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HEALTH RISK ASSESSMENT OF ATMOSPHERIC PARTICULATE-BOUND POLYCYCLIC AROMATIC HYDROCARBONS IN SHIRAZ, IRAN

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ABSTRACT:

Introduction: Benzo(a)pyren is an indicator of carcinogenic PAHs and enters the body through the respiratory system, gastrointestinal tract, and skin. This compound causes lung, kidney, and skin, cancers. In this study, the concentrations of PM_{10} and 16 PAHs compounds were measured in the particle phase in an urban and a suburban area of Shiraz and the carcinogenic risk of respiratory exposure to PAHs were assessed.

Materials and methods: A total of 60 samples were collected from Paramont and Sadra during spring 2015 using SKC sampling pump (for 24 h at a flow rate of 10 L/min). Dichloromethane/methanol mixture was used as a solvent. 16 PAHs were identificated using gas chromatography with mass spectrometry.

Results: The mean (±SD) concentrations of PM_{10} were 62.73±23.83 and 60.88±31.03 µg/m^3 in the urban (Paramont) and suburban (Sadra) stations, respectively, which exceeded the PM_{10} emission limit value of the Europe Commission (50 µg/m^3). Also, the mean concentrations (±SD) of the total PM_{10}-bound PAHs were 19.28±7.48 ng/m^3 and 17.80±9.17 ng/m^3 in Paramont and Sadra stations, respectively. Besides, the BaP_{eq} was 1.307 in Paramont and 0.814 in Sadra station. Incremental Lifetime Cancer Risk (ILCR) values for children below 10 years of age demonstrated the risk of cancer for this age group in both areas.

Conclusions: this study presented the value of PM_{10} and PAHs concentration in two sampling sites. The PM_{10} values were higher than Europe Commission and the PAHs concentrations could increase the potential risk of cancer among the children below 10 years old in both sampling areas.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are mainly formed by incomplete combustion of fossil fuels [1]. Due to characteristics, such as toxicity, mutagenicity, and carcinogenicity, most PAHs compounds have been classified as prima-

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ry pollutants by US EPA. Some of these compounds cause lung, gastrointestinal, colorectal, kidney, skin, and prostate cancers [2, 3]. PAHs are dispersed in the environment mainly in gas and particle phases according to vapor pressure. As a rule, compounds with more than five benzene rings are often seen in the particle phase, those with two or three benzene rings are seen in form of gas, and four-ring compounds such as Pyren (Py) and Fluorantene (Fl) are seen in both phases.

Benzo (a) pyren (BaP, $C_{20}H_{12}$) is a component of PAHs and has been classified in Group 1 carcinogens (definitely carcinogenic to humans). Additionally, Dibenzo[a,h]Anthracene (DBahA) has been considered in Group 2A (probably carcinogenic to human) and Naphthalene (Nap), Benzo(a)Anthracene (BaA), Chrysene (Chry), and Benzo(b)Fluoranthene (BbF) in Group B2 (possibility carcinogenic to human) by the International Agency for Research on Cancer (IARC) [4, 5]. The main sources of BaP emissions in the atmosphere are burning wood, fossil fuel combustion, automobile exhaust, and cigarette smoke [1]. BaP is a five-ring compound, which is often released in the particle phase and is known as an indicator of the carcinogenic PAHs, because the concentration of other compounds depend on many variables in the urban atmosphere [6]. PAHs, including BaP, enter the body through the respiratory system, gastrointestinal tract, and skin and tend to be stored in the kidneys, liver, spleen, and adrenal gland. Due to the potential carcinogenic effects of PAHs after prolonged contact [7], it is essential to determine the risk of carcinogenic PAHs compounds. Cancer risk of PAHs can be estimated using Toxicity Equivalent Factors (TEFs) [7, 8].

In the present study, the concentrations of 16 PAHs compound were measured in the particle phase in an urban (Paramount) and a suburban area (Sadra town) and then, the concentration of each compound was calculated based on the equivalent of benzo(a)pyren to assess the carcinogenic risk of respiratory exposure to PAHs.

MATERIALS AND METHODS

Study area

Shiraz is the capital of Fars province and the sixth most populous city of Iran. With an area of about 17889 ha, Shiraz is located in south-west of Iran in the foothills of Zagros Mountain. Paramont is one of the residential and commercial areas in center of Shiraz and has a high traffic volume. Urban development in the recent years led to formation of new settlements around Shiraz. Sadra is a new town with a population of about 9949 people, which is located 18 km from northwest of Shiraz. Ambient air samples for PAHs analysis were collected from urban (Paramont) and suburban (Sadra town) areas during spring 2015. Sampling locations have been shown in Fig.1.

Sample collection

A total of 60 samples were collected from Paramont and Sadra town (method adopted by the US EPA) every 3 days during spring 2015. SKC sampling pump (Leland Legacy, PA 15330) equipped with size selective air intake was used for sampling. The samples were taken for 24 h at a flow rate of 10 L/min by PTFE filters (47 mm ID, 0.5 µm pore size). The sampling filters were kept in a desiccator for 24 h before and after sampling. Filters' weights were measured before and after sampling to determine the concentration of PM_{10} (particles less than or equal to 10 µm in diameter). Three blank samples were also taken from each sampling site in order to determine the field contamination. It should be mentioned that none of the target PAHs was detected in the blank samples. After sampling, the samples were wrapped in aluminum foil and were kept at 18 ºC until analysis.

Sample extraction and analysis

In this study, PAHs and Py adsorbed on the PTFE filters were extracted using ultrasonic extraction method and dichloromethane (DCM)/methanol mixture (3:1 v/v) was used as a solvent. The filters were cut into four pieces and were placed in 20 mL vials. After adding10 mL of the solvent to each vial, the samples were placed in an ultrasonic

Fig.1. The map of the study area to show the two sampling sites

bath for 30 min. Then, the solvent mixture was passed through a PTFE syringe-filter (0.22 µm, 25 mm in diameters) to separate the suspended particles. The solution was dried using a stream of gentle purified nitrogen. Finally, 1 mL of the DCM)/methanol mixture was added to each vial again and kept refrigerated in dark until analysis. Identification and quantification of 16 PAHs were performed using Gas Chromatography (GC) coupled with mass spectrometry and a DB-5MS capillary column (Agilent Co., USA) in Selected Ion Monitoring (SIM) mode. The characteristics of the GC/MS and the temperature program have been presented in Table 1.

Quality control

Calibration curve was plotted with preparation of 1-2000 µg/L of PAHs standard mixture. Field and laboratory blank samples were prepared and analyzed using the same procedures as those used for the collected samples. The recovery efficiency was calculated by spiked samples analysis at a predestinated amount of the standard mixture of the 16 PAHs. The extraction recoveries ranged from 71% to 104%. Additionally, the Limit of Detection (LOD) was estimated as the mean concentration of the blank sample plus three standard deviations of the blank sample. LODs were 0.021, 0.010, 0.062, 0.052, 0.080, 0.031, 0.031, 0.083, 0.073, 0.104, 0.104, 0.104, 0.094, 0.021, 0.073, and 0.062 for Naphthalene (Nap), Acenaphtylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fl, Py, benzo (a) anthracene (BaA), Chry, BbF, benzo(k) fluoranthene (BkF), BaP, indeno(1,2,3-cd)pyrene (IcP), DBahA, and benzo(ghi)perylene (BghiP), respectively.

Risk assessment

TEFs were used for quantitative assessment of the respiratory risk of PAHs. Using TEFs, the toxicity of a mixture of PAHs compounds can be expressed in form of BaP toxicity equivalent (BaP_{eq}) [9]. In this study, the concentration of each compound was multiplied by its corresponding TEF and the concentration of each PAHs compounds

Table 1. The characteristics of GC/MS and the temperature program used for PAHs detection

Device model	GC 7890N, AGILENT & MS 5975C, MODE, EI. MS
Injection technique	Spilt less
Injector temperature	290 ºC
Injection volume	3 µL
Carrier gas	Helium
Injection rate	1mL/L
Column type	DB5/MS
Column length	30 m
Column diameter	0.25 mm
Column film thickness	0.5 µm
Initial temperature of injection	60 ºC
Isothermal	1 min
Initial rate of temperature increase	100ºC - 10ºC/m
Secondary rate of temperature increase	285ºC - 4ºC/m
Isothermal	15 min

was expressed as BaP_{eq}. TEFs used in this study were obtained from the previous studies [7, 9]. Besides, the estimated Lifetime Average Daily Dose (LADD) and Incremental Lifetime Cancer Risk (ILCR) of PAHs in the atmosphere were calculated based on the model proposed by US EPA using Eqs. (1) and (2) [10].

$$LADD = \left(\frac{C \times IR \times EF \times ED}{BW \times AT}\right) \quad (1)$$

$$ILCR = LADD \times (CSF \times (\frac{BW}{70})^{\frac{1}{3}}) \times cf \quad (2)$$

Where:
C: concentration of BaP_{eq} in air (ng/m^3)
EF: exposure frequency (day/year)
ED: exposure duration (years)
BW: body weight (kg)
AT: averaging lifetime for carcinogens (days)
CSF: cancer slope factor (mg/kg day)
cf: conversion factor (10^{-6})
The relationship between carcinogenic compounds exposure dose and increased carcinogenic risk can be expressed by CSF that is different for various age groups according to their exposure [11]. The mean of CSF for respiratory BaP was considered to be 3.14 mg/kg day according to the previous studies [7, 12]. The values of the parameters used to analyze the risk assessment have been shown in Table 2.

RESULTS AND DISCUSSION

PM_{10}, PAHs and BaP concentrations

PM_{10} emission limit value for a period of 24 h (without any effects on human health) has been considered to be 150 µg/m^3 by US EPA and 50 µg/m^3 by the Europe Commission (EC), which can be exceeded only 7 times/year [13]. Also, based on EPA, Iranian Department of Environment has proposed a clean air standard of 150 µg/m^3 with repetition limit of 7 times/year.
According to the results of the study, the mean (±SD) concentrations of PM_{10} were 62.73±23.83 and 60.88±31.03 µg/m^3 in urban (Paramont) and suburban (Sadra) stations, respectively. The concentrations of PM_{10} did not exceed 150 µg/m^3 (Iranian Department of Environment) in

any sampling day. However, PM_{10} concentrations exceeded the EC emission limit value of 50 µg/m^3 for 20 times in Paramont and 19 times in Sadra station and the difference was statistically significant (P<0.001). Therefore, air condition in terms of PM_{10} emissions in Paramont and Sadra was effective in human health in spring 2015. It should be noted that these results are only related to two areas of Shiraz and can not be extended to the city's total air condition. On the other hand, the concentration of PM_{10} in Shiraz was higher compared to that reported in many studies conducted around the world. A study in Switzerland showed that the mean concentrations were much lower than those obtained in our study (the mean annual concentrations of 40.2 and 24.8 µg/m^3 in downtown and suburban areas, respectively) [14]. Another study was investigated for PM_{10} concentration in urban and rural areas in Piedmont, Italy and was observed that the PM_{10} particles concentration ranged from 23 to 110 ng/m^3 in urban areas (an average of 58 ng/m^3) and from 15 to 48 ng/m^3 in suburban areas (an average of 26 ng/m^3) [15], which are much lower compared to the present study. Our study results also revealed higher concentrations of PM_{10} particles in Shiraz compared to Catalonia, Spain, with a mean concentration of 40.6 µg/m^3 [13]. Nonetheless, the obtained concentrations in Shiraz were almost comparable to those measured in Milan, Italy, with a mean concentration of 63 µg/m^3 [16].

In the current study, the mean concentrations (±SD) of the total PM_{10}-bound PAHs were 19.28±7.48 ng/m^3 and 17.80±9.17 ng/m^3 in Paramont and Sadra stations, respectively. Moreover, the mean (±SD) concentrations of BaP related to the particle phase were 0.73±0.88 and 0.43±0.61 ng/m^3, respectively. The box plot of BaP concentrations at the two sampling sites in Spring 2015 has been shown in Fig. 2.

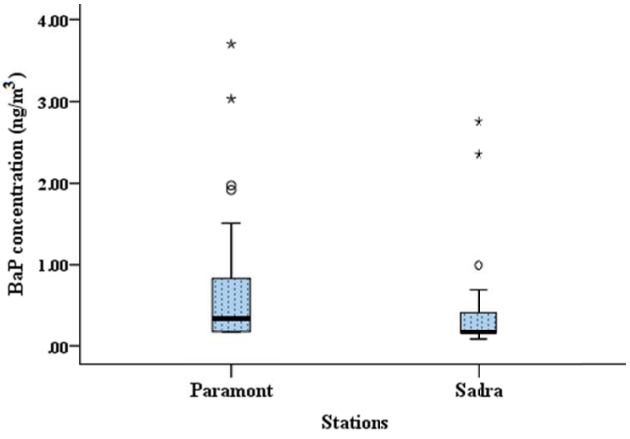

Fig.2. The box plot of BaP concentrations in Paramont and Sadra stations

Table 2. The values of the parameters used to analyze the risk assessment [7]

Parameter	Symbol	Unit	Children (Group 1)	Teenagers (Group 2)	Adults (Group 3)
Age	-	year	0-10	11-20	21-70
Body weight	BW	Kg	16.66	46.35	57.04
Inhalation rate	IR	m^3/day	8.79	13.61	12.34
Exposure frequency	EF	days/year	365	365	365
Exposure duration	ED	year	10	10	50
Averaging time	AT	days	25550	25550	25550

BaP_{eq} and risk assessment

BaP_{eq} was calculated by multiplying the concentration of each compound by its corresponding TEF. The results of these calculations during the total sampling period have been presented in Table 3. Accordingly, the amounts of BaP_{eq} were 1.307 and 0.814 in Paramont and Sadra station, respectively.

In this study, ILCR values were calculated to assess the cancer risk of PAH compounds for three age groups (a total of 6 groups) in Paramont and Sadra. Based on the results, the mean ILCR was 7.7×10^{-7} in the studied groups, which the maximum and minimum values being related to children below 10 years of age in Paramont (ILCR=1.9×10^{-6}) and adolescents between 11 and 20 years old in Sadra (ILCR =2.7×10^{-7}). US EPA suggested the chance of 1 additional cancer risk in every 10^6 people (1×10^{-6}) and stated that the ILCR values between 10^{-4} and 10^{-6} indicate a potential risk of carcinogenesis [8, US EPA]. Our study results demonstrated that the ILCR values were higher than 10^{-6} for the children below 10 years old, indicating the risk of cancer for this age group in both areas. Furthermore, comparison of the results obtained in the two areas displayed that the cancer risk was higher among the urban residents and, consequently, the children below 10 years of age were at a higher risk in Paramont. Cancer risk among different age groups in Shiraz was lower than those reported by several researchers around the world. The results of a study illustrated that respiratory ILCR was 1.04×10^{-4} for adults and below 10^{-6} for infants, which represents a potential increase in cancer risk among adults compared to infants [12]. It was also conducted a study on cancer risk assessment of PAHs compounds near an industrial area and reported the mean risk of lung cancer as 1.2×10^{-4} for the general public [4]. In the same line, other researchers assessed the risk of PAHs associated with PM_{10} in Tehran and estimated the mean of ILCR to be 7.85×10^{-6} for the general population [8].

Table 3. The mean concentration of BaP_{eq} for different PAHs compounds in the two sapling sites

Compounds	TEFs	Stations	
		Paramont	Sadra
Naphthalene	0.001	0.0007	0.0006
Acenaphtylene	0.001	0.0007	0.0007
Acenaphthene	0.001	0.0018	0.0016
Fluorene	0.001	0.0027	0.0027
Phenanthrene	0.001	0.0035	0.0035
Anthracene	0.01	0.0301	0.0279
Fluorantene	0.001	0.0004	0.0005
Pyrene	0.001	0.0857	0.0028
Benzo(a)anthracene	0.1	0.0305	0.0241
Chrysene	0.01	0.0028	0.0021
Benzo(b)fluoranthene	0.1	0.0469	0.0253
Benzo(k)fluoranthene	0.1	0.0510	0.0335
Benzo(a)pyrene	1.00	0.7380	0.4339
Dibenz(ah)anthracene	1.00	0.2673	0.2118
Benzo(ghi)perylene	0.01	0.0023	0.0019
Indeno(1,2,3-cd)pyrene	0.1	0.0422	0.0404
Σ BaP_{eq}	-	1.3073	0.8140

CONCLUSIONS

PM_{10} emission limit value for a period of 24 h (without any effects on human health) has been proposed as 150 μg/m^3 by EPA and 50 μg/m^3 by EC, which can be exceeded only 7 times/year [14]. Also, based on EPA, Iran's High Council for Environmental Protection has proposed a clean air standard of 150 μg/m^3 with repetition limit of 7 times/ year.

According to the present study results, the PM_{10} concentrations did not exceed Iranian Department of Environment in any sampling day, but were significantly higher than the EC emission limit value; i.e., 50 μg/m^3. Therefore, it can be concluded that air was polluted in terms of PM_{10} emissions in Shiraz (Paramont and Sadra areas), which was effective in human health.

Moreover, the PAHs in the sampling sites could increase the potential risk of cancer among the children below 10 years old in both sampling areas. Due to the omnipresence of PAHs in environment and their adverse effects on children's health, extensive researches are essential to detect even the smallest amounts of PAHs and to identify methods for reduction of PAHs emissions in Shiraz.

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COMPETING INTERESTS

The authors declare that they have no competing interests.

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ETHICAL CONSIDERATIONS

The manuscript is original work of authors. All authors agree to submit their manuscript to JAPH. The authors confirm that the manuscript have not been submitted or published elsewhere in any language.

REFERENCES

[1] Kakimoto K, Toriba A, Ohno T, Ueno M, Kameda T, Tang N, et al. Direct measurement of the glucuronide conjugate of 1-hydroxypyrene in human urine by using liquid chromatography with tandem mass spectrometry. Journal of Chromatography B. 2008;867(2):259-63.

[2] Ramesh A, Walker SA, Hood DB, Guillén MD, Schneider K, Weyand EH. Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. International journal of toxicology. 2004;23(5):301-33.

[3] Grainger J, Huang W, Patterson DG, Turner WE, Pirkle J, Caudill SP, et al. Reference range levels of polycyclic aromatic hydrocarbons in the US population by measurement of urinary monohydroxy metabolites. Environmental research. 2006;100(3):394-423.

[4] Ramírez N, Cuadras A, Rovira E, Marcé RM, Borrull F. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. Environmental health perspectives. 2011;119(8):1110-1116.

[5] Cancer IAfRo. Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. IARC monographs on the evaluation of carcinogenic risks to humans. 2010;92:35-818.

[6] Boström C-E, Gerde P, Hanberg A, Jernström B, Johansson C, Kyrklund T, et al. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. Environmental health perspectives. 2002;110(Suppl 3):451–488.

[7] Wang Y, Hu L, Lu G. Health risk analysis of atmospheric polycyclic aromatic hydrocarbons in big cities of China. Ecotoxicology. 2014;23(4):584-8.

[8] Hoseini M, Yunesian M, Nabizadeh R, Yaghmaeian K, Ahmadkhaniha R, Rastkari N, et al. Characterization and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in urban atmospheric Particulate of Tehran, Iran. Environmental Science and Pollution Research. 2016;23(2):1820-32.

[9] Pufulete M, Battershill J, Boobis A, Fielder R. Approaches to carcinogenic risk assessment for polycyclic aromatic hydrocarbons: a UK perspective. Regulatory Toxicology and Pharmacology. 2004;40(1):54-66.

[10] Moya J, Phillips L, Schuda L, Wood P, Diaz A, Lee R, et al. Exposure factors handbook. Washington: US Environmental Protection Agency; 2011.

[11] US EPA. Risk assessment guidance for superfund. volume I: human health evaluation manual. Washington: Office of Superfund Remediation and Technology Innovation; 2004.
[12] Chen S-C, Liao C-M. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. Science of the Total Environment. 2006;366(1):112-23.
[13] Querol X, Alastuey A, Rodriguez S, Plana F, Ruiz CR, Cots N, et al. PM_{10} and $PM_{2.5}$ source apportionment in the Barcelona Metropolitan area, Catalonia, Spain. Atmospheric Environment. 2001;35(36):6407-19.
[14] Hueglin C, Gehrig R, Baltensperger U, Gysel M, Monn C, Vonmont H. Chemical characterisation of $PM_{2.5}$, PM_{10} and coarse particles at urban, near-city and rural sites in Switzerland. Atmospheric Environment. 2005;39(4):637-51.
[15] Padoan E, Malandrino M, Giacomino A, Grosa MM, Lollobrigida F, Martini S, et al. Spatial distribution and potential sources of trace elements in PM_{10} monitored in urban and rural sites of Piedmont Region. Chemosphere. 2016;145:495-507.
[16] 1.Marcazzan GM, Vaccaro S, Valli G, Vecchi R. Characterisation of PM_{10} and $PM_{2.5}$ particulate matter in the ambient air of Milan (Italy). Atmospheric Environment. 2001;35(27):4639-50.