetables varieties were chosen for this which account for about 80% vegetables consumption in the region. The results obtained were used to calculate a preliminary estimation of the contribution of these vegetables as source of PAHs exposure in Saudi population.

Materials and Methods

Nine varieties of vegetables namely potato, turnip, carrot (root vegetable), cabbage, spinach (leafy vegetables), tomato, cucumber, eggplant and bitter gourd (fruit vegetables) were selected. In total 355 samples were collected. Samples description is given Table 1. The samples were procured from local wholesale suppliers/hypermarkets. In order to have clear picture of the levels of PAH, care was exercised to grab samples grown locally. After purchase, the vegetation samples were bagged and kept refrigerated at 4°C, till analyzed. Eight PAH congeners selected for this study were procured from Aldrich Chemical Company and Supelco Inc. (USA). Methylene chloride, acetonitrile (HPLC grade) and sodium sulfate were purchased from E. Merck. Doubly distilled, deionized water was used throughout the study.

Table 1 Vegetable description used in this study

Vegetables	Samples #	Part1	Part2	DMC (%)
Potato	41	Cores	Peels	22.7
Spinach	47	Total		7.1
Turnip	39	Cores	Peels	5.7
Carrot	40	Cores	Peels	4.9
Cabbage	46	Total		6.4
Tomato	51	Total		5.1
Eggplant	39	Cores	Peels	7.3
Bitter gourd	52	Cores	Peels	5.8

DMC dry matter content

Fresh samples were washed with tap water, deionized water, air dried and then carefully weighed. Potatoes, turnip, carrot, eggplant, cucumber and bitter gourd were separated into peel (<1 mm) and cores with a normal kitchen peeler and carefully weighed. The concentrations of PAHs in peels and cores were determined separately. For each vegetable, a composite sample of at least ten individuals was used (Table 1). All the composite samples were analyzed in triplicate. Dry matter content of the vegetables was measured by heating the samples at 95°C for 30 h (Table 1). After washing and peeling, the samples were chopped into small sections and homogenized in a blender mill. 50.0 g of homogenized sample were mixed with 100–150 g (depending upon water content) of preheated anhydrous sodium sulfate and extracted with a mixed solvent (cyclohexane:acetone, 2:1) for 8 h in a full glass Soxhlet extractor. The concentrated extract was purified by column chromatography on silica gel, as described by Camargo and Toledo (2003). A glass column (i.d 1.5 cm) was packed with silica gel and anhydrous sodium sulfate, 7.5 and 2 cm respectively, from top to bottom. The PAH extract was applied at the top of the column and eluted with 75 mL of methylene chloride. The clean extract was evaporated under gentle nitrogen flow and finally dissolved in 2 mL acetonitrile.

Analysis was conducted on Alliance HPLC system by Waters Associates (USA), equipped with a UV detector ($\lambda = 254$ nm) on ODs column (5 μm; 250 × 4.6 mm, 5 μm, C18 Waters PAH Column) at 30°C. A mobile phase composed of acetonitrile–water (75:25 v/v). At a flow rate of 1.5 mL/min was used to separate the PAHs. Blank samples were prepared to prevent and detect contamination during the treatment operation (Camargo and Toledo 2003). During analysis, two injections of a mixture of PAHs standards were made every five pairs of vegetable samples to correct any possible variation in compound responses. All the samples were analyzed for eight PAH congeners, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene,

Table 2 Average recovery and limits of detection (μg kg^{-1}; fresh weight) of various PAHs

PAH	Abbreviation	Average recovery (%)	RSD (%)	Limits of detection
Anthracene	Ant	89	9.5	0.22
Benzo(a)anthracene	B(a)A	94	8.6	0.18
Benzo(e)pyrene	B(e)P	93	11	0.09
Benzo(b)fluoranthene	B(b)F	89	6.8	0.24
Benzo(k)fluoranthene	B(k)F	96	7.5	0.76
Benzo(a)pyrene	B(a)P	94	4.5	0.11
Dibenzo(ah)anthracene	D(ah)A	88	6.9	0.17
Benzo(ghi)perylene	B(ghi)P	92	8.9	0.20

dibenzo(ah)anthracene, benzo(e)pyrene and dibenzo(ghi) anthracene (Table 2). These PAH congeners were chosen because of availability of standards and proven carcinogenicity of five of them (JECFA 2005). Recoveries of PAHs from vegetables by this method were tested by analyzing vegetable samples spiked at the level of 5 times limits. The PAH standards were spiked into the samples after the homogenization step. Average recoveries of PAHs and limits of detection attained by the present methodology are shown in Table 2. Peak identities were confirmed by running samples and standards under identical conditions (Zhong and Wang 2002).

Results and Discussion

The mean concentrations of PAHs in selected vegetables are presented in Table 3 on fresh weight basis. Normally vegetables are consumed a fresh the discussion here will be based on the results expressed on a fresh weight basis. The fact that almost all samples in the current study contained PAHs demonstrates the widespread nature of these persistent compounds. A look at total PAH contents (Table 3) reveals that root vegetables like potato and carrot showed higher values (~11 μg kg^{-1}), whereas turnip showed relatively lower contents at 9.3 μg kg^{-1}. For the fruit vegetables, all the peels were found to be more contaminated than cores. The ratios of total PAH concentrations in peels to those of cores are 1.4, 1.0, 1.5, 1.2, 1.5 and 1.2 for potato, turnip, carrot, eggplant, cucumber and bitter gourd, respectively. It can fairly be concluded that peeling of root and fruit vegetables and the removal of outer part of the leafy crop can substantially reduce the ingestion of these compounds. Lise et al. (2002) have reported elevated levels of B(a)P in potato, lettice and carrot with peel, from Denmark.

For leafy vegetables, spinach and cabbage were analyzed as a whole. Maximum PAH level was shown by spinach (10.2 μg kg^{-1}), which turned out to be more than any of the cores of fruit vegetables. Relatively lower levels (8.3 μg kg^{-1}) were shown by cabbage. These results demonstrated that due to large surface area of cabbage and spinach leaves, the absorption of airborne PAH was quite higher. This is also in accordance with Joint FAO/WHO Expert Committee on Food Additives, whereby, the PAHs that are airborne (either in the vapor phase or adhered to the particulate matter) become deposited on crops, especially crops with broad leaves (JECFA 2005). Among individual PAH congeners, Ant showed higher levels in all vegetables. For B(a)A, maximum concentration

Table 3 Concentrations (μg kg^{-1}; fresh weight) of various PAHs in vegetable parts

Vegetable	Parts	Ant	B(a)A	B(e)P	B(b)F	B(k)F	B(a)P	D(ah)A	B(ghi)P	ΣPAH
Potato	Cores	2.01 ± 1.90	0.80 ± 0.09	2.90 ± 1.10	1.02 ± 0.91	1.06 ± 0.90	1.50 ± 1.01	0.12 ± 0.09	1.05 ± 0.50	10.5
	Peels	3.80 ± 2.90	2.01 ± 0.21	4.01 ± 2.20	1.05 ± 0.97	1.06 ± 0.20	1.73 ± 0.14	0.28 ± 0.16	1.07 ± 0.30	15.0
Spinach	Total	2.85 ± 1.39	1.09 ± 0.76	1.05 ± 0.70	0.30 ± 0.16	0.66 ± 0.21	2.12 ± 1.20	1.7 ± 0.75	0.40 ± 0.29	10.2
Turnip	Cores	1.10 ± 1.01	2.21 ± 1.75	2.10 ± 1.09	0.90 ± 0.79	0.50 ± 0.25	1.01 ± 0.70	1.16 ± 0.66	0.29 ± 0.15	9.3
	Peels	1.53 ± 0.89	1.30 ± 0.92	2.18 ± 1.07	1.34 ± 0.76	0.73 ± 0.68	1.90 ± 1.12	0.13 ± 0.02	0.19 ± 0.07	9.3
Carrot	Cores	1.91 ± 1.42	2.02 ± 1.99	1.30 ± 0.66	1.33 ± 1.01	0.95 ± 1.02	2.50 ± 1.99	0.98 ± 0.55	0.59 ± 0.50	11.6
	Peels	2.29 ± 1.92	2.49 ± 2.16	2.16 ± 1.19	2.09 ± 1.32	2.05 ± 1.47	3.14 ± 2.89	1.98 ± 0.43	1.19 ± 0.90	17.4
Cabbage	Total	2.35 ± 1.92	1.04 ± 0.45	1.09 ± 0.46	0.47 ± 0.29	0.29 ± 0.09	1.27 ± 0.85	0.38 ± 0.13	1.45 ± 0.95	8.3
Tomato	Total	3.45 ± 2.80	1.66 ± 0.99	1.15 ± 0.46	0.16 ± 0.09	0.22 ± 0.12	0.19 ± 0.09	0.38 ± 0.23	0.74 ± 0.21	7.9
Eggplant	Cores	1.08 ± 1.87	1.90 ± 1.3	1.26 ± 0.45	0.78 ± 0.42	1.02 ± 0.46	1.68 ± 1.02	0.76 ± 0.07	0.34 ± 0.21	8.8
	Peels	2.07 ± 1.70	2.99 ± 1.29	1.92 ± 0.33	1.02 ± 0.36	1.05 ± 1.01	1.39 ± 0.33	0.21 ± 0.05	0.34 ± 0.11	10.9
Cucumber	Cores	0.69 ± 0.14	1.37 ± 0.77	1.03 ± 0.92	0.78 ± 0.56	0.87 ± 0.65	1.85 ± 0.99	0.33 ± 0.05	0.66 ± 0.36	7.6
	Peels	1.06 ± 0.88	2.26 ± 1.2	2.12 ± 0.78	0.92 ± 0.65	1.34 ± 0.79	2.08 ± 1.56	0.77 ± 0.53	1.03 ± 0.57	11.6
Bitter gourd	Cores	0.55 ± 0.71	0.56 ± 0.32	0.57 ± 0.44	0.97 ± 0.21	0.57 ± 0.34	1.03 ± 0.44	0.95 ± 0.21	0.09 ± 0.07	5.2
	Peels	0.65 ± 0.23	0.24 ± 0.09	0.68 ± 0.12	1.03 ± 0.76	0.61 ± 0.64	1.99 ± 0.17	1.07 ± 0.87	0.11 ± 0.37	6.4

Table 4 Average consumption of vegetables versus potential exposure of PAHs

Vegetable	Consumption (g p^{-1} d^{-1})	Ant	B(a)A	B(e)P	B(b)F	B(k)F	B(a)P	D(ah)A	B(ghi)P	ΣPAH
Potato	81	0.16	0.07	0.23	0.08	0.09	0.12	0.01	0.09	0.85
Spinach	43	0.12	0.05	0.05	0.01	0.03	0.09	0.07	0.02	0.44
Turnip	45	0.05	0.10	0.09	0.04	0.02	0.05	0.05	0.01	0.42
Carrot	58	0.11	0.12	0.08	0.08	0.06	0.14	0.06	0.03	0.63
Cabbage	50	0.12	0.05	0.05	0.02	0.02	0.06	0.02	0.07	0.42
Tomato	47	0.16	0.08	0.05	0.01	0.01	0.01	0.02	0.02	0.35
Eggplant	43	0.05	0.08	0.05	0.03	0.04	0.07	0.03	0.02	0.79
Cucumber	39	0.03	0.05	0.04	0.03	0.03	0.07	0.01	0.03	0.29
Bitter gourd	38	0.02	0.02	0.02	0.04	0.02	0.04	0.04	0.01	0.20
Total	444	0.82	0.54	0.67	0.35	0.32	0.66	0.31	0.29	4.39

(2.21 ± 1.75 μg kg^{-1}) was encountered in turnip cores. Highest B(e)P concentration was found in potato (2.90 ± 1.10 μg kg^{-1}) followed by turnip (2.10 ± 1.09 μg kg^{-1}). D(ah)A, B(ghi)P, B(b)F and B(k)F were detected in all samples studied, although at lower levels. D(ah)A and B(ghi)P are declared carcinogens (JECFA 2005; IARC 1983). Zhong and Wang (2002) have reported B(a)A levels in cabbage (5.46 ± 10.8 μg kg^{-1}), cucumber (2.33 ± 2.02 μg kg^{-1}) and eggplant (2.39 ± 1.82 μg kg^{-1}) grown in China. Camargo and Toledo (2003) have reported B(e)P and B(a)P levels in cabbage grown in Brazil. Their results for B(e)P (2.10 ± 1.21 μg kg^{-1}) were comparable to our findings, whereas B(a)P levels (0.12 ± 0.08 μg kg^{-1}) were comparable to levels in Saudi tomato (0.19 ± 0.09 μg kg^{-1}).

Irrespective of pathways of such accumulation, information on potential exposure of PAHs is of particular interest due to the fact that the general population is most frequently exposed to PAH through food. Therefore, the secondary objective of the present study was the determination of average PAHs potential human exposure through vegetables. In order to accomplish this, the mean PAH concentrations in vegetables were used in combination with average daily consumption of the vegetables. We have estimated the average daily consumption of different vegetables by adult population with the cooperation of Nutrition Division, King Fahd Teaching Hospital, Eastern Province, Saudi Arabia. Among the vegetables studied, consumption of potato was maximum (81 g p^{-1} d^{-1}), followed by carrot (58 g p^{-1} d^{-1}) and cabbage (50 g p^{-1} d^{-1}). Incidentally, potato contained the maximum total PAHs levels as well. Therefore, among the vegetables studied potato (0.85 μg p^{-1} d^{-1}) was the biggest source of PAHs exposure (Table 4), followed by egg plant (0.79 μg p^{-1} d^{-1}) and carrot (0.63 μg p^{-1} d^{-1}). According to a food survey carried out in Netherlands, the total dietary intake of B(a)P was 0.12–0.29 μg day^{-1}. In the same study, the maximum concentrations of B(a)P in leafy vegetable and potato were 0.29 μg kg^{-1} and 0.48 μg kg^{-1}, respectively. An estimated value for the average human intake of B(a)P in United Kingdom in 1979 was 0.25 μg kg^{-1}, and in Italy the daily intake of B(a)P from food was 0.17 μg kg^{-1} (Turrio-Baldassarri et al. 1996; De Vos et al. 1990; Dennis et al.1983). These reported values, although older, are similar to our findings (Table 4).

However, it should be noted that these calculations are based upon the fact that vegetables are consumed raw. In fact, vegetables are cooked, which may substantially affect the final PAH content of eaten vegetables. According to food habits of Saudi people, cucumber, carrot, cabbage and tomato are eaten as raw, without cooking. On the other hand, potato, turnip, spinach, egg plant and bitter gourd are consumed after thorough cooking. These food habits are typical of Saudi population. Therefore, the data presented could be generalized to overall adult population of the Kingdom. Keeping this in view, the data in Table 4 should be carefully handled to represent potential PAH exposure to consumers. It can safely be concluded from the present study, that all the vegetable samples analyzed contained PAHs. However, the levels of these compounds are not yet at alarming levels. These values can be considered by concerned authorities as indicative values and could be averaged to estimate the Saudi PAHs human exposure, as they are the only data available on dietary intake of PAHs by local population.

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