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Characterization, spatial distribution, and health risk assessment of polycyclic aromatic hydrocarbons and heavy metals bounded $PM_{2.5}$ in urban air of Tabriz, Iran

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ABSTRACT

Introduction: Air and its invisible components play an influential part in the existence of living beings. The two factors of urbanization and industrialization of cities increase the concentration of various compounds in the air. This study has been designed to examine seasonal characterization, spatial distribution and health risk assessment of sixteen Polycyclic Aromatic Hydrocarbons (PAHs) and eleven heavy metals bounded $PM_{2.5}$ at 16 sites in urban air of Tabriz, Iran.

Materials and methods: Glass-fiber filters, peripheral pumps and PMI holder were used with a total 3 L/min flow rate for 24 h sampling Particulate Matter less than 2.5 µm ($PM_{2.5}$) every 4 seasons at 16 sites from 20nd February to 20th December. Proper solvents are consumed for extraction purposes of these Materials. Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Gas Chromatography–Mass Spectrometry GC/MS devices used for analyzing purposes and the spatial distribution of PAHs and heavy metals bounded $PM_{2.5}$ investigated by ArcGIS 10.3. Excess Lifetime Cancer Risk (ELCR) values and carcinogenicity risk were also calculated for children and adults in different exposure pathways.

Results: The annual mean concentrations of $PM_{2.5}$ were 41.17 µg/m^3, ∑16 PAHs bounded-$PM_{2.5}$ were much higher in autumn and winter (217.47 and 178.32 ng/m^3) compared to summer and spring (162.61 and 131.89 ng/m^3). The annual mean concentrations of heavy metals bounded-$PM_{2.5}$ were 138.69 ng/m^3. Dermal carcinogenicity risk of exposure with PAHs and ELCR values of heavy metals indicated high risk for adults and children in some stations.

Conclusion: Considering the topographic location of the region, Industrial areas and the frequent presence of temperature inversion, such comprehensive researches are needed for control policies

Introduction

Air pollution mainly refers to the heterogeneous presence of gaseous and particular matters in atmospheric air [1]. Besides their natural resources, a wide variety of sources in developing

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countries, including; vehicular emissions, industrial and residential sources, derives a wide range of air pollutants [2]. Effects of air quality on people's behavioral factors and psychological health also indicate low life expectancy in polluted regions [3]. Inhalable fine fractions of Particular airborne Matters ($PM_{2.5}$) can settle in the lungs and cause many health problems among these atmospheric pollutants. These particular matters, unlike gaseous pollutants, show different chemical properties from one to another particle, different characteristics of these components, results in variable and unpredictable health effects worldwide [4].

Various sources such as vehicular exhaust publications, combustion of fossil fuels, waste incineration, and other industrial emissions can penetrate particulate matters to the air. Recent studies in urban atmospheres indicate that respiratory exposure to each milligram $PM_{2.5}$ has a different production probability of free radicals in citizens of two similar populated cities [5]. Identification of seasonal concentration variations and type detection of chemical composition bounded $PM_{2.5}$ plays the most efficient role in predicting health hazards related to particular matters [6].

The components of fine Particular Matters ($PM_{2.5}$) consist of various carbonaceous and inorganic components that can be harmful even at low concentrations [7]. As organic components, Polycyclic Aromatic Hydrocarbons (PAHs) are consist of carbon, hydrogen, and two or more benzene rings [8]. PAHs are a large group of volatile organic matters that the multiplicity of benzene rings and their connecting angles form different molecular weight, physicochemical and biodegradable properties [9]. Due to the structural diversity of PAHs, there is a classification based on the structural shape of these compounds so that if the linear structure of benzene rings in connection with the middle ring has a circular shape, it is pre-condensed. If these joints do not form a circle, it is called a cata-condensed structure [10]. The compounds of the pre-condensed group are thermodynamically stable and have less chemical reactivity [11]. Pyrogenic, petrogenic, and biological publications are possible routes of release for these pollutants, but anthropogenic sources, including pyrolysis of organic compounds and incomplete combustion, are the most common roots [12]. Acute effects of exposure to $PM_{2.5}$-bound PAHs range from eye and skin irritation to gastrointestinal motilities [13]. At the same time, exposure's chronic effects include a more comprehensive range of respiratory problems, lung abnormalities, cataracts, and even erythrocyte damage [14]. Polycyclic aromatic hydrocarbons bonded with suspended particles, unlike polycyclic aromatic hydrocarbons in the gaseous phase, are less affected by decomposition processes and are considered harmful compounds for human health [15]. Due to their wide-spread distribution, also carcinogenic, teratogenic, and mutagenic properties, among more than two hundred detected PAHs, sixteen species, including benzo[a]pyrene (BaP), benzo[a] anthracene (BaA), benzo[b]fluranthene (BbF), benzo[k]fluoranthene (BkF), chrysene (Chr), benzo[g,h,i]perylene (BghiP), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fle), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Dibenz[a,h] anthracene (DBA), Naphthalene (Nap) and indeno [1,2,3-cd]pyrene (IcdP), are regarded as priority pollutants by the United States Environmental Protection Agency (US EPA) [16].

Heavy Metals (HMs), as inorganic components bounded $PM_{2.5}$, are defined variously by their properties. However, briefly, heavy metals are

a group of intermediate elements of copper to bismuth elements in the periodic table, which is considered toxic and can be accumulated in the organs and blood [17, 18]. This group is found naturally in the Earth's crust in mixed or oxidized forms [19]. The most important members of heavy metal compounds that researchers have mostly considered are Lead (Pb), Chromium (Cr), Mercury (Hg), Cadmium (Cd), Arsenic (As), Copper (Cu), Manganese (Mn), Nickel (Ni), Zinc (Zn) and Silver (Ag) [20]. These components do not disintegrate in common biochemical processes and disrupt some organs' normal functioning [21]. International Agency for Research on Cancer (IARC) classifies a group of heavy metals, including Arsenic (As), Cadmium (Cd), hexavalent chromium (Cr^{6+}), and Nickel metalloid (Ni), as compounds with carcinogenic effects, Especially lung, liver, and kidney cancers for humans [22]. Natural and Anthropogenic sources such as dust re-suspension, fossil fuel combustion, industrial plants, and traffic emit various heavy metals [23]. The bio-chemical concerns of these heavy metals, besides their carcinogenic and mutagenic properties, have attracted the attention of many researchers [24]. This paper investigates concentrations of important heavy metals such as Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn in the ambient air of Tabriz.

Tabriz, the capital city of east Azerbaijan province, is the most significant economic and industrial core with an approximate population of 1.8 million in the northwestern part of Iran. It has a geographic area of about 324 km^2 and locates in the geographical coordinates of 46°27' E, 38°09 N with an altitude of about 1300 m above sea level. The city is bordered to the north by Un-ebnAli mountains, Garadug and Saridug mountain in the west, to the south by Sahand mountain, and about 100 km distance to Urmia salt lake by east. Tabriz has a semi-arid characteristics zone. The wind rose shows the prevailing winds from this city are from the northeast and the southwest. The primary rainfalls occur in the autumn, winter, and spring, and falls shift to snow about the third month of the autumn. The city of Tabriz is prone to unique weather conditions against western pollutants produced by some small and large industries located on the western, southwestern, and northwestern of this city. Reports of Tabriz air pollution reduction plan relates the largest share of pollutant emissions to vehicles and industrial centers, including; thermal power plant, petrochemical complex, oil refineries, machine, and tractor Manufacturing. Also, due to the preservation of the old texture of the city (such as Tabriz Grand bazaar) and inadequate street spacing, the population is more concentrated in the central areas. As a result, heavy traffic forms. Due to the region's topographic conditions mentioned above and the lack of natural air conditioning, a temperature inversion is likely to occur in the cold seasons.

Based on the above issues and even though no comprehensive study with this magnitude has ever been conducted on pollution characteristics, seasonal changes, spatial distribution and health impacts of polycyclic aromatic hydrocarbons and heavy metals bounded with $PM_{2.5}$ particles, on a yearly monitoring basis. Considering the number of preliminary studies (to the best of our knowledge), comprehensive studies that aim to promote the atmospheric ambient air of residents are required.

Considering the gaps in the relatable studies, this study aimed to: 1) Determination of the concentration of $PM_{2.5}$ particles of 16 different stations in the city during one-year monitoring, 2) Determination of the concentration and analysis

of ∑16 PAHs bounded-$PM_{2.5}$, 3) Determination of the concentration and analysis of $PM_{2.5}$-bound heavy metals 4) Determination of the spatial distribution of polycyclic aromatic hydrocarbons and heavy metal in ambient air of Tabriz, 5) Determination of the impact of meteorological parameters on the concentration of PAHs and heavy metals and, 6) Assessment of the potential health risk due to human exposure to atmospheric $PM_{2.5}$-bound heavy metals, 7) Determination of the seasonal distribution of $PM_{2.5}$ in selected important cities of different countries in compared with ones in Tabriz from March to December 2020. It is hoped that the findings of this paper would provide insights into the characteristics, seasonal changes, possible sources, and health impacts of atmospheric polycyclic aromatic hydrocarbons and heavy metal bounded $PM_{2.5}$ in the ambient air of the most significant economic urban area in the Northwestern city of Iran.

Materials and methods

Study area and site description

Tabriz is the capital city of east Azerbaijan province. It has a geographic area of about 324 km^2 and geographical coordinates of 46°27' E, 38°09 N. This descriptive cross-sectional study has been carried out to determine the concentration and analysis of ∑16 PAHs and heavy metals bounded-$PM_{2.5}$, and examined the impact of meteorological parameters, identified possible sources, and assesses the health risk in the ambient air of Tabriz. For this purpose, 16 sampling sites were chosen to screen different residential, industrial, and relatively high traffic load areas that cover the city's entire area. Fig. 1 Presents the sampling sites and their distribution. Samples of the monitoring sites were collected from 20th February to 20th December of the year 2020. The sampling was conducted on a 24 h basis in every site based on EPA-TO/13A guidelines [25, 26]. Sixteen samples from different sites every season, and 64 samples in total were taken throughout the year [27]. All sampling sites were at an approximate height of 1.8 m above the ground, on the rooftop, so it would not re-suspense the ground dust. Before taking samples, all pumps were checked for calibration, and in special situations such as pump malfunctions, sampling was postponed to another day. During sampling, meteorological parameters, including temperature, relative humidity, and wind speed, were also documented hourly for 8 h using a PHB318 portable device.

Ambient air sampling

The samples of particulate matters were collected by a gold PMI filter holder (SKC) and a high-volume peripheral pump, calibrated with a total 3 L/min flow rate for 24 h. Whatman grade GF/A circle glass-fibre filters (37 mm and 1 µm pores) were used to collect $PM_{2.5}$ samples. All devices were at an approximate height of 1.8 m above the ground, on the rooftop. Collection for $PM_{2.5}$ was conducted in four-season: winter (20nd February to 19th March 2020), spring (21nd May to 20th June 2020), summer (22nd August to 21st September 2020), and autumn (21nd November to 20th December 2020) with 16 samples for each season. Fig. 2 displays sampling pilot's schematic and pilot guide. Glass-Fibre Filters (GFFs) used for $PM_{2.5}$ sampling were desiccated in a dark place for 24 h in a laboratory desiccator. Desiccating prevents the hydration of the filter surface and gravimetric errors with 25–30% relative humidity. Filters were pre-weighted by weighing the RADWAG model As-220-R2

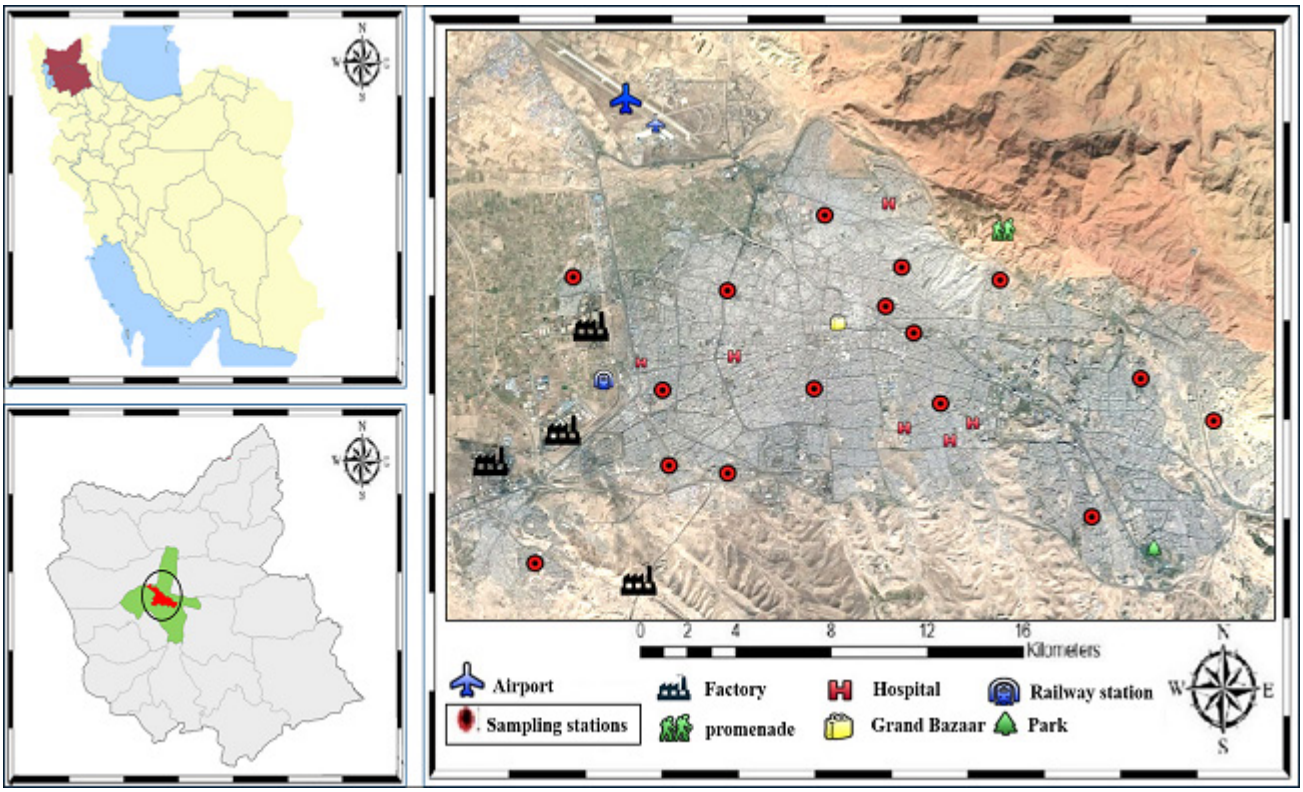


Fig. 1. Sampling sites and their distribution

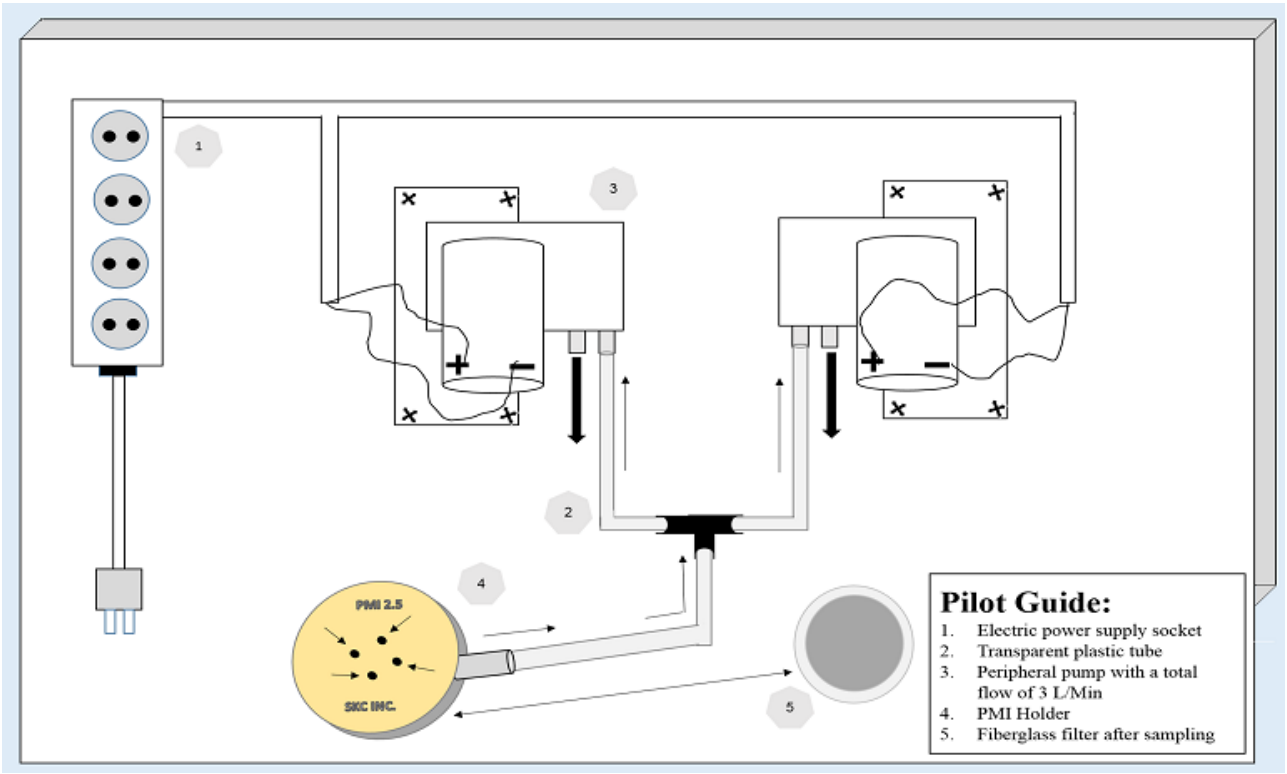


Fig. 2. Sampling pilot's schematic

before sampling and recorded data [28].

The filters, after 24 h sampling, twisted in aluminum foils to protect them from sunlight and were kept at -18 °C inside the cool box to prevent evaporation of some low molecular weight PAHs. Filters were weighed twice. After sampling the same weighing machine with 10^{-4} g sensitivity were used to obtain the gravimetric mass concentration of $PM_{2.5}$ particles based on the change in filter in primary and secondary weights. Based on primary and secondary weight, the 3 L/min flow rate, and total flow volume for 24 h, the concentration of $PM_{2.5}$ particles calculates [29].

Extraction of PAHs

Polycyclic aromatic hydrocarbons bonded with suspended particles, unlike polycyclic aromatic hydrocarbons in the gaseous phase, are less affected by decomposition processes, and only the particulate $PM_{2.5}$-bound PAHs components may be captured on the glass-fibre filters. The PAHs were extracted from Glass-fibre filters using proper solvents [30]. For this purpose, half of the numbered glass-fibre filters were taken and then cut to small fractions, all-glass wares washed with double-distilled water, acetone and pure hexane, and then placed in 200 C° oven for 4 h to dry. Half of the numbered filters were located in 20 ml vials for extraction. They were extracted with 5 ml of HPLC grade dichloromethane (DCM) and 5 ml of methanol using ultrasonic agitation for half an hour [31]. Extracted solvent filtered through a membrane filter (PVDF 0.5 mm micro syringe), and then injected into GC/MS (Agilent-MS5975 B, GC-7890 B) for analysis. The $PM_{2.5}$-bound PAHs were quantified by gas chromatograph-7890B Mass selective detector (GC/MS) system equipped with a fused silica capillary DB-5 column (30 m, 0.25 mm, 0.25 µm). The carrier gas was helium with a 28-29 cm^3/s linear velocity. The ionization was carried out in the Electron Impact (EI) mode, and the mass range scanned was from 35 to 500 amu. The temperature program was as follows: initial temperature of 70 C° was held for 4±0.1 min and increased at a final temperature of 300 C°, then held for 10 min. First, five calibration standards were injected with concentrations (0.1-0.25-0.5-1.5-1.25-2.5 ng/µl) to draw calibration diagrams. After drawing calibration curves, 2 µl volume of each sample was injected with a Special syringe in the Grob-type split less mode. As each compound enters the detector, the detector generates an electrical signal proportional to the amount of compound present. This signal is sent to a data analysis system that shows up as a peak on a chromatogram. Computation of ∑16 PAHs compounds was based on matching their retention time with a mixture of PAH standards. The area below the peak of corresponding to each analyte was used to calculate the concentration of ∑16 PAHs compounds, including benzo[a]pyrene (BaP), benzo[a]anthracene (BaA), benzo[b] fluranthene (BbF), benzo[k]fluoranthene (BkF), chrysene (Chr), benzo[g,h,i]perylene (BghiP), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fle), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Dibenz[a,h]anthracene (DBA), Naphthalene (Nap) and indeno [1,2,3-cd]pyrene (IcdP).

In each set of 16 samples, a blank sample and a spiked sample were analyzed in all laboratory steps and other samples to ensure the correctness of the peaks and the device response. Due to the high efficiency of glass-fibre filters used in adsorption and retention of compounds (except naphthalene, acenaphthylene, acenaphthene compounds), the analytical procedure for field recovery was ignored the quality control and

assurance program. All samples were analyzed with three repetitions and spiking samples of standard PAH solution containing the ∑16 PAHs used to calculate the recovery efficiencies, the range of recovery efficiency was 90%.

Analysis of heavy metals

In order to determine the concentration of heavy metals bounded $PM_{2.5}$ proper solvents are also used for extraction purposes. Another half of the weighted and numbered glass-fibre was taken, was cut to small fractions and Transferred to microwave digester's Teflon containers. A mixture of nitric acid, perchloric acid, and hydrochloric acid added 10,3 and 1 ml portions to each container. After 4 h of digestion, the containers, including acids and filters, were transferred under the hood, poured into a 25 ml Volumetric flask, and diluted using double distilled water. The mixture was filtered through a 0.45-micron syringe filter and prepared for injection into the ICO-OES (Optima 8000, Perkin-Elmer) device. Inductively coupled plasma optical emission spectrometer device determines the concentration of various heavy metal compounds present in the sample based on optical emission spectroscopy and related software and displays numerical and graphical values of each metal in Excel or PDF outputs. System equipped with a Dual, backside-illuminated, cooled, Charge-Coupled Device (CCD) detector with a Wavelength range of 165 nm to 800 nm. The Carrier gas was Argon, and Plasma Argon Flow regulated automatically within the flow range of 0 to 20.0 L/min in 1.0 L/min increments. Nebulizer Argon flow regulated in the range of 0 2.00 L/min in 0.01 L/min increments. Analyze was carried out in measurement mode of continuous nebulization and in a 5 s retention time. First, standard solutions for calibration proposes were synthesized from the mother solution in 100, 400, 700, and 1000 ppm standards to draw calibration diagrams. The ICP-OES device sprays the required volume of solution to the plasma at a flow rate of 1 ml/ min using a nebulizer. The RF generator ionizes argon gas and forms a plasma. The energy produced by this function excites atoms of the solution and emits photons at specific wavelengths. The photons produced in this process hit the light-sensitive parts of the device's CCD detector and produce an electrical signal proportional to the concentration of the desired atom, which was displayed on the ICP-OES monitor. The outputs were read as raw data in terms of mg/L. The output concentrations obtained by the device (mg/L) were subtracted from the blank sample concentration (mg/L) and multiplied by the volume of sample after preparation (m^3). In order to convert the numbers based on µg, results divided by 1000 and the concentration of observed metal in one half of the filter were obtained. This concentration is multiplied by the number 2 for total filter concentration and divided with the volume of sampled air (m^3) to achieve $\mu g/m^3$ concentrations of each heavy metal. All samples were analyzed with three repetitions, and two samples in each season were assessed by spiking samples of known concentrations to calculate the recovery efficiencies. The range of recovery efficiency was 95%.

Health risk assessment

Health risk assessment for PAHs

In the present study, samples were air particles; thus, health risk assessment was calculated through the inhalation, dermal and ingestion pathways. Health risk assessment was determined according to US Environmental Protection Agency (USEPA) standard. For this study, the related age groups were children and adults.

The Incremental Lifetime Cancer Risk (ILCR)

was used to estimate the cancer risk from PAHs exposure [30].

The equations are as follows:

$$ILCR_{Ingestion} = \frac{Cs \times \left(CSF \times \sqrt[3]{\frac{BW}{70}}\right) \times \text{IR} \times \text{EF} \times \text{ED}}{BW \times \text{AT} \times 10^{-6}} \quad (1)$$

$$ILCR_{Inhalation} = \frac{Cs \times \left(CSF \times \sqrt[3]{\frac{BW}{70}}\right) \times \text{IR} \times \text{EF} \times \text{ED}}{BW \times \text{AT} \times PEF} \quad (2)$$

$$ILCR_{dermal} = \frac{Cs \times \left(CSF \times \sqrt[3]{\frac{BW}{70}}\right) \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{SF} \times \text{ED}}{BW \times \text{AT} \times 10^{-6}} \quad (3)$$

Where Cs refers PAH concentration of air (µg/ kg), CSF is carcinogenic slope factor (mg/kg-day)−1, BW is body weight (kg), AT is the average life span (year), EF is exposure frequency (day/year), ED is exposure duration (year), IR is inhalation rate (m^3/day), SA is dermal surface exposure (cm^3/day), AF is dermal adherence factor (mg/ cm2), ABS is dermal adsorption fraction and PEF is air dust produce factor (m^3/kg) (29, 32-34).

Health risk assessment for heavy metals

The Average Daily Dose (ADD) of exposure was used to estimate the cancer risk considering a few exposure factors.

ADD was calculated based on the following:

$$ADD(ng/kg.day^1) = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad (4)$$

Where C is the concentration of the heavy metals in the air (ng/m^3), IR is the inhalation rate (15–20 m^3/day), ED is the exposure duration (years) EF is the exposure frequency (350 to 365 days/year), BW is the body weight (71±13.6 kg), and AT is the averaging time (ED×365 days).

For estimation of Lifetime Average Daily Dose (LADD) based on above equivalent, AT as the averaging time for cancer risk considers as (70×365 days), ED in the average time (AT) is (70 years) [35].

The possibility of developing any form of cancer in human body from lifetime exposure to some carcinogenic threats is defined as the carcinogenic health risk. The threshold risk is 1×10^{-6} to 1×10^{-4} [36]. values less than 1×10^{-4} considers as low risk, values in between are in an acceptable range and values greater than 1×10^{-6} indicates high Carcinogenic health risk. In this study, the age-specific groups in interest were children (2-18) and adults (19-70). Excess Lifetime Cancer Risk (ELCR) was considered to evaluate exposure risk to carcinogenic metals. The variables used to estimate ELCR were the Inhalation Unit Risk (IUR), Slope Factor (SF), and lifetime average daily dose (LADD) (29, 37).

Then, ELCR can be calculated by the following equivalents suggested by the EPA,

$$ELCR(inhalation) = LADD \times \text{SF} \quad (5)$$

$$SF = IUR \times \left[\frac{1}{IR}\right] \times BW \quad (6)$$

Where LADD is the exposure concentration for inhalation, IR is the inhalation rate (15–20 m^3/ day), BW is the body weight (71±13.6 kg), and IUR is the unit risk value (1.2×10^{-5}(µg/m^3)-1) for Pb. (SF) slope factor determined by Integrated Risk Information System (IRIS) as 0.029 (mg/ kg/day) [38].

Spatial distributions

ESRI company's software, ARCGIS 10.3, was used to examine the spatial distribution of PAHs and heavy metals bounded $PM_{2.5}$ in

the ambient air of Tabriz. For this purpose, the Geographic Information System (GIS) developed an independent raster layer of each pollutant to determine the distribution of the annual average concentration of PAHs and heavy metals bounded $PM_{2.5}$. One of the most popular non-statistical approaches of interpolating method of zonation and distribution, also used by Inverse Distance Weighting (IDW) to map the spatial distribution of environmental pollutants and anticipate their concentrations. In This method, every measuring point reflects a weight based on the distance between known and unknown points and mainly considers a procedure for distribution irregularities.

Results and discussion

Two main purposes of this study was determination of $PM_{2.5}$ levels in the Tabriz atmosphere and to know about the quantity and health risk of exposure to the PAHs and heavy metals bounded with in $PM_{2.5}$. Additionally, yearly concentrations of $PM_{2.5}$ -bound PAHs and heavy metals are given indeed.

$PM_{2.5}$ concentrations

Table 1 presents the statistical summary of Mean, Standard deviation, Maximum and Minimum meteorological parameters, including Temperature, Relative humidity, precipitation and wind speed, during the entire sampling days involving four seasons. The mass concentration levels of outdoor $PM_{2.5}$ throughout the sampling period are presented in Fig. 3. The concentration of $PM_{2.5}$ particles in 16 points of Tabriz with suitable dispersion for maximum coverage of the city was measured. During different seasons, concentrations were recorded. Due to the early arrival of cold air masses in this metropolis and considering the significant increase in scattered snowfall in winter, a slight decrease in the concentration of $PM_{2.5}$ particles was expected. Our study observed the highest particle concentration of $PM_{2.5}$ particles in autumn, followed by shorter distances in winter and then summer and spring. $PM_{2.5}$ concentrations determined in our study varied within the range 4/78 $\mu g/m^3$ in spring to 94/16 $\mu g/m^3$ in the Autumn period with a mean annual concentration level of 41/17 $\mu g/m^3$. Most stations experience levels higher than WHO's 25 $\mu g/m^3$ guidelines for annual $PM_{2.5}$ concentrations in the air. Investigating seasonal concentrations of $PM_{2.5}$ shows that concentrations in autumn (49/65 $\mu g/m^3$) > winter (47.61 $\mu g/m^3$) > summer (34.58 $\mu g/m^3$) > spring (32.85 $\mu g/m^3$). In Fig. 3, the highest concentration of $PM_{2.5}$ occurred in November and December. Station number Thirteen has the highest average annual particle concentration of $PM_{2.5}$, followed by station number Nine and Fourteen in the second and third most polluted regions by $PM_{2.5}$ particles, this is while station number Fifteen with a concentration of 9.82 $\mu g/m^3$ has the lowest particle concentration of $PM_{2.5}$. The results gathered in Fig. 3 show that the yearly mean concentrations of $PM_{2.5}$ in almost all stations exceed 10 $\mu g/m^3$ WHO guideline and in some points reaches 70 $\mu g/m^3$ concentrations in some station, which is seven times higher than WHO guidelines for $PM_{2.5}$ concentrations [39].

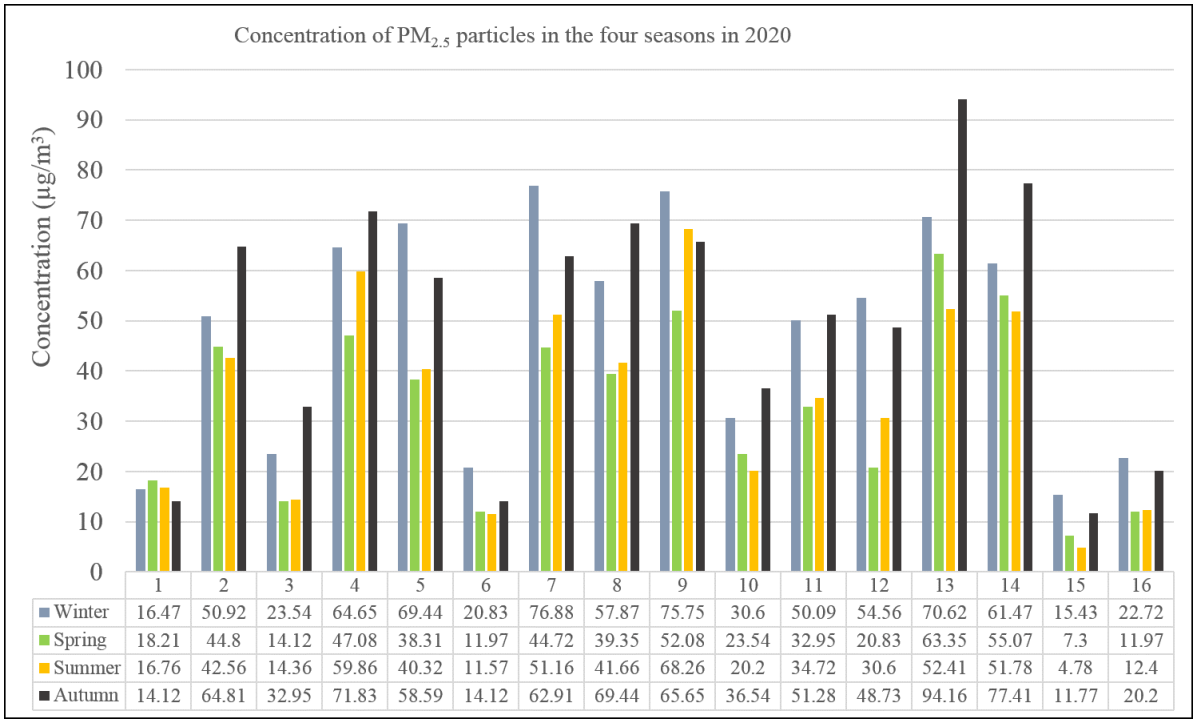
During the sampling period, the wind rose shows prevailing winds in seasonal basis. The most frequent wind direction in the study area is northeast. Fig. 4 shows seasonal variations in wind direction during the period of study. The annual dispersion of $PM_{2.5}$ particles in the ambient air of Tabriz showed in Fig. 5. According to this figure, the closer to the west, the more air pollution expansions due to different industries. The closer to the northwest of this metropolis,

the more concentration has been observed in this area due to Tabriz International Airport (Shahid Madani Airport) and heavy traffics due to narrow street structure. The mean annual concentrations of $PM_{2.5}$ in this study, compared with previous studies and shown in Table 2.

In this study, the average annual particle concentration of $PM_{2.5}$ was 41.17 µg/m^3, which is higher than the average annual concentration of 37-30 µg/m^3 in Asian countries. According to Canadian Ambient Air Quality Standards (CAAQS), this average concentration exceeds grade 1 standards of 20 µg/m^3 and grade 2 standards of 35 µg/m^3 but is lower than grade 3 standards of 70 µg/m^3 [40]. The average annual particle concentration of $PM_{2.5}$ calculated in different parts of Shaanxi, China and observed that the highest annual concentration is 59 µg/m^3 and the lowest annual concentration is 3.38 µg/m^3 [41]. Heavy vehicular traffic, industries, and biomass heating during winter months probably related to high concentrations of $PM_{2.5}$ in Tabriz city.

Table 1. Meteorological parameters, during the entire sampling days covering four seasons

Meteorological parameters	Mean	Max	Min	SD
Temperature (C°)	13.97	29.41	7.29	11.61
Relative humidity (%)	34.97	65	8	12.25
Precipitation (mm)	289	497	26	26.65
Wind speed (m/s)	8.9	19.25	1.30	4.65



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Winter	16.47	50.92	23.54	64.65	69.44	20.83	76.88	57.87	75.75	30.6	50.09	54.56	70.62	61.47	15.43	22.72
Spring	18.21	44.8	14.12	47.08	38.31	11.97	44.72	39.35	52.08	23.54	32.95	20.83	63.35	55.07	7.3	11.97
Summer	16.76	42.56	14.36	59.86	40.32	11.57	51.16	41.66	68.26	20.2	34.72	30.6	52.41	51.78	4.78	12.4
Autumn	14.12	64.81	32.95	71.83	58.59	14.12	62.91	69.44	65.65	36.54	51.28	48.73	94.16	77.41	11.77	20.2

Fig. 3. Concentration of $PM_{2.5}$ particles in the four seasons in 2020

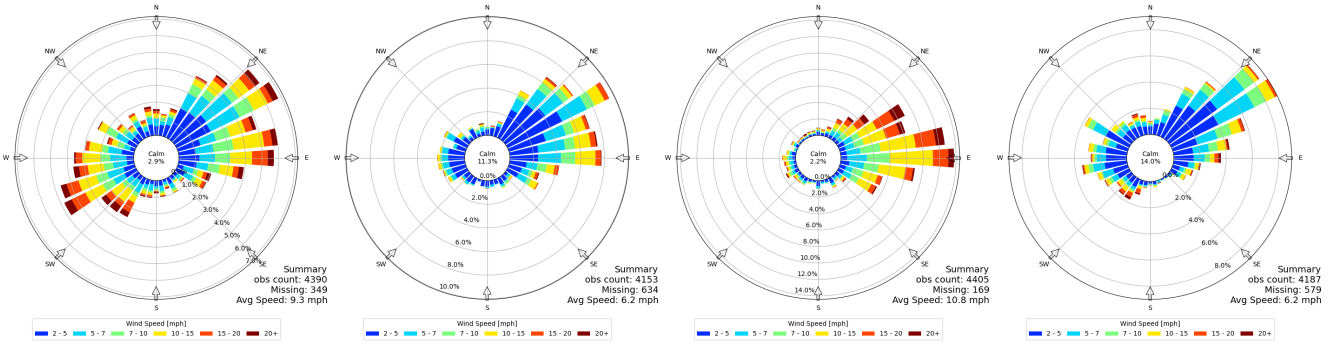


Fig. 5. Distribution of average annual concentration of $PM_{2.5}$ in stations of monitoring

Table 2. The mean annual concentrations of $PM_{2.5}$ in this study, compared with previous studies

Country	Site	Year	$PM_{2.5}$	Reference
Saudi Arabia	Jeddah	2011	28.40	[42]
Turkey	Zonguldak	2007	28.1	[43]
India	Delhi, Chennai, Hyderabad and Mumbai	2015-2018	72	[44]
China	Chengdu	2015	67.44	[45]
Pakistan	Karachi	2009	75	[46]
Iran	Urmia	2013	30	[47]
Iran	Bushehr	2016-2017	65.77	[48]
Iran	Karaj	2019	40.65	[49]
Iran	Tabriz	2020	41.17	The Present Study

PAHs concentrations

Concentrations of ∑16 PAHs during four seasonal periods (March to December 2020) in the ambient air of Tabriz are presented in Fig. 6. Concentrations of PAHs bound to $PM_{2.5}$ showed a molecular weight trend during cold and warm seasons. Low-molecular-weight PAHs including NaP, Ace, Flu, and Phen were dominant in cold seasons, whereas high-molecular-weight PAHs include BaA, BkF, BaP, DBahA, BghiP and IND are dominant PAH types in warm seasons. With higher concentrations during cold seasons period (autumn and winter)

than warm seasons period (spring and summer). High concentrations of PAHs in winter can be attributed to the topographic conditions of the city, increasing use of diesel fuel in all major industrial centers of Tabriz and occurrence of temperature inversion in the cold seasons of the year whereas in summer [50]. Generally, high wind speeds and photodecomposition of PAHs during warm seasons lead to a decrease in the concentration of PAHs compared to its values in winter. In earlier studies also the concentrations of particle-bounded PAHs in urban areas experience peak values in winter [51].

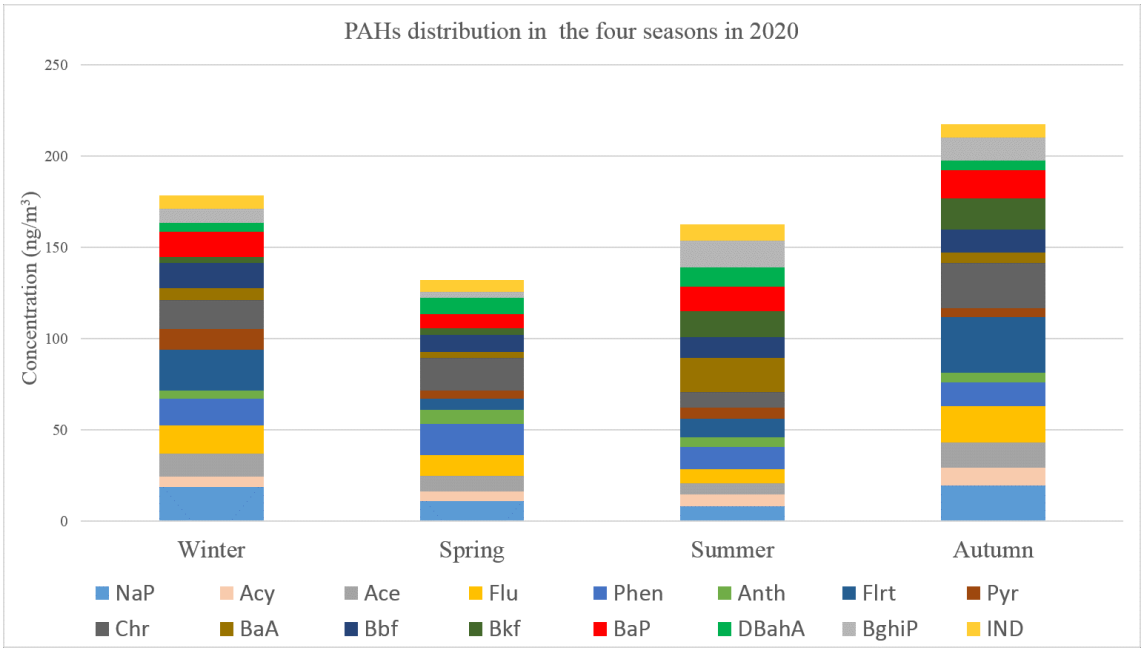


Fig. 6. ∑16 PAHs distribution in the four seasons in 2020

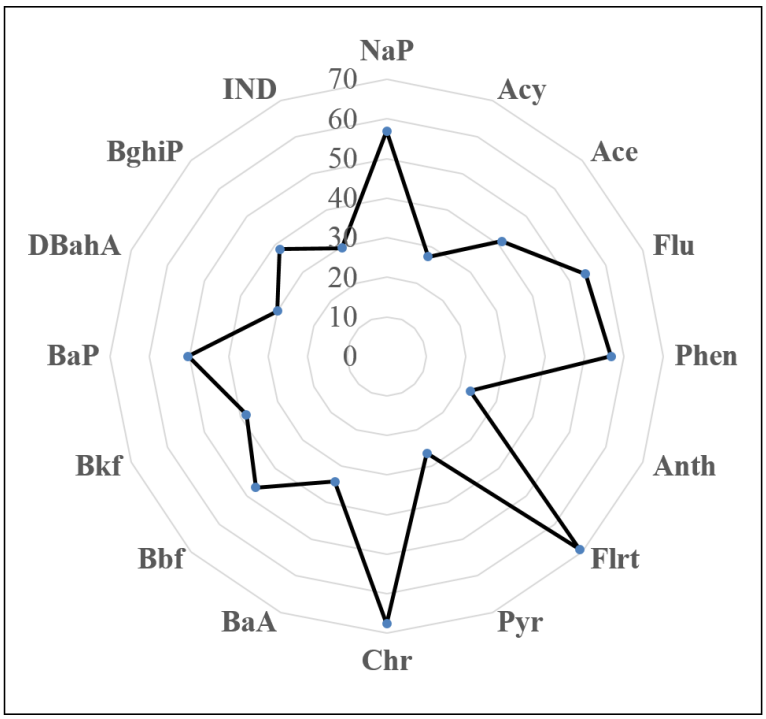


Fig. 7. The relative contribution of total ambient PAHs mass concentration for the study period

The present study's highest average annual concentration of PAHs is related to station number Thirteen with 32 ng/m^3 and station number Nine with 25/08 ng/m^3 stands in second most polluted area with PAH components. Meanwhile the lowest average annual concentration of PAH components was recorded in the station number 15 near the Einali promenade with 2/79 ng/m^3. Fig. 7 shows the relative contribution of total ambient PAHs mass concentration for the study period and Flrt composition was the dominant component followed by Chr, Phen, Nap, Flu and BaP. Fig. 8 shows the distribution of polycyclic aromatic compounds in sampling stations. It is clear that the northwestern areas of the city have the most pollution and also as we move to the east side of the city, the overall pollution of the city decreases. Measurement of different meteorological parameters during sampling periods and recording their values hourly, the relationship between temperature changes, relative humidity and air pressure on the concentration of PAHs compounds searched.

It was observed that the parameters of temperature and air pressure had a positive significant direct relationship ($P<0.05$) with the concentration of PAH compounds. These results are consistent with studies by L. Yang on the relationship between relative humidity and the concentration of various PAH compounds [52]. A direct relationship between the concentration of PAH compounds and the concentration of $PM_{2.5}$ components during all four seasons was observed. The maximum concentrations of PAH compounds were recorded in November to December, followed by February to March and the minimum concentrations recorded in August to September and May to June. The

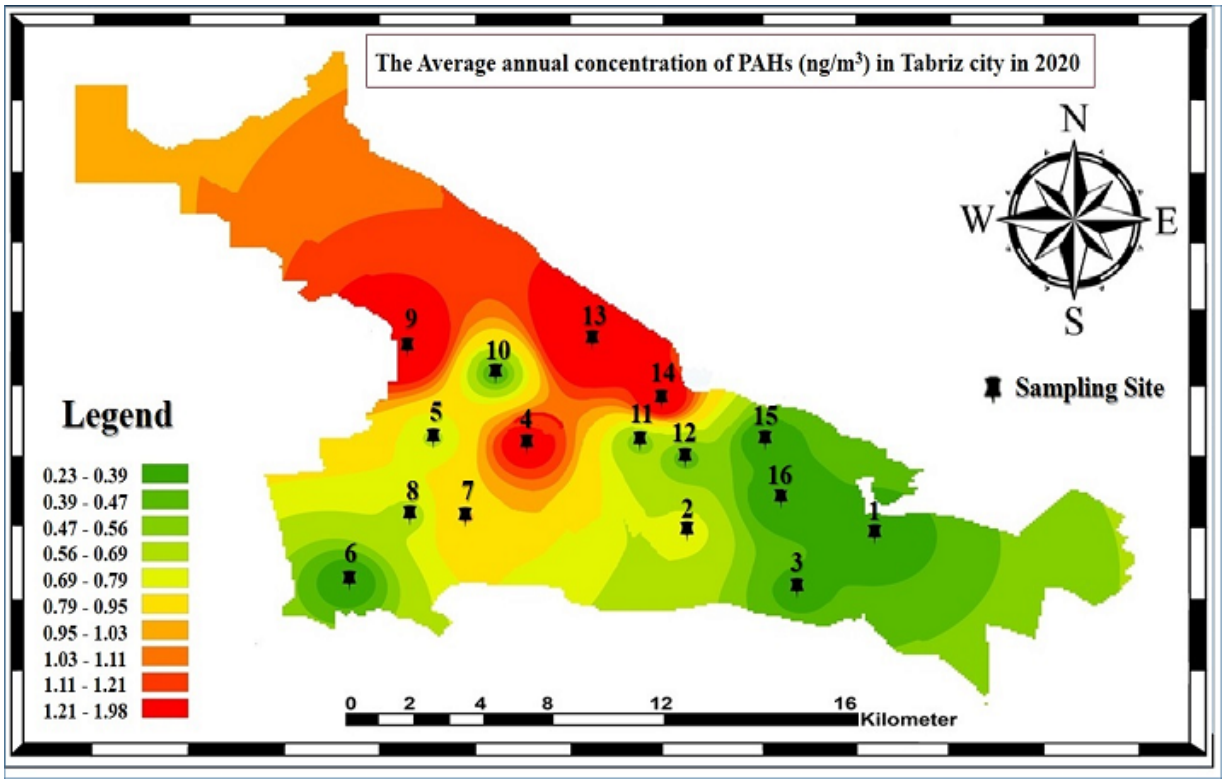


Fig. 8. Distribution of polycyclic aromatic compounds in sampling stations

carcinogenicity of ∑16 PAHs in $PM_{2.5}$ through different skin, gastrointestinal and inhalation exposures in adults and children has also been calculated (Table 3). It was observed that the risk of carcinogenicity in skin and gastrointestinal exposures with these compounds are higher than inhaled exposure pathway, and in general, Flrt and Chr compounds have the highest diffuse concentration. These results are consistent with some studies [53]. The average annual concentration of benzo(a)pyrene compound (BaP) along with a group of PAH compounds has experienced higher values than the standard value of 1 ng/m^3. It requires the presence of production control programs for the production and release of these compounds.

Table 3. The carcinogenicity of ∑16 PAHs 5 through inhalation exposures in adults and children

PAHs components	Children			Adults		
	Ingestion	Inhalation	Dermal	Ingestion	Inhalation	Dermal
Nap	1.158E-08	9.205E-08	1.853E-08	6.483E-07	3.682E-07	1.974E-08
Acy	5.273E-09	4.192E-08	8.436E-09	2.952E-07	1.677E-07	8.989E-09
Ace	8.788E-09	6.986E-08	1.406E-08	4.920E-07	2.795E-07	1.498E-08
Flu	1.055E-08	8.384E-08	1.687E-08	5.904E-07	3.353E-07	1.798E-08
Phen	1.106E-08	8.795E-08	1.770E-08	6.193E-07	3.518E-07	1.886E-08
Anth	4.756E-09	3.781E-08	7.609E-09	2.663E-07	1.512E-07	8.107E-09
Flrt	1.323E-08	1.052E-07	2.117E-08	7.409E-07	4.208E-07	2.256E-08
Pyr	5.169E-09	4.110E-08	8.271E-09	2.894E-07	1.644E-07	8.812E-09
Chr	1.210E-08	9.616E-08	1.935E-08	6.772E-07	3.847E-07	2.062E-08
Baa	7.134E-09	5.671E-08	1.141E-08	3.994E-07	2.268E-07	1.216E-08
Bbf	8.684E-09	6.904E-08	1.390E-08	4.862E-07	2.762E-07	1.480E-08
Bkf	7.754E-09	6.164E-08	1.241E-08	4.341E-07	2.466E-07	1.322E-08
Bap	1.065E-08	8.466E-08	1.704E-08	5.962E-07	3.386E-07	1.815E-08
Dbaha	5.996E-09	4.767E-08	9.594E-09	3.357E-07	1.907E-07	1.022E-08
Bghip	7.857E-09	6.247E-08	1.257E-08	4.399E-07	2.499E-07	1.339E-08
IND	6.720E-09	5.342E-08	1.075E-08	3.762E-07	2.137E-07	1.146E-08

Heavy metals concentration

Fig. 9 indicates the mean seasonal total concentration of heavy metals during the study in Tabriz. The mean concentration levels of heavy metals were 138/69 ng/m^3 and the mean percentage share of each heavy metal were in the order of Al (21%, 282/1 ng/m^3), Fe (19%, 253/1 ng/m^3), Zn (11%, 161/1 ng/m^3), Pb (11%, 149.4 ng/m^3), Cu (9%, 128/9 ng/m^3), Mn (7%, 92/2 ng/m^3), Cd (6%, 82/1 ng/m^3), Ni (6%, 81.3 ng/m^3), As (4%, 54.8 ng/m^3), Hg (3%, 36/2 ng/m^3) as seen in Fig. 10. Annual distribution of heavy metal concentrations in 16 different stations of Tabriz city presented in Fig. 11. According to this figure, the northwest and west regions of the city, including station number 13, and 14, are more polluted by heavy metals, and East parts including station number One, number 3, 16 and 15 are less polluted regions. In this study the annual average concentration of heavy metals was below the WHO standard of 500 ng/m^3 as seen in Fig. 12. Also A. Singh, calculated the average annual concentration of Pb heavy metal at 200 ng/m^3 [54]. Our results show that Al, Fe, Zn, and Pb were the largest components comprised 62% of all metals in $PM_{2.5}$ concentration levels of Al and Fe were much higher than expected. Generally, these metals' concentration was high in all stations, probably deriving from natural sources (Red Sandstones soil). Increased activities of releasing sources in cold seasons including vehicular emissions, low mixing height, and regular temperature inversion also attributes to these metals concentrations in the air [55]. When Fe is associated with Zn, anthropogenic emission sources like fuel combustion, incineration plays a significant role [56]. also when Ni is associated with Cd, diesel and gasoline exhaust might be main sources. Concentrations of metals in our study were within the permissible levels of WHO guidelines and are less than other studies. A comparison displayed in Fig. 13, between the concentration of heavy metals in the cold and hot seasons shows that levels of almost all elements (except Cd) are higher in the cold seasons period (autumn and winter) than in the hot seasons (spring and summer). Table 4 indicates risk assessment of exposure to heavy metals bounded $PM_{2.5}$. Due to the concentrations of Cd in station number Three the higher ELCR values indicates high Carcinogenic health risk for adults and also higher ELCR values for children in station number Nine. Although Pb has been phased out of gasoline and has not been consumed by cars in Iranian cities, this metal considers as fourth dominant heavy metal in the ambient air of Tabriz due to its long residence time in the environment. Average metal concentration in autumn and winter is high compared to the average metal concentration of heavy metals in summer and spring, which is predictable due to the direct relationship between the concentration of $PM_{2.5}$ particles in the air and the concentration of bounded metals. Also, various environmental phenomena, including temperature inversion in the cold seasons, increase these metals' concentration in the air.

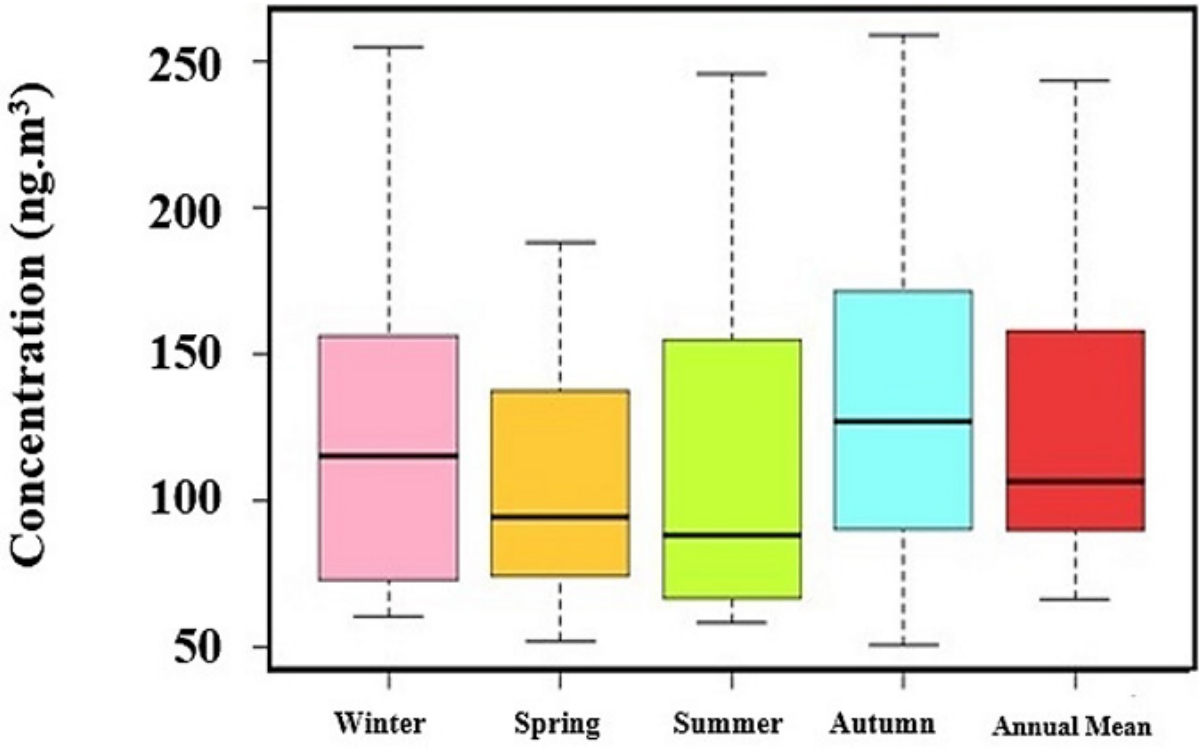


Fig. 9. The mean seasonal total concentration of heavy metals throughout the study in Tabriz

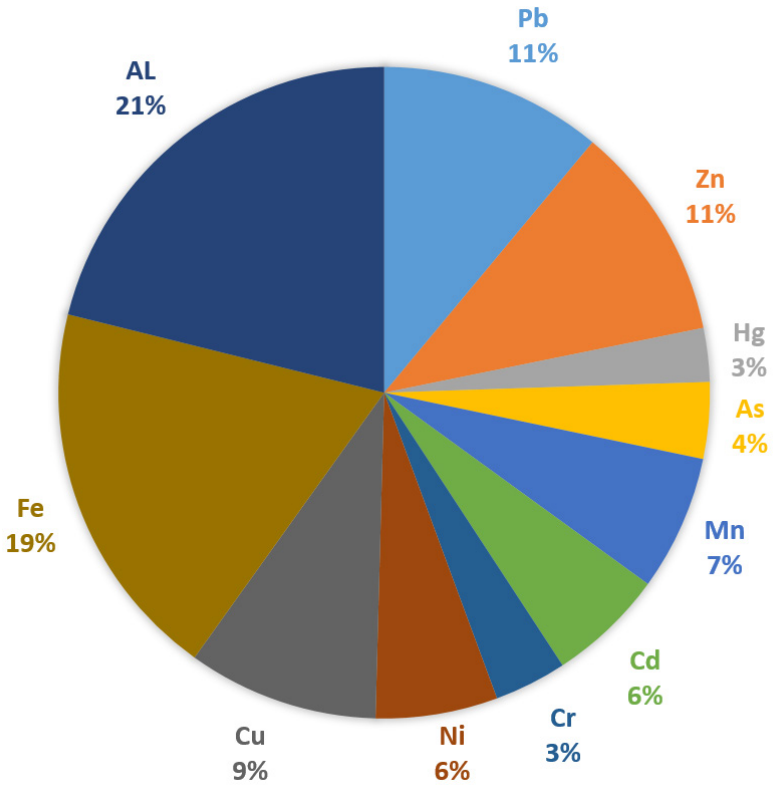


Fig. 10. The mean percentage share of each heavy metal during sampling period

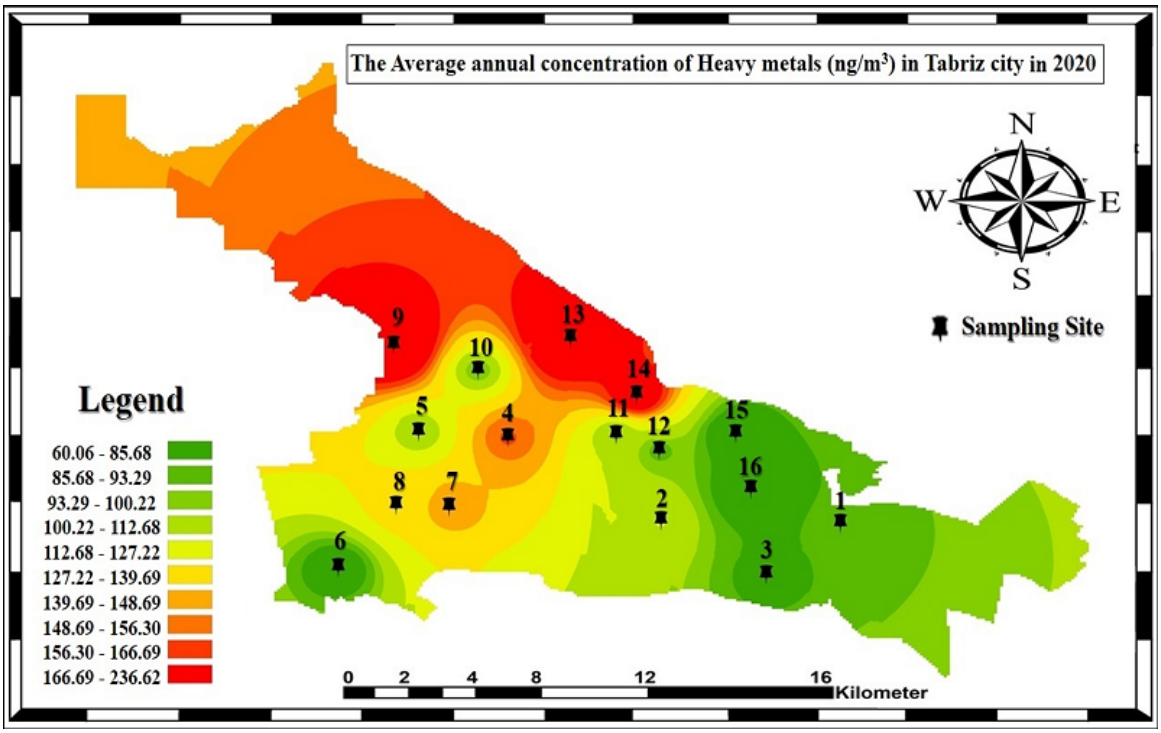


Fig. 11. Annual distribution of heavy metal concentrations in Tabriz

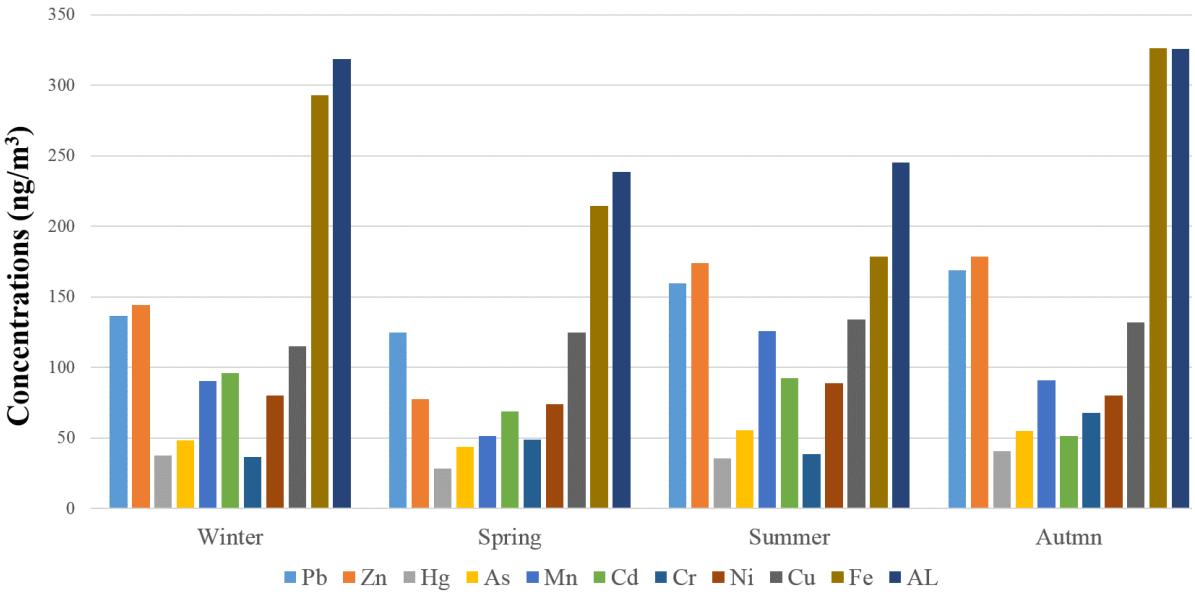


Fig. 12. Seasonal mean concentration of heavy metals in sampling stations (ng/m³)

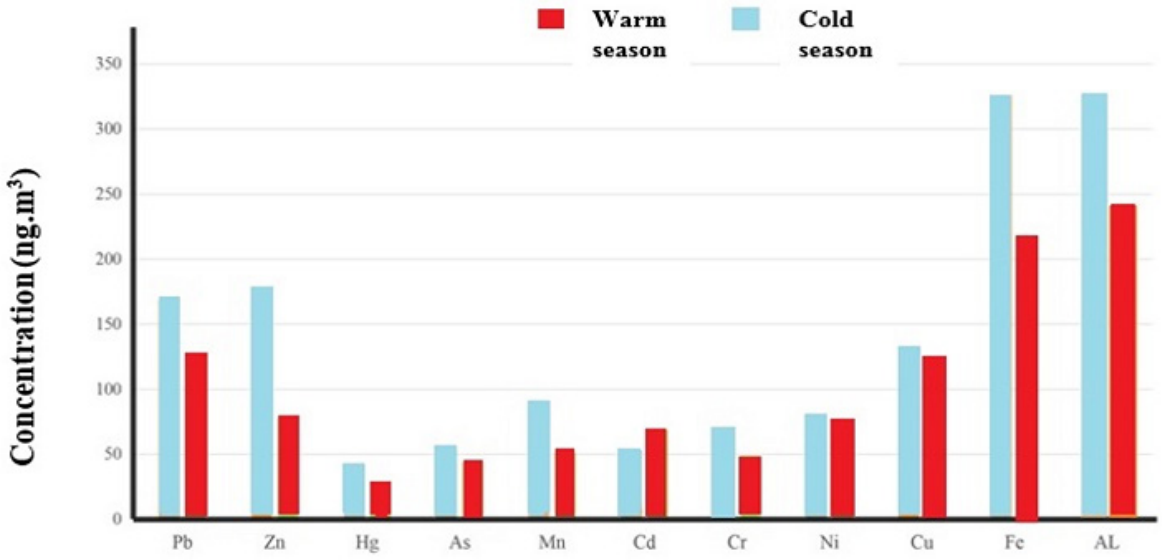


Fig. 13. Comparison between the concentration of heavy metals in the cold and hot seasons

Table 4. Risk assessment of exposure to heavy metals bounded $PM_{2.5}$

Stations	Pb		Cd	
	ELCR ADULTS	ELCR CHILDREN	ELCR ADULTS	ELCR CHILDREN
1	0.000100373	2.50932E-05	9.49479E-06	2.3737E-06
2	3.72822E-05	9.32055E-06	2.8149E-05	7.03726E-06
3	1.8549E-05	4.63726E-06	1.03693E-05	2.59233E-06
4	5.84022E-05	1.46005E-05	3.26071E-05	8.15178E-06
5	3.75123E-05	9.37808E-06	1.99595E-05	4.98986E-06
6	1.75036E-05	4.37589E-06	1.95616E-05	4.89041E-06
7	5.51967E-05	1.37992E-05	2.82477E-05	7.06192E-06
8	4.8697E-05	1.21742E-05	2.21063E-05	5.52658E-06
9	8.79879E-05	2.1997E-05	4.84471E-05	1.21118E-05
10	3.9051E-05	9.76274E-06	2.06104E-05	5.1526E-06
11	2.88592E-05	7.21479E-06	1.99726E-05	4.99315E-06
12	2.34411E-05	2.34411E-05	2.03047E-05	2.03047E-05
13	9.08877E-05	9.08877E-05	4.45184E-05	4.45184E-05
14	6.52373E-05	6.52373E-05	3.70488E-05	3.70488E-05
15	3.56449E-05	3.56449E-05	6.75288E-06	6.75288E-06
16	1.79671E-05	1.79671E-05	1.18389E-05	1.18389E-05

Conclusion

The findings of this comprehensive study add to the understanding of the concentration, spatial distribution, seasonal variations, and health risk assessment caused by exposure to $PM_{2.5}$-bounded PAHs and heavy metals from February to December 2020 in Tabriz city. The results indicated that the mean concentration of the $PM_{2.5}$ during the sampling period was 41/17 $\mu g/m^3$. Relatively higher concentrations of $PM_{2.5}$ in cold seasons were observed compared to warm seasons. ∑16PAHs bounded-$PM_{2.5}$ were much higher in autumn and winter (217.47 and 178.32 ng/m^3) compared to summer and spring (162.61 and 131.89 ng/m^3). The most common PAHs found were Flrt, Chr, Phen, NaP, Flu and BaP and risk of carcinogenicity in skin and gastrointestinal exposures were higher than inhaled exposure pathway. Levels of heavy metals were measured high in Tabriz's ambient air by mean concentration of 138/69 ng/m^3 and dominate metals were: Al, Fe, Zn, Pb, Cu, Mn, Cd and Ni. ELCR values indicated high carcinogenic risk for adults and children in some stations. In general, considering the topographic location of the region and the frequent presence of temperature inversion in cold seasons in this city with considering importance of these information for future assessments and control policies, further comprehensive researches are needed.

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Competing interests

The authors have no competing interests to declare.

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Ethical considerations

"Ethical issues (Including plagiarism, Informed Consent, misconduct, data fabrication and/or falsification, double publication and/or submission, redundancy, etc.) have been completely observed by the authors."

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