Polycyclic Aromatic Hydrocarbons in Vegetables and Fruits produced in Saudi Arabia

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Abstract:

Popular varieties of vegetables were collected from Eastern Province, KSA and analyzed for polycyclic aromatic hydrocarbons (PAH) contents. Eight important PAH congeners were analyzed; most of them are suspected carcinogens. Total PAH contents of the root vegetables like potato and carrot showed higher values (~13µg/kg), whereas turnip showed relatively lower contents at 10.9□g/kg. 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 1.45, 1.26, 1.31, 1.44, 1.40 and 1.36 for potato, turnip, carrot, eggplant, cucumber and bitter gourd, respectively. For leafy vegetables, maximum PAH level was shown by cabbage (11.6 µg/kg), 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 (3.44±2.10 µg/kg) was encountered in turnip cores. Highest benzo(e)pyrene concentration was found in potato (3.19±1.67 µg/kg) followed by turnip (2.74±1.22 µg/kg). 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 Pakistani intake rates. The study revealed that cumulative dietary exposure of Saudi population to PAHs ranges from 0.25 $\mu g\text{-}p^{-1}\text{-}d^{-1}$ to 1.16$\mu g\text{-}p^{-1}\text{-}d^{-1}$.

Keywords: PAH; Vegetables; Risk Assessment; Human Exposure

Introduction

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).

PAHs occur as contaminants in different food varieties and beverages. 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 (Kipopoulou et al 1999; Vousta & Samara 1998; Wild et al 1992) and contamination of PAHs was often found in various food categories including vegetables (Tao et al 2004; Camarago & Toledo 2003; Zhong & 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 (Meudee 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 (Meudee et al 2006; Wild et al 1992).

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 scientists and 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. However, the potential for agricultural production is limited in Saudi Arabia due to the lack of arable land and renewable water resource. Saudi Arabia, being the biggest oil producer in the Gulf, extensive activities regarding exploration, refining and petrochemicals production go on 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

Sampling

More than half of the Kingdom's cultivated area (57%) is in the central Riyadh and Qasseem Regions. In the south of the country, Jizan, Asir, 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 this area supply the local as well as neighboring markets. 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 259 samples were collected. Samples description is given Table 1. The samples were procured from local wholesale markets. 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^{o}C, till analyzed.

Reagents

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.

Sample Treatment

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 (<1mm) and cores with a normal kitchen peeler and carefully weighed. The concentrations of PAHs in peels and cores were determined separately. Other vegetables were measured totally according to Pakistani dietary habits. 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^{o}C for 30 hours (Table 1). After washing and peeling, the samples were chopped into small sections and homogenized in a blender mill.

Sample Extraction

50.0g of homogenized sample were mixed with 100 to 150g (depending upon water content) of preheated anhydrous sodium sulfate and extracted with a mixed solvent (cyclohexane/acetone, 2:1) for 8 hours in a full glass Soxhlet extractor. The concentrated extract was purified by column chromatography on silica gel, as described by Camargo & Toledo (2003). A glass column (i.d 1.5cm) was packed with silica gel and anhydrous sodium sulfate, 7.5cm and 2cm respectively, from top to bottom. The PAH extract was applied at the top of the column and eluted with 75mL of methylene chloride. The clean extract was evaporated under gentle nitrogen flow and finally dissolved in 2mL acetonitrile.

Sample Analysis and Validation

Analysis was conducted on Alliance HPLC system by Waters Associates (USA), equipped with a UV detector (λ=254nm) on ODs column (5µm; 250x4.6mm, 5µm, C18 Waters PAH Column) at 30^{o}C. A mobile phase composed of acetonitrile-water (75:25v/v). at a flow rate of 1.5mL/min was used to separate the PAHs. Blank samples were prepared to prevent and detect contamination during the treatment operation (Camargo & 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, 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 & Wang, 2002).

Results and Discussion

Analytical Results

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 (~13µg/kg), whereas turnip showed relatively lower contents at 10.9□g/kg. 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 1.45, 1.26, 1.31, 1.44, 1.40 and 1.36 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 cabbage (11.6 µg/kg), which turned out to be more than any of the cores of fruit vegetables. Similar levels (11.5 µg/kg) were shown by spinach as well. 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 (3.44±2.10 µg/kg) was encountered in turnip cores. Highest B(e)P concentration was found in potato (3.19±1.67 µg/kg) followed by turnip (2.74±1.22 µg/kg). B(b)F and B(k)F showed relatively lower levels in all samples studied. D(ah)A could not be detected in spinach, carrot and tomato, whereas B(ghi)P could not be detected in bitter gourd, turnip, carrot and eggplant. Both are declared carcinogens (JECFA, 2005; IARC, 1983). Zhong & Wang (2002) have reported B(a)A levels in cabbage (5.46±10.8 µg/kg), cucumber (2.33±2.02 µg/kg) and eggplant (2.39±1.82 µg/kg) grown in China. Camargo & 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) were comparable to our findings, whereas B(a)P levels (0.12±0.08 µg/kg) were comparable to levels in Pakistani tomato (0.11±0.06 µg/kg).

Dietary Exposure

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. Second 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 in Saudi Arabia, with the cooperation of Nutrition Division, KFTH Dammam. Among the vegetables studied, consumption of potato was maximum (75 $g\text{-}p^{-1}\text{-}d^{-1}$), followed by carrot (60 $g\text{-}p^{-1}\text{-}d^{-1}$) and cabbage (55 $g\text{-}p^{-1}\text{-}d^{-1}$). Incidentally, potato contained the maximum total PAHs levels as well. Therefore, among the vegetables studied potato (1.157 $\mu g\text{-}p^{-1}\text{-}d^{-1}$) was the biggest source of PAHs exposure (Table 4), followed by carrot (0.812 $\mu g\text{-}p^{-1}\text{-}d^{-1}$) and cabbage (0.629 $\mu g\text{-}p^{-1}\text{-}d^{-1}$). According to a food survey carried out in Netherlands, the total dietary intake of B(a)P was 0.12-0.29µg/day. In the same study, the maximum concentrations of B(a)P in leafy vegetable and potato were 0.2 µg/kg and 0.4 µg/kg, respectively. An estimated value for the average human intake of B(a)P in United Kingdom in 1979 was 0.25 µg/kg, and in Italy the daily intake of B(a)P from food was 0.17 µg/kg (Turrio-Baldassari et al. 1996;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. 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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Table 1: Vegetable description used in this study

Vegetables	Samples #	Part1	Part2	DMC(%)
Potato	28	Cores	Peels	22.1
Spinach	27	Total		7.2
Turnip	32	Cores	Peels	5.3
Carrot	30	Cores	Peels	5.1
Cabbage	26	Total		6.2
Tomato	31	Total		4.7
Eggplant	30	Cores	Peels	7
Bitter gourd	26	Cores	Peels	5.6

DMC Dry Matter Content

Table 2: Average recovery and limits of detection (µg/kg; 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	1.07
Benzo(k)fluoranthene	B(k)F	96	7.5	0.76
Benzo(a)pyrene	B(a)P	94	4.5	0.07
Dibenzo(ah)anthracene	D(ah)A	88	6.9	0.17
Benzo(ghi)perylene	B(ghi)P	92	8.9	0.20

Table 3: Concentrations (ug/g; 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	10.46
	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	15.01
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	10.17
Turnip	cores	1.10±1.01	2.21±1.75	2.09±1.09	0.90±0.79	0.50±0.25	1.01±0.70	1.16±0.66	0.29±0.15	9.26
	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	11.58
	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	17.39
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	8.34
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	7.95
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	8.82
	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	10.99
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	7.58
	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	11.58
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	5.29
	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	6.38

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	0.163	0.065	0.234	0.083	0.086	0.122	0.010	0.085	0.848
Spinach	43	0.122	0.046	0.045	0.013	0.028	0.091	0.073	0.017	0.435
Turnip	45	0.050	0.099	0.094	0.041	0.023	0.045	0.052	0.013	0.417
Carrot	58	0.111	0.117	0.075	0.077	0.055	0.145	0.057	0.034	0.629
Cabbage	50	0.118	0.052	0.055	0.024	0.015	0.064	0.019	0.073	0.420
Tomato	47	0.162	0.078	0.054	0.008	0.010	0.009	0.018	0.016	0.355
Eggplant	43	0.046	0.082	0.054	0.034	0.044	0.072	0.033	0.015	0.794
Cucumber	39	0.027	0.053	0.040	0.030	0.034	0.072	0.013	0.026	0.295

Bitter gourd	38	0.021	0.021	0.022	0.036	0.022	0.039	0.036	0.003	0.200
Total	444.000	0.819	1.198	0.673	0.346	0.317	0.659	0.311	0.282	4.393