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A Study of Polycyclic Aromatic Hydrocarbons (PAHs) and Trace Elements in Ambient Air $PM_{2.5}$ in an Urban Site of Tehran, Iran

***Majid Kermani*[1], *Zahra Asadgol*[1], *Hossein Arfaeinia*[1, 2*]**

1) Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran
2) Department of Environmental Health Engineering, School of Public Health, Bushehr University of Medical Sciences, Bushehr, Iran
**Author for Correspondenc:*.arfaeiniah@yahoo.com

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ABSTRACT

The concentrations of thirteen polycyclic aromatic hydrocarbons (PAHs) and six trace elements adsorbed to a fine fraction of particulate matter ($PM \leq 2.5$ µm) were determined at an urban site in Tehran (Iran) during the spring period in 2013. The average concentration of $PM_{2.5}$ was 41.19 µg/m^3, which was 1.64 and 1.2 times higher than the annual average of WHO guidelines and EPA ambient air quality standards, respectively. The trace elements measured in the $PM_{2.5}$ samples were Pb, Cd, Cr, Ni, As and Zn with the mean concentrations of 38.05, 18.2, 4.24, 4.19, 1.34, and 69:92 ng/m^3 ,respectively. Hg was not found in any sample in this study. Results from correlation tests between PM2.5 concentrations and different toxic metals; which were studied in various days of the week, including holidays, 1 day after the holidays, and the other days showed that variability between groups was significant at 0.05 level. Exception is Hg and Zn. The mean concentrations of $PM_{2.5}$ and trace elements in 1 day after the holidays were higher compared other 2 groups. Total PAHs concentrations in $PM_{2.5}$ were found to be 7.92 ng/m^3.The most abundant PAHs found were high molecular weight homologues (4-6 ring PAHs) such as Inp, Bgp, Dba, Bkf and Bbf, which are contributing to constituents of vehicular emissions. In general, high molecular weight PAHs are more correlated than low molecular weight PAHs. Moreover, a moderate correlation was observed between total PAH concentration and $PM_{2.5}$ mass.

Key words: $PM_{2.5}$, Polycyclic Aromatic Hydrocarbons (PAHs), Trace Elements, Tehran

INTRODUCTION

A wide range of adverse health consequences has been recorded due to short- and long-term exposure to particulate matters, at levels usually experienced by urban populations[1-3]. Particles with smaller size have important health implications because they have a greater ability to penetrate deeply into the airways and lungs[4-6]. Due to these adverse health effects, in the recent decades, particles with aerodynamic diameter less than 10 µm (PM_{10}) and 2.5 µm ($PM_{2.5}$) have been received much attention [6, 7]. Some epidemiological studies have found relationship between exposure to PM (especially PM_{10} or $PM_{2.5}$) and increase in lung cancer risk[8, 9]. Also some study has shown that exposure to $PM_{2.5}$ or secondary particles such as sulfates can increase risk of respiratory diseases[10]. Moreover, there are many researches which have been shown association between health effects and particular aerosols characteristics such as particle size, number, concentration, and chemical composition, including sulfate, trace elements and metals such as Si, V, Fe, Pb, Cd, Ni, and Zn and elemental carbon [11, 12]. It has been shown that heavy metals content of particulate matters can be toxic to humans and other organisms at certain levels; and there are many researches regarding measurement of Pb, Cd, Hg, and other heavy metal levels in air and their toxic effects [13-16].

In addition to trace elements, the association of particulate matters (especially$PM_{2.5}$) with carcinogenic and mutagenic chemicals such as polycyclic aromatic hydrocarbons (PAHs) which is formed during incomplete combustion of organic materials and constitute the organic fraction of PM in ambient outdoor air may contribute to a range of adverse health effects [17, 18]. Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants formed by the incomplete combustion of organic materials such as coal, oil, wood, diesel oil and petroleum [19]. The formation of these compounds occurs in relatively high temperatures (more than 500℃) in conditions of insufficient oxygen in gas-burning facilities, motor vehicles, waste incinerators and industrial activities, such as oil refining, coke and asphalt production, aluminum production, steel and iron industries, etc. [20]. The formation of free radicals produced by the rupture of C-C and C-H bonds and consequently reaction with each other is one of a known mechanism of PAHs production. Levels of PAHs produced depend on the conditions such as temperature of combustion and the nature of the organic matter involved in the process [21].

These pollutants are widely studied due to their toxicity because some of them are known to be mutagenic or carcinogenic in the atmosphere. PAHs are released in both gaseous or particulate phases [22]. The most volatile compound of PAHs exists almost exclusively in the gas phase. In general PAHs having 2-rings (Naphthalene) exist in the gas phase while those having 3- and 4-ring (Anthracene, , Benz[a] Anthracene, Chrycene, Pyrene, Phenanthrene, Flouranthene) can be present in both the gas and particulate phases and the carcinogenic 5- and 6-ring species (Benzo[a]Pyrene, Benzo[b] Flouranthene, Benzo[k] Flouranthene, Benzo[e]Pyrene, Benzo[ghi]Perylene, Dibez[a,h]Anthracene, Indeno[1,2,3-cd]Pyrene) are predominantly associated with particles. The majority of particle-bound PAHs are found on small particles with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) [23].

The atmospheric concentrations of PAHs have been measured and reported in many geographical locations of the world such as Higashi Hirushima ,Japan [24], Kozani, Greese [25], France [26], and Madrid, Spain [27]. Tehran is one of the most polluted cities in the Asia and even in the world in which [23]extreme sources of pollution include heavy industry, local heating systems combusting fossil fuels, and old cars that are not equipped with up-to-date catalysts and particle filters may be expected.

Hoseini *et al.[*28] reported that the total average concentrations of PAHs in urban atmospheric Particulate of Tehran ranged from 56.98±15.91 to 110.35±57.31 ng m−3 in summer and from 125.87±79.02 to 171.25±73.94 ng m−3 in winter. In the other study, Moeinaddini *et al.* found that the average concentrations of total PAHs and total n-alkanes in respirable particles of Tehran were 16.7 and 591 ng/m^3, respectively. Nevertheless, there are sporadic studies regarding the atmospheric concentrations of trace elements and particle-bound PAHs in Tehran. Thus, the present study aimed to assess the relative abundance of trace elements and PAHs on PM2.5 particles to provide a database for other studies and regulatory action to improve air quality in Tehran.

MATERIALS AND METHODS

Sampling sites and method

Tehran, the capital of Iran, has a geographic area of 686.3 km2 and is situated at 35º 45' 20. 90''N ,51º 23'40. 40''E, and 1,200 above sea level. The monitoring site located between two large squares in the center of Tehran. There are many busy roads with unique transportation, which includes buses, gasoline passenger car, taxis and diesel trucks near the sampling site.

Moreover, around 100 m from the sampling site, many local roads intermingle together and have a large number of motor vehicles. Traffic congestion at the sampling site was about 600-700 vehicles / hour during the sampling period. Moreover, there are a large number of workshops, commercial centers and a bus terminal adjacent to the sampling site. Fig.1 illustrates the sampling site in Tehran.

Samples for $PM_{2.5}$ were collected using afrmOMNItm Ambient Air Sampler Operating at 5 l/min. PTFE filters of 47mm in diameter from Sartorius Stedim Biotech GmbH (Germany) were used to collect particle matters. The instruments were kept at 10 m above the ground level. Thirty $PM_{2.5}$ samples were collected every three days from 21 March to 22 June, 2013. Sampling duration was 24 h with yielding sample volumes of 7.2 m^3. The filters were weighed twice, before and after sampling using an analytical balance with reading precision of 10 μg (Model: Sartoris 2004 MP) to obtain $PM_{2.5}$ concentration. Afterwards, for protection samples against sunlight, they were wrapped in aluminum foil and then they were frozen at -20°C to prevent of volatilization of PAHs until extraction and analysis.

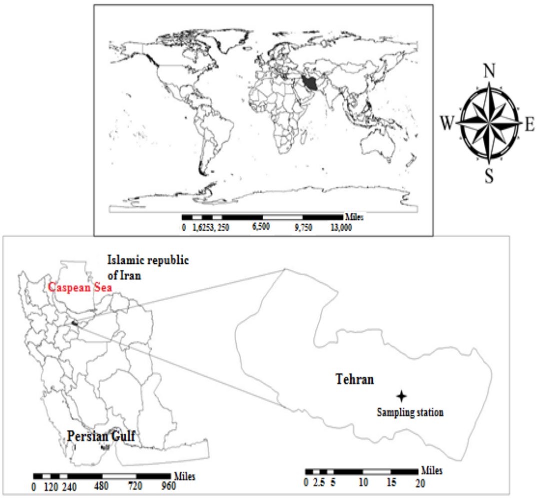

Fig.1: Location of the sampling site in Tehran

In order to determine the trace elements (Pb, Cd, Cr, Ni, Hg, As and Zn) contents, one-fourth of each PTFE filter was digested twice with 5mL of concentrated HNO_3 and 5ml of $HClO_4$ in a Teflon bomb to solubilize the metals in ionic form. These samples were heated to dryness at 170 $^{\circ}$C for 4 hours and then was added 2.5 ml HNO_3 (1N) initially and was rinsed with distilled–deionized water (with a resistivity of 18 Ω) up to a final volume of 25mL, finally. The analysis was carried out by using ICP-AES (Arcousmodel,Germany) [29, 30]. Each element was quantified under specific wavelength conditions with the corresponding dilutions using Milli-Q water, and using standards which were simultaneously analyzed with experimental samples. The standard deviation was checked at the beginning and at the end of each measured trace element. In order to determination of background values of each species during the study period, blank samples (i.e., unexposed control filters) were chemically analyzed routinely. Then, the real concentration of each species was calculated by subtracting the blank values from the results of the chemical analysis conducted on the exposed filters.

Extraction procedure and analysis of PAHs

To extract PAHs, a half of each filter paper was cut and shredded into 10-ml vial. After that, filters were covered with approximately 5mL of HPLC grade dichloromethane (DCM) and sonicated for 30 min in an ultrasonic bath (Elmasonic S 80 H). To achieve maximum extraction, extraction procedure was repeated two times more. The extracts were filtered through 0.22 µm Millipore PTFE filters (Schleicher &Schuell) and the volume reduced to~2 mL. Afterwards, extracts were injected into GC-MS for analysis. Before chromatographic analysis, 0.6 ng of semi-volatile internal standard (Dioxane) was added to all extracts. The analysis was performed on an Agilent 7890 Gas Chromatograph-5975C Mass selective Detector (GC-MS) system equipped with a fused silica capillary Hp-5 column (30* 0.25mm i.d., 0.25mm film thickness). The mass range scanned was from 50 to 550 am under full scan acquisition mode with an initial flow of 1.0 ml min-1 and using helium as a carrier gas. The ionization was done in the electron impact mode at 70 eV and an initial temperature of 70 °C was held for 2 min, increased at a rate of 7 °C per min to 280 °C, then held for 5 min. The volume of injection was 1 µl of each sample in the spiritless mode and the purge time was 2 min. Detecting and quantifying of PAHs compounds were based on conforming their retention time with a mixture of PAH standard (Supelco-EPA 610 PAH mix, Supelco, USA). In order to determine the background values of each PAHs during the study period, control samples (i.e., unexposed control filters) were similarly extracted. Then, the real concentration of each species was calculated by subtracting the control sample values from the results of the chemical analysis conducted on the exposed filters.

Quality assurance

All data for this study were achieved under strict control procedures and quality assurances. The recovery rate ranged from81-94% with relative standard deviation of 3-9%. To monitor the quality control, procedural blanks were analyzed with every 5 samples. PAHs were not detected in any of the analytical blanks. Quantitative analysis was carried out on a five-point linear calibration of PAH solution, acquired by dilution of the 16-PAH mixture. Limit of detection (LOD) were measured with a signal-to-noise ratio (S/N) of 3. The MDLs were between 0.1 and 1 ng/g. Satisfactory linearity was obtained with values of the correlation coefficient R above 0.99.

Statistics analysis

The obtained findings were statistically analyzed using SPSS for Windows version 19 (SPSS Inc, Chicago, IL). Data analysis including mean, maximum and minimum concentrations, and standard deviation using statistical methods was performed. Linear correlation Pearson analysis was applied to test the relationship between $PM_{2.5}$, heavy metal and PAH concentrations. The following data were used to analysis: (a) the rate of each PAH; (b) the total of 16 PAHs; (c) the total of six PAHs with low molecular weight; (d) the total of 10 PAHs with high molecular weight and (e) the total of potentially carcinogenic PAHs.

RESULTS AND DISCUSSION

Particles mass and trace element concentrations

Mass concentration of $PM_{2.5}$ and its trace elements content (mean ± SD) are shown in Table 1.

Table1: Particles mass and trace element concentrations

Components	unit	Mean ± SD	Median	Range
$PM_{2.5}$(µg/m^3)	µg/m^3	41.19±11.9	37.98	17.98 - 76.45
Pb	ng/m^3	38.05±11.96	37.98	14.98 - 66.51
Cd	ng/m^3	18.20±6.13	19.04	5.97 -33.26
Cr	ng/m^3	4.24±1.44	4.43	1.40 - 7.80
Ni	ng/m^3	4.19±1.38	4.33	1.35 - 7.49
Hg	ng/m^3	ND	ND	NDa
As	ng/m^3	1.34±0.99	1.23	0.12- 3.65
Zn	ng/m^3	63.92±19.94	61.33	22.24 - 109.27

aNot Detection

As showed in Table 1, the $PM_{2.5}$ concentrations ranged from 17.98 to 76.45 μg m^{-3} during the sampling period with an average of 41.19μg $m{-}3$. As the results shown, $PM_{2.5}$ concentrations in some days were higher than EPA daily standards (EPA 1997) which have been adopted adapt in Iran. In comparison with other studies, these levels fall in the low to moderate range [31, 32].

Mean concentrations of $PM_{2.5}$–associated metals measured in this study the following order: Zn >Pb> Cd > Ni> As. As can be seen, the most abundant heavy metal species in the $PM_{2.5}$ fraction were Zn and Pb, respectively. The As, Ni, and Cr showed a lower contribution to the total trace element contents, with average concentrations lower than 5 ng/m_3. Results obtained by KhaiwalRavindra *et al*.have shown that Ni and Cr were classified as trace elements with mean concentrations below 10 ng m^{-3} [33]. As well as, Hg was found in none of the samples. As mentioned above, Zn and Pb were determined as the most abundant trace element species in the $PM_{2.5}$ fraction, and there a good correlation between Pb and $PM_{2.5}$ as showed in Fig. 2, with R2 of 0.598. Furthermore, Zn showed a poor correlation with the $PM_{2.5}$ with R2 of 0.141 (Fig. 3). Similar results have been reported for Pb by a previous study in Chemical composition of TSP and PM_{10} in a central area of Tehran [34].

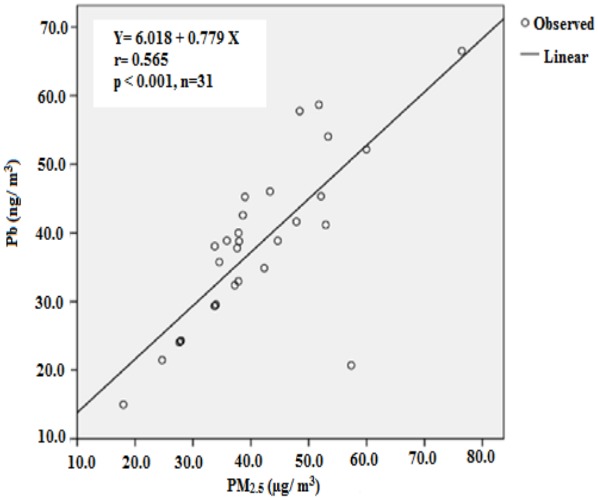

Fig.2: Correlation between $PM_{2.5}$ and trace element of Pb mass concentration

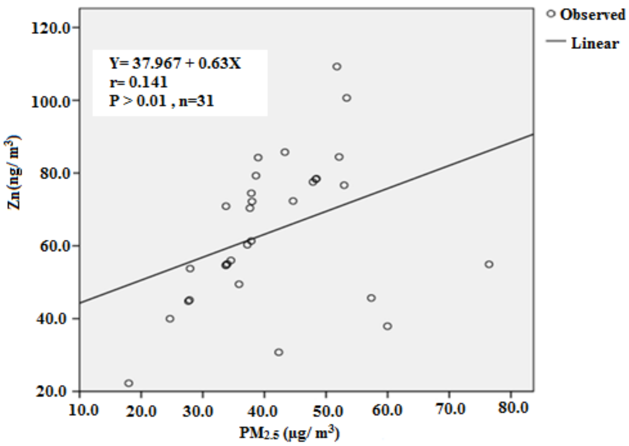

Fig.3: Correlation between $PM_{2.5}$ and trace element of Zn mass concentration

The levels of $PM_{2.5}$-related trace element concentrations could be compared with other studies. According to Thomaidis et al, high Pb levels and slightly, lower values of other metals were observed. They have found that the trace elements concentrations followed in order Pb>Ni>As>Cd. As and Ni is produced largely by metals industries such as steel industry and smelters, together with emissions associated with diesel, oil and coal burning. As well as, Zn production is associated with abrasion and incineration of the tire, brake pads and engine oil [35]. It has been found that Pb in urban sites is related to motor vehicle releases and the wear of construction materials such as brick, metal, wood and paint. Furthermore, Cd was related to brake pad wear, emissions of diesel and motor oil [35].

Moreover, trace element levels in $PM_{2.5}$ found to be higher than those reported by Philadelphia and Pheonix in the USA [36], Pérez Nand *et al.*, in Spain [29]and Kendall Mand *et al*., in Turke [37](Table 2). These remarkable differences, between trace element concentrations, especially for Pb and Cd, could be attributed to the differences in geographical conditions and the large number of vehicles and industries in Tehran. Due to plenty of pollution sources and restricted control, it seems difficult to determine the particular sources of these metals. It is estimated that emissions be associated with consumption of fossil fuels (coal, oil and etc.) for producing energy in residents and industries.

Table 2: Mean concentrations (ng/m^3) of 7 trace elements measured in urban background $PM_{2.5}$ in Tehran over the period March to June 2013 and compared with other studies.

	Pb	Cd	Cr	Ni	Hg	As	Zn
This study	38.05	18.2	4.24	4.19	ND	1.34	63.92
Urban USAa	28	-	1.4	8.5	-	0.4	56
Urban Spainb	26	0.5	6	6	-	1.1	103
Urban Turkeyc	32	1.3	9.4	7.7	-	4	215

a: Philadelphia, USA in 1994 [36], b: Metal concentrations in PM_{10} in Barcelona, Spain during 2003–2006 [29], c :Metal concentrations in $PM_{2.5}$ in Bursa, Turkey during 2007-2008 [37

Comparison considered parameters between various days:

For comparison purposes, the measured levels of the considered parameters between various days of the week, data from the study classified into the following three categories: holidays, 1 day after the holidays, and the other days. The results of grouped data for $PM_{2.5}$, and total metal concentrations are presented in Table 3.

The one-way ANOVA procedure was used to search for significant variability's among these groups. Using this procedure, it was found that variability's between groups (holidays, 1 day after the holidays, and workdays) was significant at the 0.05 level. An exception was Hg (Pvalue=0. 238) and Zn (Pvalue=0. 177). The total levels of Pb, Cd and Cr were lower than those previously reported for TSP and PM_{10} in a central area of Tehran [34, 38] and other Asian urban area [39].

The results of grouped data for total metal concentrations are presented in Table3. As can be seen, mean concentrations of $PM_{2.5}$ and their trace element contents in 1 day after the holidays were higher than 2 other groups(except Zn). This result is likely due to the huge amount traffic on the large number of cars on the streets these days automotive in 1 day after the holidays that could be the reason for the increased emissions in these days.

Table3: The differences between concentration and content of ambient $PM_{2.5}$in holidays, 1 day after holidays, and the other days

	Components	**Mean ± SD**	**Median**	**Min – Max**
The other days	$PM_{2.5}$($\mu g/m^3$)	36.91 ± 7.46	37.65	24.67 - 52.12
	Pb (ng/m^3)	35.74 ± 9.58	37.79	21.46 - 58.68
	Cd	17.87 ± 4.79	18.90	10.73 - 29.34
	Cr	4.19 ± 1.12	4.43	2.52 - 6.88
	Ni	4.03 ± 1.08	4.26	2.42 - 6.61
	Hg	ND	ND	ND
	As	1.23 ± 0.92	0.98	0.12 - 2.98
	Zn	66.99 ± 17.3	70.37	39.97 - 109.27
Holidays	$PM_{2.5}$($\mu g/m^3$)	38.68 ± 12.37	39.10	17.98 - 52.93
	Pb (ng/m^3)	37.23 ± 13.73	37.32	14.98 - 57.76
	Cd	14.03 ± 6.2	14.16	5.97 - 21.07
	Cr	3.29 ± 1.45	3.32	1.4 - 4.94
	Ni	3.16 ± 1.4	3.90	1.35 - 4.75
	Hg	ND	ND	ND
	As	1.21 ± 0.83	1.29	0.23 - 2.45
	Zn	52.26 ± 223.10	52.72	22.24 - 78.46
1 day after holidays	$PM_{2.5}$($\mu g/m^3$)	57.99 ±11.63	57.34	47.87 - 76.45
	Pb (ng/m^3)	44.62 ± 16.76	42.06	20.70 - 66.51
	Cd	20.70 ±7.70	21.03	12.32 - 33.26
	Cr	5.14± 1.96	4.88	2.54 - 7.8
	Ni	4.92± 1.96	4.74	2.14 - 7.49
	Hg	ND	ND	ND
	As	1.74±1.48	1.23	0.23 - 3.65
	Zn	58.87± 18.41	54.92	37.92 - 78.31

PAHs concentrations in $PM_{2.5}$:

List of PAHs reported abbreviations, formula, molecular weight, vapor pressure. Concentrations (mean ± SD) and their contribution to the total PAHs in $PM_{2.5}$ measured are presented in Table 4.

As showed in Table 4, the average concentrations (ng m−3) of PAHs during sampling period ranged from 0.075ngm^{-3} (Chry) to 1.21ng m^{-3} (Dba). These values are lower than those previously reported in PM_{10} samples in urban air of Tehran [40]. For example, for Dibenz[a,h]anthracene, the most abundant PAH observed in this study, the mean level (1.21ng m^{-3}), was Two-third of the value reported in PM_{10} of Tehran by Halek *et al.* (1.81ng m^{-3}).

The concentrations of seven carcinogenic PAH in this study were in order Dba>Bkf>Inp>Bbf>Bap>Baa >Chry. This study also revealed that seven carcinogenic PAHs had a maximum level of total

PAHs with almost two-third of the total PAHs concentration, presumably due to the large number of vehicles in Tehran. Similar findings were reported for atmosphere of Tehran by Hoseini *et al.* [28].

PAHs were classified based on their aromatic rings as follows: PAHs with 3-ring include Phen, Anth; 4-rings include Fluo, Pyr, Baa, Chry; 5-rings include Bbf, Bkf, Bap,Bep, Dba; 6-rings include Bgpand Inp. The percentage of each group to total PAHs in $PM_{2.5}$ samples during the sampling period was shown in Fig.3. As illustrated in this figure, high molecular weight PAHs with 4-6 rings has a higher fraction about 70% in total PAHs, while low molecular weight PAHs with 2-3 ring participates a lower fraction. The higher fraction of high molecular weight PAHs in $PM_{2.5}$ samples are mainly due to fossil fuel consumption. Similar observations have also been reported by Liu and Cheng [41]and D.P. Singh [42].

With comparisons of $PM_{2.5}$ related 4-6 ring PAH concentrations in present study with those reported values for other major cities around the world, (Supplementary information; Tables 4 and 5), it was seen that values obtained in this study, were much higher than those reported in other parts of the world [43, 44].

Table 4: List of PAHs reported, abbreviations, formula, molecular weights, vapor pressure, mean concentrations and their contribution to the total PAHs in $PM_{2.5}$

PAH Compounds	Formula	Molecular weight	Vapor pressure (mm Hg)a	Mean ± SD (ng/m^3)	% of total PAHs
3-Rings, C12-C14					9.5
Phenanthrene (Phen)	C14H10	178	6.8×10-4	0.51±0.97	6.4
Anthracene (Anth)	C14H10	178	1.7×10-5	0.25±0.55	3.1
4-Rings, C16-C18					19.44
Fluoranthene (Fluran)	C16H10	202	5×10-6	0.88±1.28	11.1
Pyrene (Pyr)	C16H10	202	2.5×10-6	0.39±0.7	4.9
Benzo[a]anthracene (Baa)	C18H12	228	2.2×10-8	0.20±0.56	2.5
Chrysene (Chry)	C18H12	228	6.3×10-7	0.07±0.41	0.94
5-Rings, C20					36.24
Benzo [e] pyrene (Bep)	C20H12	252	5.7×10-9	0.83±1.39	10.47
Benzo[b]fluoranthene (Bbf)	C20H12	252	5×10-7	0.73±1.23	9.2
Benzo[k]fluoranthene (Bkf)	C20H12	252	5.59×10-11	1.04±1.88	13.1
Benzo[a]pyrene (BaP)	C20H12	252	5.6×10-9	0.28±0.71	3.47
6-rings, C22					34.85
Dibenz[a,h]anthracene (Dba)	C22H14	278	1.0×10-10	1.21±1.57	15.23
Benzo[ghi]perylene (Bgp)	C22H12	276	1.03×10-10	0.67±1.02	8.42
Indeno[1,2,3-cd]pyrene (Inp)	C22H12	276	10-11-10-6	0.89±1.38	11.20
∑PAH	-	-	-	7.92±7.01	100
$PM_{2.5}$(µg/m3)	-	-	-	41.19±11.9	-

Table5: Mean concentrations (ng/m^3) of PAHs measured in urban background PM$_{2.5}$at the sampling site over the period March2013 to June 2013, Comparison have made with urban background data from the USA (1999), Suburban Atlanta (2003–2006) and India (2011)

Location	**Current study**	**Urban Los Angeles**	**Urban Atlanta**	**Urban India**
Sampling season	**March to June 2013**	**Throughout the year, 2001-02**	**June, 2003-04**	**Summer, 2007-08**
Phen	0.51	NA	NA	1
Anth	0.25	NA	NA	1.6
Fluo	0.88	0.03	0.04	2.7
Pyr	0.39	0.05	0.04	1.5
Baa	0.2	0.03	0.02	1.8
Chry	0.07	0.05	0.05	2.8
Bep	0.83	-	0.06	NA
Bbf	0.73	0.08	0.09	5.4
Bkf	1.04	0.04	0.3	6.9
Bap	0.28	0.08	0.4	5.1
Dba	1.21	0.01	-	2.1
Bgp	0.67	0.08	0.07	6.4
Inp	0.89	0.17	0.14	4.2
Reference	Current study	[44]	[43]	[42]

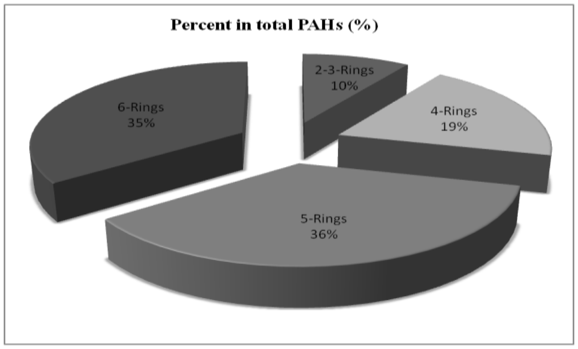

Fig.4: Distribution of grouped PAH by ring size in PM$_{2.5}$

The levels of PM$_{2.5}$-bound PAHs were compared with other international researchers. Comparing the obtained results of the current study with those reported that Collected in Rio de Janeiro, Brazil by S.L. Quiterio [45], shows that our values are 0.13 ngm^{-3} (for Phenanthrene) to 0.87 ngm^{-3} (for acenaphthene) upper. In general, concentrations of most PAHs compounds, determined in present study, except Chrysene, Benzo[a]pyrene and Benzo[ghi]perylene, were higher than those measured in an area away with obvious lack of primary particle sources, located at the country side of Thromacedones, Greece [46].

As showed in Table 4, PAHs levels in PM$_{2.5}$ samples were higher than those reported by Eiguren-Fernandez *et al.*, in the Los Angeles [44], Zheng Li *et al.*, in the Atlanta [43]. But our results are lower than those reported by D.P. Singh *et al.*, in urban environments of Delhi [42]

It is worth mentioning that levels of PAHs depend on several factors such as geographical and meteorological conditions, sampling methods, extraction methodology of the study, sampling seasons and sources of emissions and these can be reasons for the difference in the results between different geographical locations around the world. Comparisons between literature data are vague and may lead to inaccurate conclusions.

Relationship between PAHs with 3, 4, and 5–6 aromatic rings and relationship between PAHs concentration and PM$_{2.5}$ concentration

Linear regression analyses have performed on the concentrations of measured PAHs as well as among the total PAHs concentration and PM$_{2.5}$ concentration concurrently measured in all samples. Not surprisingly, a good correlation was observed between individual PAHs of similar molecular weight with each other (Table 6), and in general, high molecular weight PAHs are more correlated than low molecular weight PAHs. The Pearson correlation coefficients (r) between PAHs with 3, 4 and 5–6 aromatic rings also were found to be: 3-rings: 0.06-0.71, 4-rings:0.19-0.93 and 5,6-rings:0.71-0.97. Also, similar results for the correlation between PAHs have been reported by Wu *et al.*, in China [47].

Moreover, moderate correlation was observed between total PAHs concentration and PM$_{2.5}$ mass (Fig. 5). Our findings differ from a study conducted on the Atlanta atmosphere, where particulate PAHs were better correlated with PM$_{2.5}$ mass [43]. However, such differences are not surprising, given the various sources and atmospheric chemistry affecting the Tehran airshed as compared with air over the Atlanta.

There are number of limitation in which further study could be carried out. First, since the vehicles are the main origin of PAHs in Tehran, there is a need to do further comprehensive analysis using finer fraction of atmospheric aerosols, such as PM1. Source apportionment of PAHs by using positive matrix factorization (PMF) and chemical mass balance (CMB) as well as dispersion modeling with higher number of samples can be performed in order to provide more information about PAH sources and distribution. Second, regarding risk assessment, there is a need to conduct further research to characterize better those parameters that contributed most significantly to the risk estimates.

Table6 Correlation matrix of the individual PAH compounds.

	Phen	Anth	Fluo	Pyr	Baa	Chry	Bep	Bbf	Bkf	Bap	Dba	Bgp	Inp
Phen	1.00												
Anth	0.71	1.00											
Fluo	0.54	0.66	1.00										
Pyr	0.39	0.59	0.92	1.00									
Baa	0.13	0.21	0.53	0.71	1.00								
Chry	0.21	0.31	0.61	0.73	0.93	1.00							
Bep	0.09	0.24	0.38	0.63	0.76	0.81	1.00						
Bbf	0.13	0.28	0.52	0.64	0.83	0.76	0.97	1.00					
Bkf	0.13	0.26	0.51	0.62	0.82	0.79	0.96	0.96	1.00				
Bap	0.06	0.21	0.34	0.59	0.81	0.83	0.96	0.95	0.96	1.00			
Dba	0.08	0.19	0.38	0.51	0.69	0.64	0.73	0.84	0.83	0.8	1.00		
Bgp	0.12	0.28	0.42	0.66	0.82	0.79	0.74	0.97	0.96	0.79	0.82	1.00	
Inp	0.10	0.21	0.47	0.62	0.81	0.74	0.93	0.92	0.93	0.94	0.71	0.96	1.00

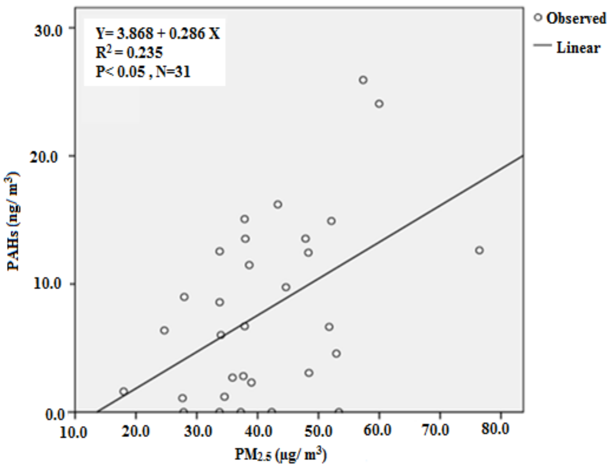

Fig.5: Correlation between PAHs and $PM_{2.5}$ concentrations

CONCLUSION

This study describes the level and distribution characteristics of $PM_{2.5}$ and its related trace elements and PAHs in an urban site in Tehran (Iran) during the spring period of 2013. As the results showed the average concentration of the $PM_{2.5}$ for the sampling period was 1.64 and 1.2 times higher than the annual average of WHO guidelines and EPA ambient air quality standards, respectively. Trace element concentrations in atmospheric $PM_{2.5}$ collected at the sampling site were lower than several reported values for other urban areas with high or medium vehicular traffic and/or industrial input. Also the measured values were lower than those previously reported for TSP and PM_{10} in Tehran. Regarding $PM_{2.5}$-bound PAHs, the results illustrated that the concentrations of $PM_{2.5}$-bound PAHs in ambient air at the sampling site were higher than several reported values for other urban areas around the world. The most abundant PAHs found were Inp, Bgp, Dba, Bkf and Bbf, which are contributing to constituents of vehicular emissions. In general, high molecular weight PAHs are more correlated than low molecular weight PAHs. Moreover a moderate correlation was observed between total PAHs concentration and $PM_{2.5}$ mass. In addition to this, these findings provide a valuable data base database health risk assessment of the local population and prioritization of control actions.

ETHICAL ISSUES

Ethical issues have been observed by the authors.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

AUTHORS' CONTRIBUTION

Authors contribute on this study as following items:
Majid Kermani:Study design .
Hossein Arfaeinia: Statistical analysis and reviewing the final version of the manuscript.
Zahra Asadgol:Data coordinator and data mining

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