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Original Article

Personal Exposure to Polycyclic Aromatic Hydrocarbons in Newsagents in Tehran, Iran

Fatemeh REZAEI [1], Hossein KAKOOEI [1], Reza AHMADKHANIHA [2], Kamal AZAM [3], Leila OMIDI [1], Seyed Jamaleddin SHAHTAHERI [4]*

1. *Dept. of Occupational Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*
2. *Dept. of Human Ecology, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*
3. *Dept. of Epidemiology & Biostatistics, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran*
4. *Dept. of Occupational Health Engineering, School of Public Health, Institute for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran*

***Corresponding Author:** Email: shahtaheri@tums.ac.ir

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Abstract

Background: Vehicle exhaust is a major source of exposure to Polycyclic Aromatic Hydrocarbons (PAHs) found in the urban atmosphere. Newsagents usually work close to heavy traffic flow. The purpose of this study was to assess the breathing zone exposure of newsagents to PAHs found in the urban atmosphere of Tehran City during summer and autumn seasons and comparing the levels of exposure in both seasons.

Methods: Fifteen non-smoking newsagents were randomly selected from north, south, east, west, and center of Tehran. Particle and gas phases PAHs were collected on polytetrafluoroethylene (PTFE) filter and XAD-2 adsorbent. Gas chromatography–mass spectrometry (GC/MS) was used to determine PAHs concentrations in newsagent's breathing zone samples.

Results: The highest and lowest values of exposures during summer and autumn in all sampling stations were recorded for benzo[a]anthracene and benzo[ghi]perylene, respectively. Mann-Whitney test results showed that seasonal variation had significant influence on concentrations of all studied PAHs (P= 0.001) except benzo[ghi]perylene (P= 0.089). An increase in concentrations of PAHs was observed in autumn.

Conclusion: The workers of the newsstands in the south area of Tehran City were experiencing higher levels of exposures to PAHs. Newsagents' breathing zone exposures to PAHs during the cold period were two to three folds higher than those during the warm period were. The levels of exposures in all sampling stations were below the OSHA and NIOSH's recommended exposure limits.

Keywords: Polycyclic aromatic hydrocarbons, Newsagents, Exposure, Breathing zone, Seasonal variation

Introduction

One of the most significant current discussions in occupational health is the exposure to chemical agents in the outdoor environment. Polycyclic Aromatic Hydrocarbons (PAHs) are a group of organic compounds, which are found in the crude oil, mineral oil, and coal tar. These compounds are also produced during the incomplete combustion of fossil fuels and petroleum products (1, 2). PAHs can be emitted into the air from several industrial processes including aluminum electrolysis, foundries, and petroleum refineries (3). The other PAHs emission source is traffic emissions (4). PAHs exposure is the cause of many human cancers such as bladder, lung, and skin cancers (5).

International Agency for Research on Cancer (IARC) has classified some of them in different categories such as benzo[a]pyrene in group 1 'known human carcinogens' and dibenzo-[a,h]anthracene in group 2A 'probably carcinogenic to humans'. These compounds are considered as genotoxic and mutagenic and may have an effect on human immune system. PAHs have been identified as persistent organic pollutants since they are not readily biodegradable (6-8).

Emission of PAHs from vehicle exhaust is not the only source of exposure to these compounds in the urban atmosphere. Other sources of exposure include tire wear, asphalt particles, stationary combustion sources, furnace, power generation units, and petroleum refineries. Cigarette smoking increases PAHs concentrations in indoor environment (9, 10). The PAHs are present in the gaseous and particulate phases in the atmosphere. Low molecular weight compounds such as phenanthrene and anthracene are often present in the gas phase. Four ring PAHs such as fluoranthene, pyrene, and chrysene are distributed between the gas and particulate phases. Five and six rings PAHs including benzo[a]pyrene, benzo[a]anthracene, and dibenzoanthracene are present in the particulate phase in the atmosphere (4). The distributions of these compounds in the gas and particle phases depend on vapor pressure, air temperature, concentration and the amount of adsorbed PAHs on suspended particles (11, 12). Previous studies have reported increases in the PAHs concentration in indoor air and outdoor atmosphere (11, 13). The effect of the seasonal variations on PAHs concentration in outdoor atmosphere has been presented in many research projects (13). Moreover, the concentration of PAHs in winter is higher than that in summer and the existence of combustion source can induce an increase in the concentration of PAHs in indoor air (14). Benzo[a]pyrene was selected as an indicator for the classification of PAH compounds. A good correlation has been observed between the benzo[a]pyrene and other PAHs (15). However, little attention has been paid to assess personal exposure to PAHs found in urban atmosphere in workers occupationally exposed to these compounds (e.g., traffic police) or in a general population. Most studies have examined specific biomarkers as an indicator of exposure to PAHs in workers occupationally exposed to these compounds such as police officers, drivers, and newsagents but the existing research fail to provide accurate estimates from the breathing zone concentrations of PAHs (16).

Newsagents usually work close to heavy traffic flow and many hours a week. It is thought that this group of workers is the best representative of non-driver employees exposed to PAHs found in the urban air pollution. The mean exposure level of benzo[a]pyrene found in the urban air for non-smoking newsagents was 1.00±0.32 ng/m^3 during the cold period and 0.65±0.25 ng/m^3 in the warm season. The annual average benzo[a]pyrene exposure for non-smoking newsagents was 0.82±0.33 ng/m^3. That is to say, that high level of exposure to benzo[a]pyrene in these workers was reported (16). Occupational Safety and Health Administration (OSHA) has set a permissible exposure limit (PEL) of 0.2 mg/m^3 for benzo[a]pyrene, anthracene, pyrene, chrysene, and phenanthrene and 10 mg/m^3 for naphthalene (17).

Despite the considerable amount of PAHs found in the urban atmosphere, little attention has been paid to measure the personal exposure of newsagents to PAHs. The purpose of this study was to assess the breathing zone exposure of newsagents to PAHs found in the urban atmosphere of Tehran city during summer and autumn seasons and comparing the levels of exposure in both seasons.

Materials and Methods

Study participants

This cross sectional study was performed at newsstands across Tehran during summer and autumn 2013 supervised by municipality and Air Quality Control Company (AQCC) of Tehran. Considering high traffic streets and squares in 22 regions of city, 15 non-smoking newsagents were randomly selected from north, south, east, west, and center of Tehran. The average age of newsagents was 37.23± 10.81. They worked from 7 a.m. to 9 p.m.

in naturally ventilated newsstand with one open window (18).

This study was performed according to the principles outlined in the research involving human subjects. All of the participants filled out a consent form. Eight PAHs were selected for sampling as an indicator of exposure to PAHs found in urban atmosphere and vehicle exhaustion including chrysene, benzo[*a*]pyrene, benzo[a]anthracene, dibenzo[a,h]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[ghi]perylene, and indeno[1, 2, 3-cd]pyrene (9, 19).

Personal sampling

For the estimation of the effect of seasonal variations on PAHs concentrations, newsagent's breathing zone exposure was evaluated during summer and autumn seasons. A total of 90 breathing zone samples were collected during both seasons (July– August and November–December 2013). Personal breathing zone samples were measured by calibrated personal sampling pump (SKC Inc, USA) using NIOSH method 5515 (20). For time weighted average sampling, particle and gas phases PAHs were collected on polytetrafluoroethylene (PTFE) filter (37 mm diameter, 2.0 µm pore size) and XAD-2 adsorbent at a flow rate of 2 liters per minute. After sampling, filter was removed with forceps, placed in the plate, and wrapped in aluminum foil to protect from exposure to ultraviolet radiation. Following this, XAD-2 adsorbent was wrapped in aluminum foil. On completion of sampling, the samples were stored at 4°C and transferred to the analysis laboratory. PAHs were extracted from the filters and XAD-2 adsorbent with methylene chloride using an ultrasonic bath for 30 minutes at room temperature. Stock solutions of PAHs (Sigma-Aldrich Co, UK) in acetonitrile were used to prepare the standard curves (21). Gas chromatography–mass spectrometry (GC/MS) (Agilent Technologies 6890 (Palo Alto, CA, USA)) was used to determine PAHs concentration in newsagents' breathing zone samples (22). The initial temperature of the column was set at 70°C for a minute and then raised at a rate of 10 °C up to 300 °C. The retention time of the PAHs in the column was 30 minutes. The injector temperature was set at 290°C. The helium carrier gas flow rate was 1 ml/min. A 1 µl volume of samples was injected into the gas chromatography column. The area under each peak in the chromatogram was considered as the proportion of individual concentrations of PAHs in the samples. Concentration of standard PAHs solution was 1 ppm. Concentrations of PAHs in newsagent's breathing zone were calculated using Eq. [1].

$$C(mg/m^3)=\frac{W-B+W_f+W_b-B_f-B_b}{V} \quad [1]$$

Where C is the concentrations of PAHs, W (µg), W_f, and W_b are the amount of analyte present in PTFE filter, in front sorbent, and in back sorbent, respectively. B, B_f, and B_b are the amount of analyte present in blank filter, in front sorbent, and in back sorbent, respectively. V is the volume of sampled air (L).

Retention time of individual PAHs, the limit of quantification (LOQ) and limit of detection (LOD) were considered in the study and determined using blank determination method with 10 blank samples (18, 23). The intra assay and inter assay coefficient of variation (CV) were used to determine the internal validation of methods of analysis and repeatability of experiments. For this purpose, three independent experiments in different three days were performed in the laboratory with the same GC/MS technician, materials, and equipment. Correlation coefficient was used to measure the linear association between the concentration of PAHs and area under the peak according to calibration curves. Indoor air parameters such as air velocity, air temperature, and relative humidity were examined during the sampling period in each kiosk (24). Comparisons of PAHs concentration between the two seasons were made using Mann-Whitney test with SPSS 22.

Results

The average of the relative humidity during summer (Sum) and autumn (Aut) of 2013 was approximately 40%. Table 1 shows the results obtained from the investigation of indoor air parameters.

Table 1: The results of investigating the indoor air parameters

Indoor air parameters	Summer	Range	Autumn	Range
Air temperature (°C)	30.94± 4.32	22.80- 43.73	17.02± 3.53	10.35- 22.30
Relative humidity (%)	40.94± 1.95	38.16- 45.03	40.31± 2.20	37.30- 43.83
Air velocity (m/s)	0.30± 0.22	0.04- 0.68	0.07± 0.02	0.04- 0.11

As shown in the table, maximum and minimum air temperature in the newsstands was 22.8 and 43.73 °C in the summer and 10.35 and 22.30 °C in November–December. The mean relative humidity at studied kiosks was in recommended ranges (25). The effects of air velocity inside the kiosks on worker's exposures were negligible.

Table 2 illustrates the results of the retention time of individual PAHs in the column, regression equations and correlation coefficient, the limit of quantification (LOQ), and limit of detection (LOD). A good linearity was observed from the regression analyses of concentrations of individual PAHs with correlation coefficients ranging from 0.9992 to 0.9998. The longer and shorter retention times of 24.87 and 18.53 were obtained for benzo[ghi]perylene and benzo[a]anthracene in the column, respectively. Considering the areas of peak, the low intra assay coefficient of variation was calculated for benzo[a]anthracene (5.95%) and high coefficient of variation was calculated for benzo[*a*]pyrene (7.93%). All calculated coefficients of variations for studied PAHs were less than 10%. Table 3 shows the precision coefficient of variation for each PAH.

Table 2: Parameters associated with analytical methods of PAHs

PAHs	Retention time (min)	LOD (ng/ml)	LOQ (ng/ml)	Regression equation	Correlation coefficient
Benzo[a]anthracene	18.53	0.25	0.50	y = 342697x - 171.17	0.9992
Chrysene	18.61	0.25	0.50	y = 968686x + 269.57	0.9998
Benzo [b] fluoranthene, Benzo [k] fluoranthene	20.95	0.37	0.75	y = 1E+06x - 621.23	0.9997
Benzo[*a*]pyrene	21.68	0.37	0.75	y = 676278x - 1082.20	0.9994
Dibenzo[a,h]anthracene, Indeno [1, 2, 3-cd] pyrene	24.76	0.37	0.75	y = 265592x - 540.61	0.9996
Benzo[ghi]perylene	24.87	0.37	0.75	y = 965358x + 111.61	0.9995

Table 3: The coefficients of variations for studied PAHs

PAHs	Coefficient of variation (%)	
	Intra assay	Inter assay
Benzo[a]anthracene	5.95	7.14
Chrysene	7.03	8.72
Benzo [b] fluoranthene, Benzo [k] fluoranthene	6.62	6.77
Benzo[*a*]pyrene	7.93	9.10
Dibenzo[a,h]anthracene, Indeno [1, 2, 3-cd] pyrene	6.86	7.05
Benzo[ghi]perylene	7.22	6.93

Measuring results of PAHs in the breathing zone air of newsagents suggested that the highest and lowest values of exposures during summer and autumn in all sampling stations were recorded for benzo[a]anthracene and benzo[ghi]perylene, respectively. Table 4 presents the results obtained from the measuring of PAHs in the breathing zone air of newsagents at different locations of the newsstands in the city of Tehran.

Table 4: The results of measuring PAHs in the breathing zone air of newsagents

PAHs (μg/m³)	Locations of the newsstands in the city									
	North		South		East		West		Center	
	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut	Sum	Aut
Benzo[a]anthracene	0.36±0.13	1.28±0.22	0.59±0.07	1.66±0.21	0.52±0.01	1.47±0.24	0.40±0.18	0.99±0.58	0.52±0.05	1.44±0.15
Chrysene	0.13±0.04	0.44±0.08	0.20±0.02	0.58±0.07	0.18±0.01	0.51±0.09	0.14±0.06	0.35±0.18	0.18±0.01	0.50±0.05
Benzo[b]fluoranthene, Benzo[k]fluoranthene	0.07±0.04	0.27±0.04	0.12±0.01	0.34±0.03	0.11±0.01	0.32±0.05	0.09±0.02	0.22±0.09	0.12±0.01	0.33±0.03
Benzo[*a*]pyrene	0.08±0.05	0.34±0.02	0.14±0.01	0.47±0.04	0.13±0.01	0.38±0.06	0.10±0.03	0.26±0.10	0.14±0.01	0.39±0.04
Dibenzo[a,h]anthracene	0.12±0.07	0.49±0.05	0.22±0.01	0.63±0.07	0.20±0.01	0.59±0.09	0.15±0.05	0.39±0.16	0.21±0.02	0.58±0.06
Indeno[1, 2, 3-cd]pyrene	0.12±0.07	0.46±0.11	0.22±0.01	0.65±0.06	0.22±0.02	0.65±0.13	0.15±0.05	0.40±0.17	0.22±0.03	0.61±0.07
Benzo[ghi]perylene	0.00±0.01	0.00±0.01	0.02±0.01	0.02±0.01	0.02±0.01	0.05±0.02	0.00±0.01	0.02±0.03	0.02±0.01	0.02±0.01

Mann-Whitney test results showed that seasonal variation had significant influence on concentrations of all studied PAHs (P= 0.001) in newsagent's breathing zone except benzo[ghi]perylene (P= 0.089). An increase in concentrations of PAHs was observed in autumn.

Discussion

This study set out with the aim of assessing the breathing zone exposure of newsagents to PAHs found in the urban atmosphere of Tehran City during summer and autumn seasons. Ambient and indoor air exposure to air pollutants is the leading routes of human exposure to contaminants. The most important risk factors for the burden of disease imposed on society according to the World Health Organization (WHO) were exposure to indoor air pollution from solid fuels and urban air pollutions (13). Considering that city bus and taxi drivers have high exposure to PAHs, newsagents are thought to have high levels of exposure to these compounds (16). They work many hours a week (12 hours per day) and close to heavy traffic flow and some research studies reported high levels of PAHs exposure in this occupation category (16, 18). Seasonal variations and traffic related urban air pollution play important roles for exposure to PAHs (13, 16).

The current study found that benzo[a]anthracene had the highest concentration among all PAHs in the breathing zone air of newsagents during summer and autumn seasons. Benzo[ghi]perylene had the lowest values in both seasons. The highest concentrations of benzo[a]anthracene were recorded in the south area of Tehran. The measured levels of breathing zone exposure to benzo[a]anthracene for newsagents in the south area were 0.59± 0.07 and 1.66± 0.21 μg/m³ during summer and autumn seasons, respectively. As it is shown in the results section, the east area with the average of 0.52± 0.01 and 1.47± 0.24 μg/m³ had the highest concentration of benzo[a]anthracene after the south area of Tehran city. IARC classified benz[a]anthracene as a group B2 carcinogens (probable human carcinogens) (26) and American Conference of Governmental Industrial Hygienists (ACGIH) has not determined occupational exposure limit for this compound but has recommended exposure to benzo[a]anthracene through all routes of exposure should be minimized (27). The results of this study indicated that newsagents had significant exposure to benzo[a]anthracene found in the urban atmosphere during summer and autumn seasons (P= 0.001). It seems possible that the differences in air pollution concentrations in different areas of city were due to differences in the volume of traffic, the total population of people in each studied area, the dominant wind direction, and the distance between newsstands and industries (16, 28).

The results showed that the workers of the newsstands in the south area were experiencing higher levels of exposures to chrysene, dibenzo[a,h]anthracene, benzo [k] fluoranthene, benzo [b] fluoranthene, and indeno [1, 2, 3-cd] pyrene than workers of the newsstands in other areas of the city. The lowest levels of benzo[ghi]perylene in the breathing zone air was seen in the workers

of newsstands in the north area of city during the warm and cold period (0.00± 0.01 μg/m^3).

The highest concentration of benzo[a]pyrene found in the urban atmosphere was observed in the breathing zone air of newsagents in the south area with the average of 0.14± 0.01 and 0.47± 0.04 μg/m^3 during the warm and cold period, respectively. The lowest concentration of benzo[a]pyrene was reported in the north area. Recommended exposure limits for benzo[a]pyrene found in the urban atmosphere in many countries, such as Germany and Italy ranged from 1 to 10 ng/m^3 (9). This study confirmed that the levels of newsagent's breathing zone exposure to benzo[a]pyrene were higher than those recommended. It seems possible that these results are due to the high volume of the traffic, the large number of vehicles, vehicle types, and fuel quality and type that have effects on the concentration of these substances in the urban atmosphere. The results of the present study confirm that urban traffic is the most important source of exposure to PAHs emitted by vehicles, automobiles, and diesel engine exhaust and a dramatic increase in PAHs concentration can be seen in the area with the high volume of traffic. The results of particulate polycyclic aromatic hydrocarbons in urban air of Tehran showed that the concentrations of total PAHs in a year sampling period in the north, south, east, west, and center of Tehran were 70.20 ng/m^3, 79.10 ng/m^3, 44.10 ng/m^3, 130 ng/m^3, and 96.50 ng/m^3, respectively (29). In their study, the highest concentrations of carcinogenic PAHs were reported in the west area of Tehran, which was lower than the values measured in the present study. The annual average daily exposure of non-smoking newsagents to benzo[a]pyrene in Genoa was 0.82± 0.33 ng/m^3 (16). Their results also suggested that the level of newsagent's breathing zone exposure to PAHs in the warm period was 35% lower than that in the cold period (16). The concentration values of benzo[a]pyrene found in this study were higher than those found in Piccardo et al. study (16). The importance of exposure to urban pollutants was observed in another study (18). The results of assessment of 50 personal exposures to PAHs in the atmospheric gas phase in breathing zone air of newsagents and peddlers with similar analytical method to that used in the current study revealed that low concentrations of chrysene, benzo[a]py-rene, benzo[a]anthracene, and dibenzo[a,h]ant-hracene were reported. Higher concentrations were observed for benzo[k]fluoranthene, ben-zo[b]fluoranthene, and benzo[ghi]perylene (18). This rather contradictory result may be due to differences in the sampling (both gas and particulate phases sampling in the current study against only gas phase sampling in other studies), higher traffic flows in Tehran, and difference in the fuel quality and type used in vehicles. In confirmation of previous work (9, 13, 16, 18), the results showed that newsagent's breathing zone exposures to PAHs during the cold period were two to three fold higher than those during the warm period. These results might be related to the impacts of inversion phenomenon, the reduction of the reaction of PAHs and increases in use of fossil fuels during the cold period, and other factors, such as wind direction, temperature, atmospheric stability, aerosol concentrations, and increase the release of free radicals in the cold seasons (9, 13, and 18). Smoking in indoor environments with poor or insufficient ventilation such as newsstands can increase the risk of PAHs exposure (16). The findings of a number of studies have shown that the occupational or work related exposure to PAHs in some occupations such as professional drivers might increase the risk of cancer among them (9). Although the level of breathing zone exposure of newsagents to PAHs in the study was significant, the levels of exposure in all sampling stations were below the OSHA and National Institute for Occupational Safety and Health (NIOSH)'s recommended exposure limits (30).

Conclusion

This paper has investigated the levels of newsagent's breathing zone exposure to PAHs found in the urban atmosphere of Tehran city during summer and autumn seasons. The most obvious finding to emerge from this study is that newsagents work close to heavy traffic flow and had

significant exposure to PAHs. Benzo[a]anthracene had the highest concentration among all PAHs during summer and autumn seasons. The workers of the newsstands in the south area of Tehran city were experiencing higher levels of exposures to PAHs. The second major finding was that newsagents' breathing zone exposures to PAHs during the cold period were two to three fold higher than those during the warm period were.

Ethical considerations

Ethical issues (including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy) have been completely observed by the authors.

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