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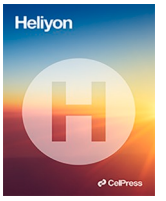

Research article

A comprehensive study on the spatial and temporal variation of BTEX and asbestos in the northwest of Iran: Human risk assessment

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ABSTRACT

Substances like asbestos and other air pollutants, such as BTEX (benzene, toluene, ethylbenzene, and xylene), are hazardous compounds due to their adverse effects on human health. This study aims to investigate the levels, seasonal variations, spatial distribution, potential sources, and associated health risks associated with BTEX compounds and asbestos fibers in the ambient air of Tabriz. Air samples were taken at 16 different locations during the 2020–2021 period. Glass containers with charcoal were used for sample collection, and the BTEX content was determined using the GC-FID method. Phase-contrast microscopy (PCM) analysis was conducted with a low-volume peripheral pump for asbestos fiber sampling. The results showed that the average concentration of ∑BTEX was 37.94 and 27.98 μg/m^3 in autumn and spring, respectively. The same parameter was 2.26 and 1.68 f/L for asbestos in the autumn and winter, respectively. The contribution of BTEX to ozone formation potential (OFP) in the research area showed that xylene and toluene were the major contributors to ozone production in different seasons. The risk of exposure to benzene compounds was 24×10^{-4} in children and 55.9×10^{-4} in adults, while the risk of exposure to ethylbenzene was 3.78×10^{-4} in children and 3.25×10^{-4} in adults. The estimated lifetime cancer risk was found to be the highest for benzene, followed by ethylbenzene. The estimated cancer risk for benzene and ethylbenzene exceeded the threshold values set by EPA, which signals a significant carcinogenic risk due to exposure to these substances in the ambient air of Tabriz. According to the EPA guidelines, the low carcinogenicity risk levels are between 10^{-4} and 10^{-6}. According to the findings for the exposure to asbestos fibers, the maximum values of excess cancer risk (ECR) and estimated lifetime cancer risk (ELCR) were observed in the 16–30 age range across all locations, suggesting increased exposure to asbestos fibers compared to other age groups.

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1. Introduction

Air pollution is a leading global cause of death and disability, affecting billions of people annually. Efforts to reduce it have had limited success despite various initiatives [1]. Rapid technological development, urbanization, and population growth have exacerbated the issue, particularly its impact on health [2]. Ambient air pollution is associated with premature deaths and numerous diseases, like cancer, cardiovascular, respiratory, reproductive, endocrine, and neurological diseases [3–7]. Volatile organic compounds (VOCs), including BTEX (benzene, toluene, ethylbenzene, xylene), are major contributors to air pollution, primarily released from car exhausts, industrial activities, and urban processes. Exposure to them has received considerable global attention due to their adverse health effects, including cancers and neurological disorders [8]. Asbestos is a collective term used to describe a collection of naturally occurring minerals and silicon-based mineral compounds characterized by long, thin, fibrous, brittle, or flexible fibers. There are six types of asbestos fibers: chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite [8,9]. Thanks to their strength, flexibility, and resistance to heat and chemicals, these fibers are used in various industries (8). The most common type of asbestos used in the industry is chrysotile, accounting for approximately 95 %, followed by crocidolite and amosite [10]. Asbestos is widely used in various industries due to its unique chemical and physical properties, including low thermal conductivity, high mechanical resistance, flexibility, and resistance to chemical and biological attacks. It finds applications in cement production, automotive manufacturing, construction materials, insulation, adhesives, flooring, ventilation ducts, and pipes as a fire retardant [11,12]. However, despite its benefits, the International Agency for Research on Cancer (IARC) classifies asbestos as a carcinogen [13,14]. During braking, both light and heavy vehicles release significant amounts of asbestos fibers into the air due to friction between asbestos-containing brake pads and wheel drums or discs. Although air pollution, including acid rain, can contribute to asbestos release from cement sheets, its impact is considered minor [15]. Exposure to this substance can lead to diseases such as malignant mesothelioma, lung cancer, throat cancer, ovarian cancer, asbestosis, and pleural disease (plaques and thickening of the pleura) [16]. The emission patterns of air pollutants indicate that polycyclic aromatic hydrocarbons (PAHs) are discharged by both diesel automobiles and industrial operations. Both BTEX and asbestos are predominantly released into the environment by automobiles. The United States Environmental Protection Agency (USEPA) classifies some VOCs, such as benzene, toluene, ethylbenzene, and isomeric xylenes (together referred to as BTEX) as air toxins or hazardous air pollutants (HAPs). These chemicals are suspected to possess carcinogenic properties and may cause other significant adverse health consequences [17]. Toluene and ethylbenzene can impact the central nervous system, leading to cognitive disorders and eye irritation. Additionally, xylene can result in skin inflammation and respiratory problems.

Despite the notable health impacts associated with exposure to BTEX in the surrounding atmosphere, both WHO (World Health Organization) and EPA have not yet identified any definitive acceptable exposure thresholds. In 2000, the European Commission recommended an annual average of 5 $\mu g/m^3$ of benzene in the surrounding atmosphere. This recommendation was later revised in 2006 to a lower threshold of 1 $\mu g/m^3$. Finally, in 2010, the European Commission reached the objective of attaining the goal of achieving zero or undetectable levels of benzene in ambient air. According to risk assessment based on inhalation exposure, asbestos, BTEX, and PAHs have higher carcinogenic risks than the limits recommended by US EPA and WHO (1×10^{-4}) [18]. Moreover, they can alter the atmosphere, particularly the troposphere, through photochemical processes. As a result, they increase secondary pollutants, such as ozone (O_3), peroxyacetyl nitrate (PAN), and secondary aerosols that are undetectable, which damage the environment and ecosystems [19]. In developing nations, ineffective air quality regulations, unsustainable development, urbanization, and population growth contribute to air pollution by affecting mobility and transportation resources [20]. Tabriz, the largest city in northwest Iran, faces severe air pollution due to industrial activities, uncontrolled urban expansion, population growth, increased motor vehicle traffic, and fossil fuel consumption. Mobile sources, including personal cars, motorcycles, and taxis, constitute the majority of air pollution sources in Tabriz. Atmospheric conditions, such as limited natural ventilation and temperature inversions during the cold season, exacerbate pollution [21,22]. Health-related effects of pollutants like BTEX and asbestos have become significant concerns in Tabriz and other Iranian cities, necessitating research and regulatory measures to address air quality issues. Studies in Tehran and other cities have highlighted the contribution of mobile sources to the emission of VOCs, emphasizing the need for mitigation strategies [23]. In general, the polycyclic aromatic hydrocarbon pollutants and $PM_{2.5}$-bound heavy metals, asbestos, and BTEX compounds have health-related effects, and we have focused on BTEX and asbestos in this research. Various studies have been conducted in Tehran and other cities regarding BTEX in ambient air [20,24,25]. A substantial portion of VOCs in Tehran in 2013 originated from mobile sources, mostly from personal cars, motorcycles, and old taxis, among other sources, according to the research by Shahbazi and colleagues [26]. Maleki et al. measured the amounts of asbestos fibers and BTEX in Tehran's ambient air during the warm and cold seasons. The findings of the spatial study also indicated that the highest concentrations of BTEX and asbestos occurred in regions with significant traffic and proximity to industries and industrial sites. Furthermore, the results showed that temperature inversions can affect air stability and the buildup of contaminants [19]. This study aims to assess the environmental concentrations of BTEX compounds and asbestos fibers, examine seasonal variations, map their geographic distribution, pinpoint likely sources, and calculate the potential for ozone formation (OFP) and the potential health risks associated with these substances in the Tabriz's ambient air.

2. Material and methods

2.1. Case study area description and sampling

This investigation focuses on the city of Tabriz, which is the fourth most populated city in Iran, with over two million residents. It is the capital of East Azerbaijan and covers an area of 324 square kilometers, located approximately at 46.27° east and 38.09° north. Tabriz is economically and industrially significant in the northwestern region of Iran, surrounded by mountains such as Eynali,

Qaradaq, Saridagh, and Sahand, with Lake Urmia to the east [27].

For this study, 128 samples (64 BTEX and 64 asbestos) were collected throughout Tabriz city (16 stations) in different seasons of a year from 2020 to 2021) (Fig. 1).

2.2. Chemical analysis

Sampling of BTEX compounds was carried out at various locations throughout the city of Tabriz. GC-FID instrument was used and BTEX material was sampled by method 1501 [28]. The duration of sampling was at least 45 min at a height of 2 m. Sampling of volatile BTEX compounds was initially performed at a flow rate of 0.2 L/min using a micro sampling pump (AirLine No. 110-100, SKC, USA) with a charcoal tube. It was calibrated using the soap bubble method, and the apparatus was inspected for any potential leaks. After setting up at the sampling locations, the sampling pump was turned on, and both ends of the glass charcoal tubes were inserted into the pump in the direction of airflow and in the proper manner. Temperature, air pressure, and relative humidity were measured with a portable instrument at the beginning and end of the sampling to standardize the air volume used. After sampling, both ends of the broken charcoal tubes were sealed with special plastic caps, marked, and securely sealed with Teflon tape. They were then stored in a cold box at −4 °C until they were transferred to the laboratory to minimize the degradation of BTEX compounds. For the analysis of the samples, the main part of the charcoal tube (the front cotton wool section) was removed, and the contents of the front adsorbent were poured into vials containing 500 mL of carbon disulfide (CS_2) solvent. Afterward, to completely remove VOCs, the samples were subjected to an ultrasonicator for 20 min. They were then extracted and phased into a liquid form from the adsorbed pollutants on the black adsorbent beads using a gas chromatography mass spectrometer (7890B/5975B Agilent, USA) equipped with a flame ionization detector (GC-FID) for 10 min of analysis. In this way, the polyurethane foam in the rear part of each charcoal tube was also removed, and for the content of the rear section's 50-g adsorbent, the same procedure as the front section was followed, and the vials were numbered accordingly. The numbering of vials for each charcoal tube was done separately for the front and rear sections, with numbers 1F–16F and 1B–16B, respectively [20,29].

To ensure the absence of background contamination in the sampling charcoal tubes, one charcoal tube was used as a control sample. This control sample was designated as blank-F and blank-B and was used in all stages of extraction and instrumental analysis. It should be noted that if the concentration of target pollutants in the analyzed vials of the rear section is more than 10 % of the concentration in the front section, the sample has an error, which is referred to as a "breakthrough" error according to the data provided by the instrument. The concentration of BTEX compounds was determined based on this equation (1):

$$C = \frac{((Wf\text{-}Wb)\text{-}(Bf\text{-}Bb))}{V} \quad (1)$$

In this equation, C is the pollutant concentration in μg/m^3, W_f and W_b are the pollutant concentration in the front and rear parts in μg/

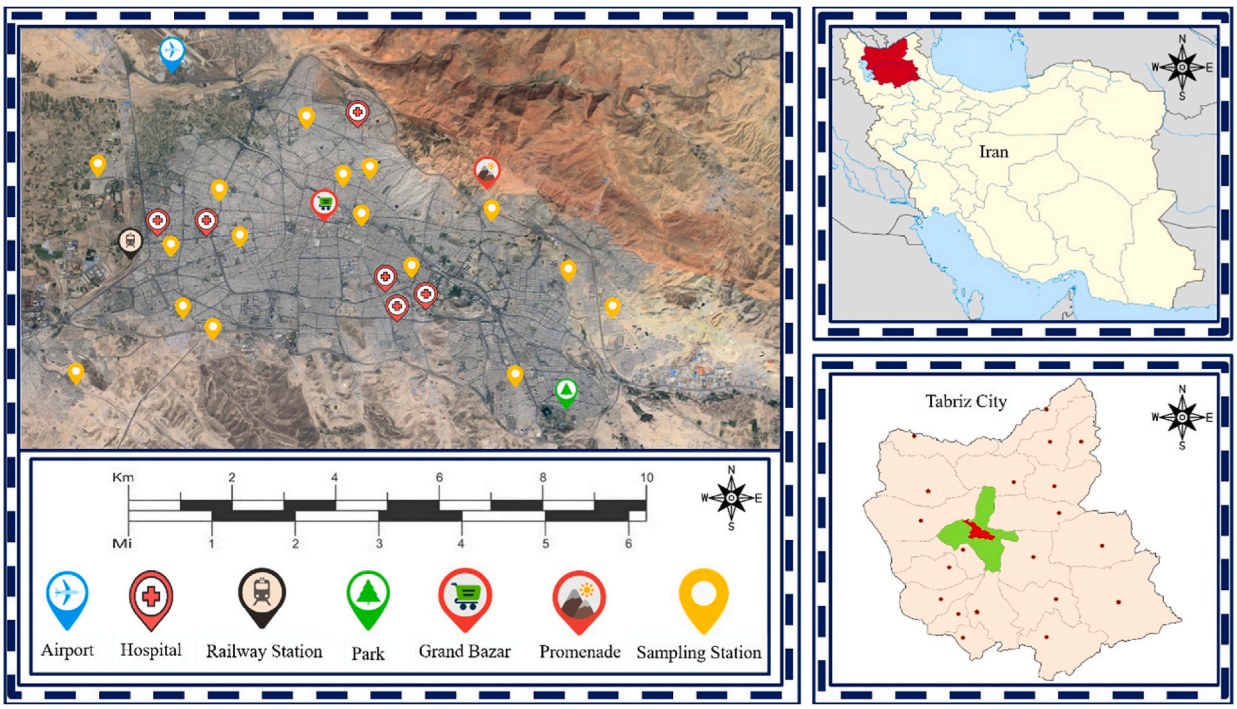

Fig. 1. Geographical location and sampling points of the study area.

m^3, B_f and B_b are the pollutant concentration in the front and rear parts of the control sample in $\mu g/m^3$, and V represents the volume of the sampled air in m^3. In order to ensure the proper performance of the device and determine the optimal sampling time, samples were taken from various sampling points and examined in the laboratory. After analyzing the samples, it was determined that the optimal sampling time is 1 h with a flow rate of 0.2 L/min. Additionally, the determination of the optimal flow rate and sampling time was done based on the appropriate adsorptive concentration in the charcoal tube without causing errors.

A total of 64 air samples were taken from different places inside Tabriz City for the study of airborne asbestos. These samples were obtained from a diverse range of 16 sites around the city. In order to evaluate the fluctuations in fiber content throughout the year, air samples were systematically gathered at identical sites for each of the four distinct seasons. Millipore cellulose ester membrane filters with 0.45 μm pore sizes were used to obtain the specimens. An open-face filter holder (type FP050/2, Schleicher and Schull, Dassel, Germany) was used to achieve this.

The sampling procedure involved using an IP 30L suction pump at a flow rate of 6 L per minute for 4–8 h. Samples were collected in an unobstructed environment at a 1-m elevation. The BS ISO 2002:14966 standard was employed to quantify the numerical concentration of non-organic fibrous particles. The fibers present in the samples were subjected to analysis using phase-contrast microscopy (PCM) in order to determine their kind. Additionally, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were employed for further examination. Using a phase-contrast electron microscope (AXIOM model, Germany) with a 400x–450× magnification range and a G22 Walton-Bechette graticule, asbestos fiber surface area was measured in compliance with NIOSH 7400 NIOSH 1989 criteria. Using a steam distillation apparatus, the filter was first cleaned in this manner. The objective lenses were changed to 40× to 45× magnification for fiber counting, and the microscope was set to 10× magnification. Ultimately, the phase-contrast microscope's overall magnification was adjusted to 400× to 450x [30]. According to this technique, asbestos fibers are defined as having a length-to-diameter ratio of 3:1 and a diameter of less than 3 μm, or more than 5 μm. Despite PCM's relative speed and affordability, its drawbacks make the employment of an alternative technique for asbestos fiber numerical counting necessary [31]. To report the fiber density on the filter surface, the fibers were counted on the filters, and the fiber count (fibers per milliliter of air samples) was determined using the following equation (2):

$$E = \frac{\frac{F}{nf} - \frac{B}{nb}}{AF} \tag{2}$$

Where:

E: is the fiber density of the filter surface, C: Airborne fiber concentration (fibers/ml), F: Total number of fibers >5 μm counted, nf: Total number of fields counted on the filter, B: Total number of fibers >5 μm counted in the blank, nb: the total number of fields counted on the blank, and the result was divided by the area of the graticule field (AF) (equivalent to 0.00785 square mm).

For reporting fiber concentration (C) (f/L), the following equation (3) was used:

$$C = \frac{Ac \times E}{V \times 1000} \tag{3}$$

A_C: Useful surface area of the filter, E: Density of particles on the filter, V: Volume of sampled air in Liters.

SEM equipped with EDX allows for the examination of thinner fibers and determination of fiber composition. Differentiating between asbestos types and non-asbestos fibers requires knowledge of fiber morphology and chemical composition. This technique is used in combination with other methods such as selected area electron diffraction and/or energy-dispersive X-ray analysis (EDX) to identify asbestos fibers among a wide spectrum of non-fibrous particles [32]. Fibers that satisfy the following criteria—a length-to-diameter ratio of 1:3, a diameter of less than 3 μm, and a length greater than 5 μm—are classified as asbestos using the Czech WEGA/TESCAN SEM model at magnifications ranging from 500× to 2500x. Moreover, an EDX system was used in conjunction with SEM to distinguish between absolute asbestos fibers and non-asbestos fibers, as well as other kinds of fibers. According to estimates, the SEM instrument can detect fibers at a sensitivity of between 0.0001 and 0.1 per milliliter of air [33]. The same equation used for PCM was used to calculate the SEM findings. Finally, after classifying the fibers and counting their quantity using SEM, the concentration may be computed using the following formula:

$$C = \frac{100N \times r^2}{V \times n \times a} \tag{4}$$

N: is the total number of asbestos fibers found. V: indicates the volume of an air sample obtained, n: is number of counted fields of images and a: displays the area of calibration of each image (mm^2), while r: stands for the filter radius (mm).

2.3. Potential for the generation of ozone

The creation of ozone is significantly influenced by VOCs. The quantity and reactivity of an organic chemical in the atmosphere determine its OFP [34]. Maximum incremental reactivity (MIR) and concentrations are used to calculate the OFPs of various VOC species. Ozone is produced when the amount of VOCs per mass is calculated using MIR coefficients [35]. In the current investigation, the OFP of BTEX was ascertained using equation (5).

$$OFP = BTEX\ (\mu g\ /m^3) \times MIR\ (gO_3/g\ VOCs) \tag{5}$$

2.4. Health risk assessment

BTEX including pollutants such as benzene, toluene, ethylbenzene and xylene take part in the formation of air secondary aerosols and are considered among dangerous air pollutants. Benzene has lots of harmful effects on human health and is recognized as group 1 carcinogens [36,37]. USEPA assesses health risks of cancer and non-cancer diseases through inhalation routs [38,39]. To estimate the carcinogenicity risk of BTEX compounds in inhalation rout, the EPA first determines the concentration of BTEX volatile compounds and then defines an acceptable framework in which there is the probability to make respond per consuming one chemical unit in lifespan under enhancement factor. This factor has had different dosages for different BTEX compounds based on mg/kg/d and the carcinogenicity risk of these compounds calculated using equation (5).

$$\mathrm{CDI} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \tag{6}$$

This factor has had different dosages for different BTEX compounds based on mg/kg/d and is used to calculate the carcinogenicity of these compounds. In this equation:

CDI: daily received dosage, C: breathing (0.83–0.65 m^3/h), IR: inhalation rate, ED: the duration of exposure, EF: the number of exposures, BW: body weight, AT: the duration of carcinogenicity.

Carcinogenic risks of benzene and ethylbenzene were assessed by the excess life time cancer risk (ELCR) provided by the USEPA [39] as follows:

$$\mathrm{ELCR} = \mathrm{EC}\left(\mu g / m^3\right) \times \mathrm{IUR}\left(\mu g / m^3\right) \tag{7}$$

The USEPA's Integrated Risk Information System (IRIS) supplied information on Inhalation Unit Risk (IUR). Table 1 displays all of the variables. The WHO study considers ELCR values between 1×10^{-5} and 1×10^{-6} to be "an acceptable limit for humans," but the USEPA recommends ELCR values below 1×10^{-6} [40].

Equation (8) was also used to assess the non-carcinogenicity risk of BTEX compounds in terms of the hazard quotient (HQ) parameter. The ratio of reference concentration (RfC) (mg/kg/day) to chronic daily intake (CDI) (mg/kg/day) is used to express it.

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RfC}} \tag{8}$$

In equation (8), coefficient of RfC is 0.03 mg/kg/day for benzene, 5 mg/kg/day for toluene, 1 mg/kg/day for ethylbenzene and 0.1 mg/m^3 for xylene compounds [41]. In this equation, for HQ values greater than 1, the risk value is significant and beyond the threshold [42]. While HQ ≤ 1 indicates that the risk created by exposure to BTEX will not be significant and has no potential effect on human health and its level is negligible [43].

The risk assessment for asbestos is conducted by utilizing the particle counting technique (PCM), as stated in the references from the United States Environmental Protection Agency's Integrated Risk Information System (USEPA IRIS) [44]. An estimate of the ELCR linked to breathing in asbestos fibers found in Tabriz City's ambient air was conducted in order to evaluate the health effects of asbestos. In order to accomplish this goal, the exposure concentration (EC) was adjusted using a unit factor (URF) in order to obtain the effective ELCR (Equation (7)). This metric plays a crucial role in determining the likelihood of cancer development based on the cumulative exposure to asbestos throughout an individual's lifetime. The calculation of EC was performed using following equations 9 and 10 [45].

$$\mathrm{EC} = \mathrm{C_a} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} / \mathrm{AT}\left(\mathrm{f} / \mathrm{cm}^3\right) \tag{9}$$

$$\mathrm{ELCR} = \mathrm{EC} \times \mathrm{URF} \tag{10}$$

Table 1
Risk parameters applied for ELCR and HQ assessment.

Exposure Parameter	Unit	Value	Reference
Average time (AT)	Years	Carcinogenic:70 Non- carcinogenic:35	[40]
Body Weight (BW)	Kg	70	[40]
Concentration (C)	µg/m^3 or f/m^3	–	–
Exposure Duration (ED)	Year	35	[40]
Exposure Frequency (EF)	Day/year	350	[41]
Exposure Time (ET)	Hour/day	24	[42]
Inhalation Rate (IR)	m^3/day	18.7	[40]
Inhalation unit risk (IUR)	µg/m^3	Benzene:7.8×10^{-6} Ethylbenzene:2.5×10^{-6} Asbestos:0.23	[42,43]
Reference concentration	mg/m^3	Benzene:0.029 Toluene:5 Ethylbenzene:1 Xylene:0.1	[42]

Within these fpormulas:

EC stands for "chronic exposure concentration," which is averaged over a 70-year lifetime. ED stands for "exposure duration", AT for "averaging time (h), URF for "unit risk factor for asbestos inhalation" $(f/cm^3)^{-1}$, C_a for "asbestos concentration" (f/cm^3), and ET for "exposure time in hours per day".

2.5. Statistical analysis

The statistical analysis of asbestos in this study was conducted using R 3.5.0 software and Microsoft Excel 2013 (v15.0). Subsequent to the determination of asbestos fiber concentration by the use of PCM and SEM techniques. The normality of the data was assessed using the Kolmogorov-Smirnov test. Subsequently, the concentration of asbestos fibers was spatially delineated using ArcGIS software. The statistical analysis of BTEX was conducted utilizing SPSS software (version 22) and Microsoft Excel. The B/T, E/B, and X/B ratios were computed for the samples in order to evaluate the photochemical aging process and identify the sources of BTEX compound emissions.

3. Results & discussion

3.1. Metrological parameters

We measured meteorological factors (temperature, pressure, humidity) during the sample period for the current study. The city of Tabriz has a semi-arid. It is evident from the box plot of seasonal temperature fluctuations over a one-year period that the summer season has the greatest temperatures among the four sample seasons (Fig. 2a). Following that, the spring season ranks second, the autumn season ranks third, and the winter season ranks fourth in terms of temperature.

Also, the maximum air pressure occurs in the autumn season, while the minimum is recorded in the summer season (Fig. 2b). According to Fig. 2c, the seasons of autumn, winter, summer, and spring, in that order, exhibit the highest to lowest relative humidity levels.

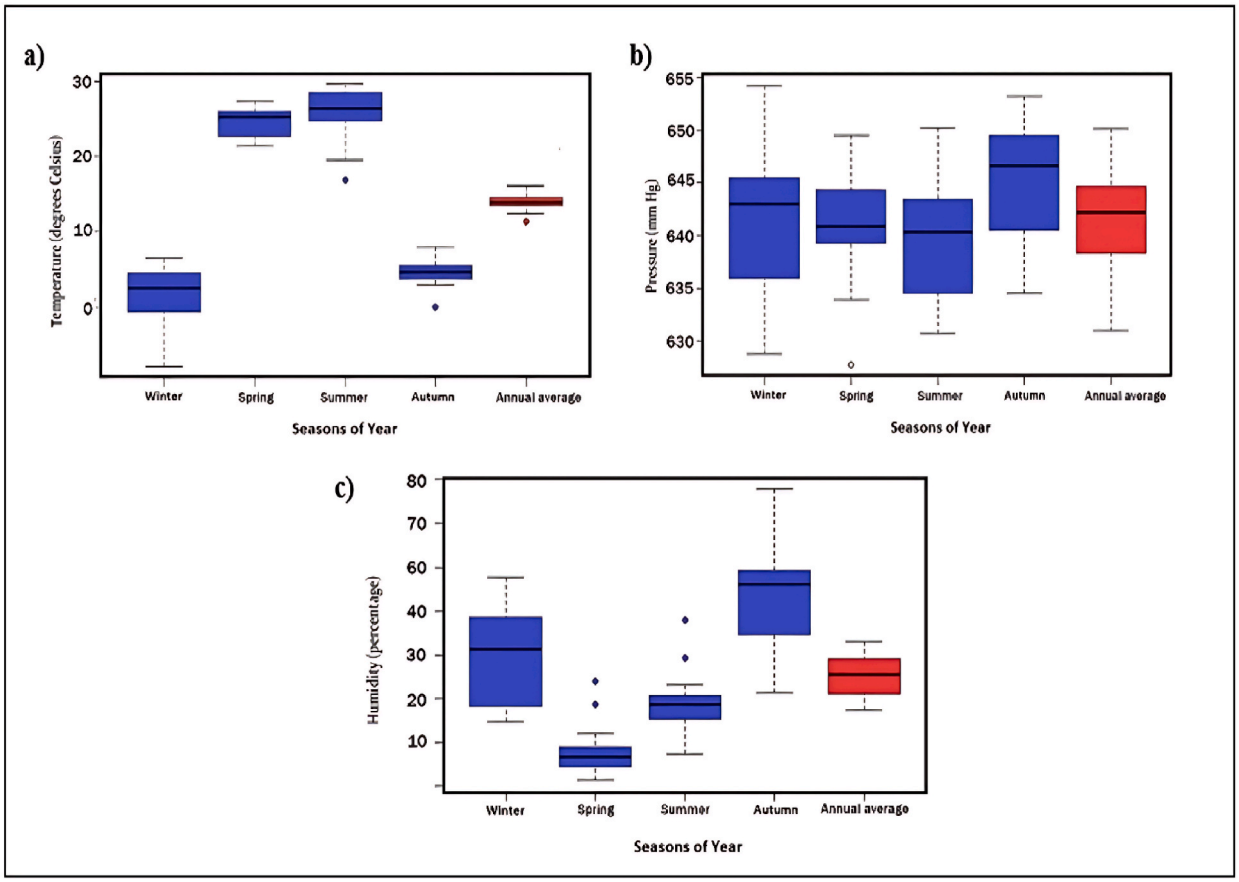

Fig. 2. Box plot of seasonal temperature, pressure, humidity variations in Tabriz city (2020–2021).

3.2. Concentrations of the BTEX compounds

Table 2 presents a summary of the BTEX levels in ambient air in Tabriz city over the course of four seasons. According to this table, the most seasonal average of BTEX compounds has been recorded in the autumn, and the lowest seasonal average of BTEX compounds has been recorded in the spring as 27.98 μg/m^3. Benzene, as the most important BTEX compound has experienced a seasonal average less than 5 μg/m^3 during the year. The highest concentration of this compound has been in the summer, and its lowest seasonal concentration has been in the winter.

Summer and winter have allocated the most and the least concentration of benzene to themselves (Fig. 3a). EPA guidelines have considered the legal limit of BTEX compounds in the air as 160 μg/m^3; that this guideline is more than the concentration of BTEX compounds as 33.03 μg/m^3 in Tabriz. Also, the total average of benzene was achieved at 3.25 μg/m^3 during the study. The distribution of benzene concentration based on the annual average in Tabriz city is shown in Fig. 4a. According to this figure, the more we approximate the west of the city, the higher the benzene concentration becomes due to the existence of more factories and industries. On the other hand, less benzene is observed in the east of Tabriz. This study has been consistent with the study conducted by Y. Hajizadeh et al., and this study shows a significant reduction in BTEX compounds concentration from summer to winter [46]. The summer and the spring have allocated the most and the least toluene concertation to themselves (Fig. 3b). Toluene high concentration in the ambient air due to the slow reaction of aromatic rings with O_3 and NO_3 radicals [47]. Toluene is only able to do one photochemical reaction with OH radicals in the ambient air [48]. Also, the total average of toluene pollutant during the study was achieved 17.06 μg/m^3. On the other hand, Fig. 4b shows toluene concentration distribution based on annual average in the ambient air of Tabriz. According to the figure, the more we approximate the north of the city, the more toluene concentration becomes due to the existence of more factories and industries, and there is less toluene on the east side of the city. The Industrial areas surrounding major cities have led to the production of significant amounts of uncontrolled anthropogenic emissions. Additionally, the increase in the use of personal vehicles and insufficient public transportation options, along with the presence of dust and particulate matter, are among the reasons for the high levels of air pollutants in Iran [49].

Fig. 3c shows that the summer and the spring have allocated the most and the least ethylbenzene concentration to themselves, respectively. According to Fig. 4c, the more we approximate the north and northwest of the city, the greater the ethylbenzene concentration becomes due to the existence of more factories and industries. On the other hand, there is less ethylbenzene on the east side of the city. The box plot shows that the autumn and the spring have allocated the most and the least O-xylene concentration, respectively (Fig. 3d). The total average of the most and the least O-xylene was achieved at 5.75 μg/m^3 during the study. In the north and center of the city, due to the presence of more factories and industries, the concentration of O-xylene increases. On the other hand, there is less O-xylene on the eastern side of the city (Fig. 4d). The box plot shows that the autumn and the winter have allocated the most and the least P-xylene concentration, respectively (Fig. 3e). The total average of the most and the least P-xylene was achieved 5.19 μg/m^3 during the study. Fig. 3f, shows that the autumn season has the highest concentration of total BTEX compounds. EPA guidelines set the limit of total BTEX compounds in the air as 160 μg/m^3, which is higher than the concentration of BTEX compounds present in Tabriz city at 33.03 μg/m^3. Places with high traffic and near industries have higher concentrations of BTEX compound (Fig. 4f).

Generally, toluene has allocated the highest concentration recorded in all seasons to itself in comparison with benzene, toluene, ethylbenzene, o-xylene, and p-xylene compounds. However, even the maximum value of toluene recorded in autumn, 35.52 μg/m^3, remains below the standard permissible values for this compound release. These results have been consistent with the findings of study conducted by M. Miri et al. and L. Miller et al. [43,50] on BTEX compounds, where toluene compounds generally constituted the largest share of urban BTEX compounds.

The results of this study on the seasonal concentration of BTEX compounds do not agree with those of studies by Miri et al. in

Table 2
Seasonal concentrations of BTEX compounds (μg/m^3).

BTEX compounds	Spring			Summer		
	Min	Max	Mean	Min	Max	Mean
Benzene	0.58	6.87	2.72	1.41	8.41	3.84
Toluene	8.59	31.2	14.90	6.87	32.41	18.64
Ethylbenzene	2.57	7.62	4.08	2.97	10.21	6.18
O-xylene	2.28	6.51	3.44	3.67	10.23	6.56
P-xylene	2.79	9.30	5.15	3.43	6.31	4.92
BTEX	17.93	59.75	27.98	16.80	64.51	36.03
BTEX compounds	**Autumn**			**Winter**		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**
Benzene	1.54	6.12	3.77	0.95	5.57	2.62
Toluene	9.25	35.52	18.54	9.82	33.65	16.15
Ethylbenzene	1.43	6.54	4.75	3.64	7.68	5.56
O-xylene	3.31	13.36	7.79	2.54	12.67	5.19
P-xylene	2.30	12.97	6.63	2.63	6.13	4.52
BTEX	23.56	70.82	37.94	16.79	61.18	30.16

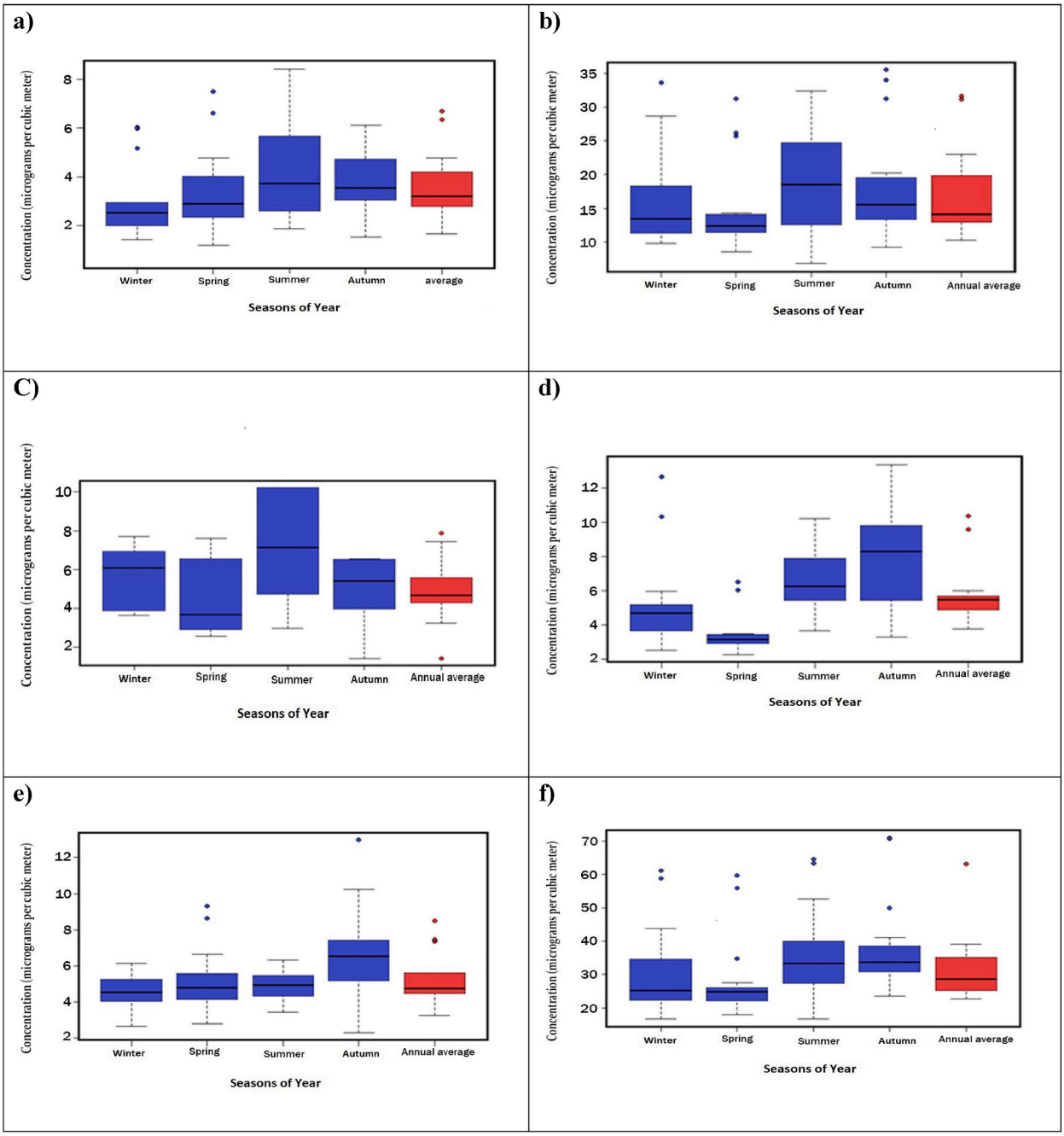

Fig. 3. Seasonal variation of Benzene (a), Toluene (b), Ethylbenzene (c), O-xylene (d), P-xylene (e), and BTEX compound (f) concentration.

Teheran, Iran [43] and Seron Breton in Leon, Mexico [51] which found that the spring and summer months saw the highest concentrations of BTEX compounds. Rainy days during the sampling period and variable sampling settings could be the cause of this, as rain transfers BTEX atmospheric chemicals to other media, including plants and soil.

To determine the emission resources of BTEX compounds, toluene/benzene (T/B) compound ratio has been used as indicator, so that values close to 1 indicate automobile resources and values more than 3 indicate industrial resources. The ratio of toluene to benzene compounds varies from 4.8 to 6 throughout the year, indicating that Tabriz's air contains these chemicals primarily from industrial sources. According to figures (4a, 4b, 4c, 4d, 4e) and the dispersion diagram of BTEX compounds in Fig. 4f and the high concentration of such compounds on the west side of the city, it is possible to consider the concentrated industrial factories as the most important resource of BTEX compounds emission, and it is impossible to ignore the emission share of Industrial town of west of Tabriz, petrochemical factories, oil refinery company of Tabriz, thermal power station, machine and tractor manufacturing companies in the

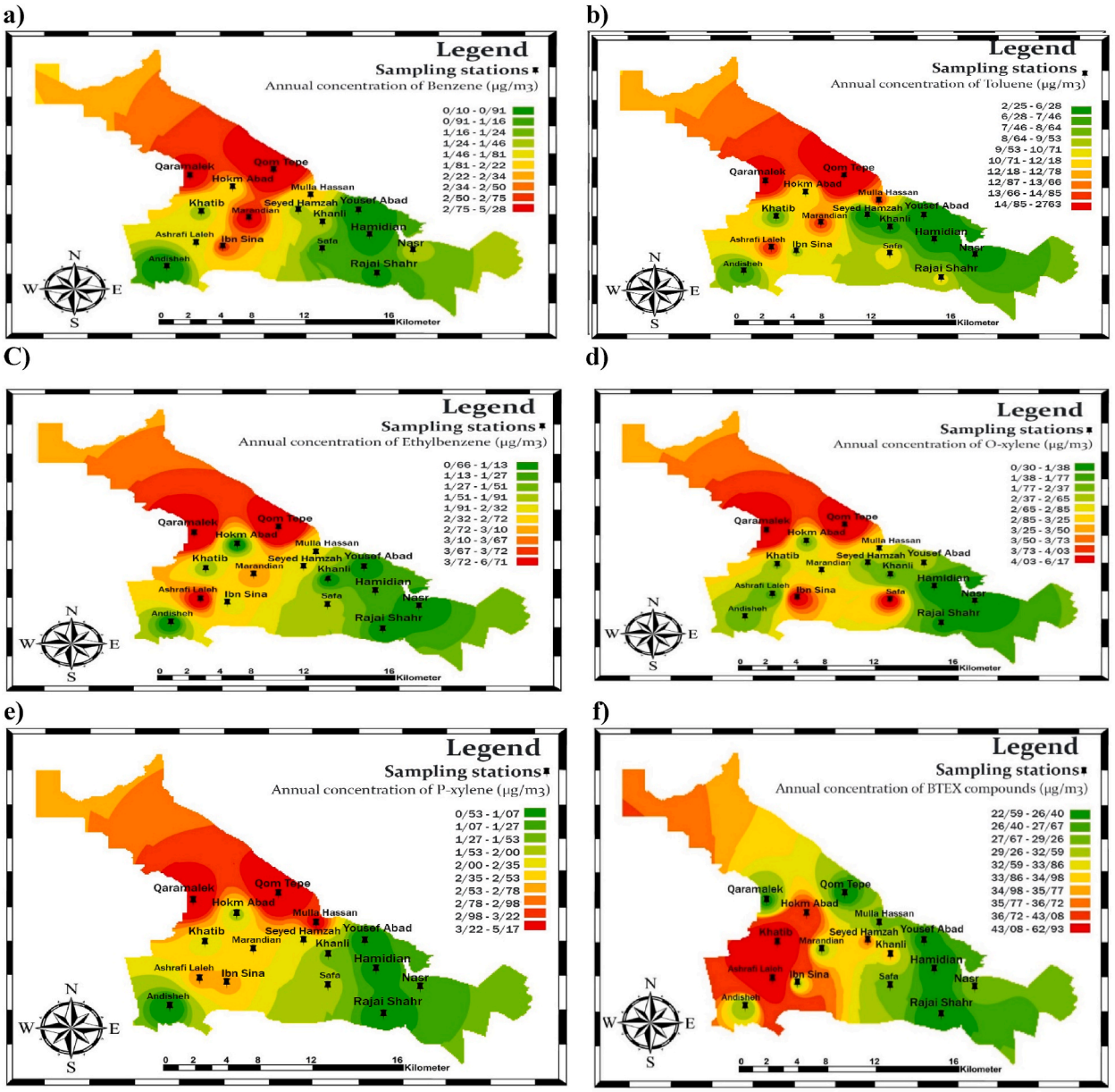

Fig. 4. Spatial distribution of annual concentration of Benzene (a), Toluene (b), Ethylbenzene (c), O-xylene (d), P-xylene (e), and BTEX compound (f).

west of this city. Tabriz, as the largest city in the northwest of the country, faces numerous challenges related to air pollution, stemming from both small and large-scale industrial activities and the traffic of light and heavy vehicles. The presence of automobile and tractor manufacturing factories, which are upwind from the city, the presence of railway lines, and the existence of numerous thermal, gas, and hydroelectric power plants, especially in recent years, have compounded the environmental problems of this city.

3.3. Ozone formation potential

To create methods for reducing air pollution, it is necessary to comprehend how VOC emissions affect the production of ozone. The photochemical production of ozone is initiated to widely varied degrees in the troposphere by interactions between VOCs and OH radicals [52]. During several investigations, OFP has been used to predict the ability of different species of VOCs to produce ozone in ambient air [34]. Fig. 5 shows the contribution of BTEX to OFP in the research area in different seasons. For example, each chemical contributed to OFP in spring: toluene (58 %) > xylene (28 %) > ethylbenzene (12 %) and benzene (2 %). Compared to other components in this research, toluene and xylene and contribute more to ozone production. The MIR scale indicates that among BTEX, o,

p-xylenes were the primary contributors to ozone production, with toluene coming in second and ethyl benzene in third. Similar studies have indicated this trend [5,34,52,53].

Increasing the concentration of any BTEX species increases ozone production because OFP of VOCs are proportional to their concentration in ambient air [34]. Propene (13 %), xylenes (12 %), propanal (12 %), toluene (11 %), acetaldehyde (11 %), isoprene (6 %), methanol (4 %), isobutene (3 %), acetone (3 %), and 1,3-butadiene (3 %), were the top 10 VOCs that constituted more than 80 % of the total ozone production [52]. More in-depth research should be done to determine whether other volatile organic compounds have the ability to produce ozone.

3.4. Concentrations of asbestos fibers

Asbestos fibers are one of the pollutants studied in this research. PCM analysis was used to calculate the amount of asbestos fibers (Fig. 6). In 2021, the average asbestos concentrations in the winter, spring, summer, and fall were 1.68, 1.90, 1.93, and 2.26 f/L, respectively. In the current study and according to the analysis, Qoom Tapa Station, with 3.81 f/L annual concentration average, was the most polluted center to asbestos fibers, which shows the highest concentration of fibers recorded in 16 centers in all seasons of the year. Qaramalek Station is the second center contaminated with asbestos fibers, with an average annual concentration of 2.65 f/L. Marandian and Nasr Stations, with an average annual concentration of 2.51 f/L, share the third place among the most polluted points in Tabriz. The cleanest sampling stations are Hokmabad, Yousef Abad, and Ashrafi-ye-Laleh Stations, with an average annual concentration of 0.67 f/L, 1.08 f/L, and 1.15 f/L, respectively. Also, the lowest standard deviation is related to Hokmabad Station, with a numerical value of 0.13, and this station has the lowest pollution to asbestos fibers in half of the seasons of the year among the sampling stations, and ND values have been recorded in the remaining 50 % seasons. The most polluted season of the year for asbestos fibers is the autumn, with 2.26 f/L, and the cleanest season of the year is winter, with an average concentration of 1.68 f/L, which is consistent with the study conducted by Ghorbani et al., who found that the autumn has been the most polluted season with regard to the asbestos fibers [54].

According to the box plot, autumn and winter have experienced the highest and the lowest concentrations of asbestos fibers, respectively (Fig. 7). The total average of asbestos fiber concentration was 1.94 f/L during the study period.

The annual average graph of Tabriz's ambient air is used to determine the asbestos fiber distribution (Fig. 8). This graph indicates that the concentration of asbestos fibers increases with proximity to the south of the city, which can be attributed to the presence of factories and other enterprises. However, due to the presence of the main entrance route, petrochemicals, main highways connecting the city to other parts of the country, and significant traffic, a large concentration is seen on the northern side of Tabriz. Also, the closer we get to the west side of the city, the less asbestos concentration is observed. Considering the location of Shahid Madani International Airport of Tabriz to the northwest of the city and its several daily flights, and given the proximity of Pasdaran Square as one of the biggest intercity squares, which connects Pasdaran Highway to Azerbaijan Highway and Sattar Khan Street, and a daily traffic of hundreds of thousands of light and heavy automobiles coming/departing from the beltway, the concentration of asbestos fibers is high due to the brake lining of planes and automobiles. The central regions of Tabriz, including Marandian and Safa Stations, experience high levels of asbestos due to heavy traffic and the non-development of the old tissue of the city in contrast with the ever increasing traffic. Nasr Station is the closest station to the University of Tabriz, Shahid Madani Hospital, Imam Reza Hospital, Imam Khomeini

Fig. 5. Contribution of BTEX to OFP in seasons of year: A) Spring B)Summer C)Autumn D)Winter.

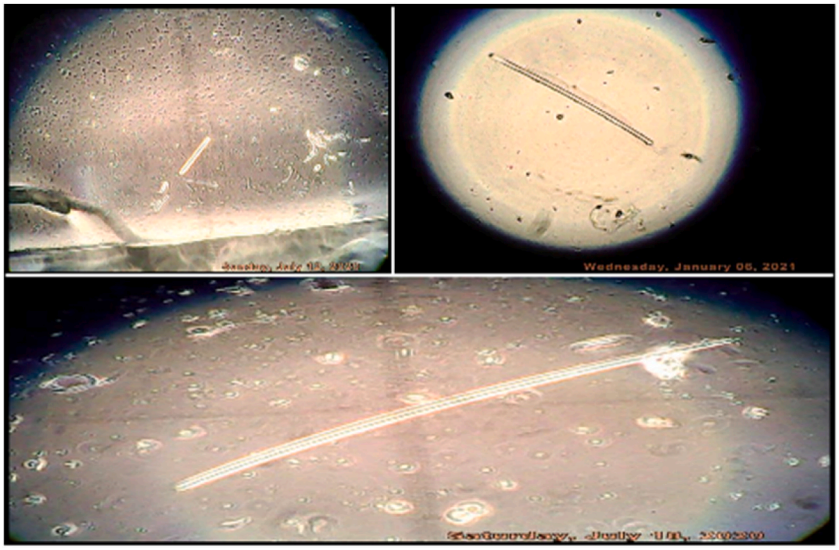

Fig. 6. Asbestos fiber sample under the phase contrast microscope in the reference laboratory.

Hospital, Sina Hospital, and Tabriz University of Medical Sciences, and the increase of asbestos tissue emitted from automobiles was more noticeable due to the Covid-19 pandemic and the increased volume of traffic going to medical and testing centers. Eastern regions of the city, including Nasr and Rajaei Stations, are considered newly-built and underdeveloped regions, and, at the moment, there are great projects of constructing residential houses and industrial and recreational centers on the agenda of these urban regions. Rajaei Shahr Station is the closest station to Shah Goli Park, the most important touristic and recreational center of Tabriz. Every day, this region receives hundreds of intercity travelers and the residents of Tabriz itself. The increased concentration of these fibers in these areas poses a health risk to the local population due to the release of asbestos, caused by construction and vehicle exhausts. Hamidian, Yousef Abad, and Andisheh Stations were the cleanest regions of the city in terms of asbestos fibers, which is ascribable to lower traffic and the absence of industrial regions. The average annual concentration of asbestos fibers in Karaj was found to be 0.0018 f/mL PCM by Kermani et al., which is in line with the findings of the present investigation [33].

Numerous studies showed comparable positive and negative relationships between a few meteorological parameters and the amount of asbestos fibers in the air of the studied cities; an increase in wind speed is positively correlated with the amount of asbestos fibers in the air, whereas an increase in temperature, relative humidity, and air pressure shows a negative correlation [55]. Ghorbani et al. investigated traffic and urban transportation as the most important factors in the dispersion of asbestos fibers into the air of Isfahan, which is consistent with the results of asbestos fibers dispersion map for the air of the city studied in the current research [54]. Mokhtari et al. reported that the average asbestos tissue concentration in cold seasons was higher than the values recorded in the same stations in the summer, which is inconsistent with the results of the current study because of the different meteorological conditions of Yazd and Tabriz [56].

3.5. Health risk assessment

3.5.1. BTEX

This study used the health risk of BTEX compounds for the assessment of the carcinogenic (ELCR) risks of benzene and ethylbenzene compounds due to their carcinogenetic properties and depicted the health risk caused by such compounds for children and adults.

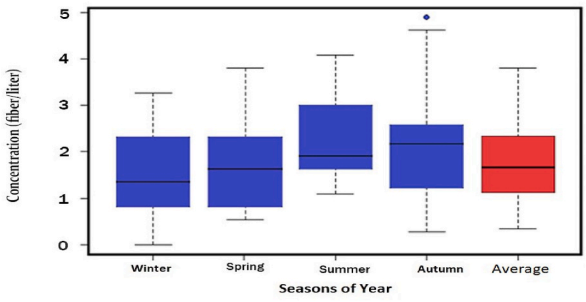

Fig. 7. Seasonal variation of asbestos fibers concentration.

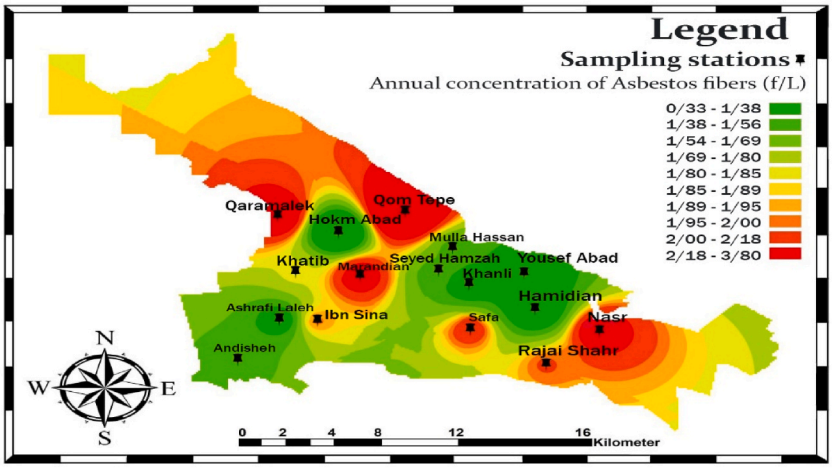

Fig. 8. Spatial distribution of annual asbestos fiber concentration.

USEPA has determined ELCR below 1×10^{-6} as an acceptable level [57], while WHO has recommended values between 1×10^{-5} and 1×10^{-6} [58].

According to Table 3, the risk of exposure to benzene compounds is 24×10^{-4} in children and 55.9×10^{-4} in adults, and the risk of exposure to ethylbenzene is 3.78×10^{-4} in children and 3.25×10^{-4} in adult. According to lifetime cancer risk predictions, benzene and ethylbenzene had the strongest correlations. There is a considerable risk of cancer from exposure to benzene and ethylbenzene in Tabriz's ambient air because the estimated cancer risk for these compounds is higher than what the EPA and WHO threshold values for these compounds are. Similar results have been reported in Ardabil (Iran), Shiraz (Iran), Beijing (China), India and Mexico [28,36,51,59–61]. Calculating the non-carcinogenicity risk of these compounds determined under the HQ factor, and values lower than 1 show a low risk, and values higher than 1 show the presence of non-carcinogenicity risk. According to Table 3, HQ factor has been greater than 1 for benzene compound, both for children and adults, at 4.24 and 9.26, respectively, and this factor has been determined to be less than 1 for ethylbenzene compound. Therefore, a high non-carcinogenicity risk has been attributed to benzene compound for all groups in exposure. EPA represented reports based on neural disorders and symptoms like weakness, loss of appetite, tiredness, dizziness, nausea, and irritation in eyes, skin, mucous membrane, and respiratory system are instances of the non-carcinogenic effects of benzene compounds, and there is a low non-carcinogenicity risk for ethylbenzene, which shows recklessness on the non-carcinogenicity of this compound in the study region [62].

3.5.2. Asbestos fibers

Less research has been done on the non-carcinogenic effects of asbestos exposure than the carcinogenic effects. As a result, the study's predicted positive health impacts have only been linked to asbestos because of the increased risk of cancer from asbestos-polluted air. As to the carcinogenicity categorization, asbestos with the CAS number CAS 4-21-1332 is considered carcinogenic to humans in Group 1. The present investigation has assessed the risk of asbestos fibers using data derived from the PCA approach, taking into account the EPAR IRIS references.

Tables 4 and 5 indicate that when the ELCR rises, the EC will likewise rise. The 16–30 age range, which has the greatest interaction with asbestos fiber relative to other age ranges, is associated with the biggest levels of EC and ELCR at all points. The carcinogenicity risk of airborne chemicals ranges from 1×10^{-4} to 1×10^{-6}, which has been designated as the target level, as per the EPA advisory value.

The age group of 16–30 has the most contact with asbestos fiber when compared to other age groups, and this age range has been associated with the largest values of these results in all points. The estimate of the carcinogenicity risk resulting from this investigation falls between 1×10^{-4} and 1×10^{-6}. This is in contrast to the study conducted in Limpopo by M. Malatji et al., where the majority of the centers exceeded the recommended limits [63]. Because the use of asbestos equipment has decreased in those cities over a ten-year planned period, the average annual concentration in three Italian cities was around 0.56 f/L PCM, which is less than the standard

Table 3
Assessing risk caused by BTEX compounds.

Compounds	ELCR		HQ		HI	
	Children	Adults	Children	Adults	Children	Adults
Benzene	24×10^{-4}	55.9×10^{-4}	4.24	9.26	80.30	124.85
Toluene			1.19	2.22		
Ethylbenzene	3.78×10^{-4}	3.25×10^{-4}	0.325	0.215		
Xylene			74.55	112.39		

value. As a result, the current study is consistent with the study carried out by Gualtieri [64].

This study has limitations that need to be investigated in future studies, including the fact that sampling was done at only 16 locations, which may not adequately reflect changes in pollution levels across the city. Therefore, it is suggested to increase the number of sampling points in Tabriz to increase the accuracy of the assessment of the overall air quality of the city. The assessment of carcinogenicity risks for asbestos exposure was examined using a simple approach, which led to ambiguities. The method tends to overestimate risks due to its conservative approach. Additionally, the analysis fails to differentiate between types of asbestos fibers and overlooks confounding factors for age-specific risks like smoking and lifestyle factors among exposed individuals.

4. Conclusion

The data on the concentrations, geographic distribution, seasonal variations, and risk assessment of airborne asbestos fiber and BTEX chemicals in Tabriz's ambient air have been provided by this study. The investigation results showed that fall had the highest concentration of all BTEX chemicals. High-traffic locations and the vicinity of businesses were shown to have a higher correlation with BTEX concentrations. One of the pollutants examined in this study and measured using PCM is asbestos fiber. The seasons with the highest and lowest amounts of asbestos fibers were autumn and winter, respectively. From a geographical point of view, the closer one gets to the south of the city, the concentration of asbestos fibers increases. This is due to the presence of industries and other industrial activities, traffic, weather patterns, and geographic location. The inhabitants' health is at risk due to the rising concentration of these fibers in those places.

Both WHO and the EPA have set threshold values, and the estimated cancer risk associated with benzene and ethylbenzene exceeded those values. This suggests that there is a significant risk of cancer caused by these compounds, which are found in Tabriz's ambient air. The study findings indicate that individuals aged 16–30 years had the greatest EC and ELCR maximum values in all sites, indicating their higher exposure to asbestos fibers compared to those in other age groups. According to the EPA standards, the objective limit for carcinogenicity risk associated with airborne chemicals ranges between 1×10^{-4} and 1×10^{-6}. These findings underscore the significance of controlling asbestos fibers and Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) in urban areas, particularly those with industrial origins. It is evident that comprehensive future research is necessary to identify and control the sources of pollutant emissions and mitigate their levels. In order to solve this problem, steps like conducting in-depth studies, improving fuel and vehicle regulations, establishing reliable public transit systems, and moving businesses to suburban areas can all make a big difference in the reduction of BTEX and asbestos emissions.

Abbreviations

Abbreviation	Definition
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CDI	Chronic daily intake
ECR	Excess cancer risk
ELCR	Estimated lifetime cancer risk
HAPs	Hazardous air pollutants
HQ	Hazard quotient
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
IUR	Inhalation Unit Risk
MIR	Maximum incremental reactivity
OFP	Ozone formation potential
PAHs	Polycyclic aromatic hydrocarbons
PAN	Peroxyacetyl nitrate
PCM	Phase-contrast microscopy
RfC	Reference concentration
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
WHO	World Health Organization

Data availability statement

Data will be made available on request.

Additional information

No additional information is available for this paper.

CRediT authorship contribution statement

Elnaz Zarezadeh: Writing – review & editing, Writing – original draft, Methodology, Investigation. **Ahmad Jonidi Jafari:** Writing

Table 4
Chronic contact with asbestos fibers.

EC_{0-2}		EC_{2-6}		EC_{6-16}		EC_{16-30}	
Min	Max	Min	Max	Min	Max	Min	Max
1.21 E−06	4.96 E−06	2.14 E−05	4.12 E−05	3.28 E−05	5.09 E−05	5.41 E−05	6.69 E−05

Table 5
Additional carcinogenic risk caused by asbestos during lifetime.

$ELCR_{0-2}$		$ELCR_{2-6}$		$ELCR_{6-16}$		$ELCR_{16-30}$	
Min	Max	Min	Max	Min	Max	Min	Max
1.04 E−06	2.19 E−06	1.19 E−05	3.38 E−05	2.74 E−05	4.64 E−05	4.29 E−05	5.36 E−05

– review & editing, Writing – original draft, Methodology, Investigation. **Mitra Gholami:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition. **Mahdi Farzadkia:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Ehsan Ashouri:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Abbas Shahsavani:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Majid Kermani:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Pegah Nakhjirgan:** Writing – review & editing, Writing – original draft, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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