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Characterization and source identification of trace elements in airborne particulates at urban and suburban atmospheres of Tabriz, Iran

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Abstract Concentration of particulate matter (PM_{10} and total suspended particulate (TSP)) and their elemental constituents were measured to identify the major sources of elements in urban and industrial suburban sites in Tabriz, Iran, from September 2012 to June 2013. TSP and PM_{10} samples were collected using high-volume samplers. Concentrations of 31 elements in aerosols and crustal soil were determined by ICPMS. The most abundant detected metals in the urban sampling sites were Al (217.5–4019.9 ng m^{-3}), Fe (272.5–7658.0 ng m^{-3}), Pt (4.7–1994.4 ng m^{-3}), and P (13.6–2054.8 ng m^{-3}(for TSP and Al (217.6–3687.3 ng m^{-3}), Fe (197.1–3724.9 ng m^{-3}), Pt (65.9–2054.5 ng m^{-3}), and P (11.0–756.6 ng m^{-3}(for PM_{10}. In the suburban sampling site, the most abundant detected metals were Al (2083.0–9664.0 ng m^{-3}), Fe (360.0–7221.5 ng m^{-3}), P (229.4–870.5 ng m^{-3}), and Ti (137.3–849.7 ng m^{-3}) for TSP and Al (218.5–4179.6 ng m^{-3}), Fe (106.3–2005.1 ng m^{-3}), P (251.9–908.4 ng m^{-3}), and Ba (10.6–584.9 ng m^{-3}) for PM_{10}. For the crustal soil, the most abundant detected elements included Al (60,088–60,694 ppm), Fe (19,886–20,474 ppm), Ti (894–3481 ppm), and Si (365–4246 ppm). Key emission sources were identified, and the concentrations contributed from individual sources were estimated. Enrichment factor (EF) explaining a preponderance of the variance in the data was applied to the datasets. EF calculations revealed that non-crustal trace elements were more enriched in the urban than suburban sampling sites. Results of the factor analysis on the elements showed that emissions from road traffic (involving oil and fuel combustions by vehicles, platinum group elements from vehicle exhaust, and resuspension of particulate matter from polluted soil) and construction dust from nearby construction sites and electricity generation plant were the major contributors of anthropogenic metals at ambient atmosphere in Tabriz. Results of this study elucidated the need for developing pollution control strategy, especially vehicle exhaust control, and creating green spaces around the city.

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Keywords Particulate matter · Metals · PCA · Source apportionment · Tabriz

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Introduction

Atmospheric particulate matter (PM) may be generated by various natural processes or human activities, such as soil dust, wood stoves, diesel trucks, power plants, and industrial

processes (Lin et al. 2008). International Agency for Research on Cancer (IARC) has recently classified outdoor air pollution and PM components of outdoor air pollution as carcinogenic to humans (IARC group 1) (Loomis et al. 2013). PM is one of six "criteria" pollutants, and its effects on human health and the environment varies with the physical and chemical compositions (Lin et al. 2008). Numerous epidemiological studies have reported that exposure to PM is associated with a variety of adverse acute and chronic health effects and increased risk of adverse birth outcomes (Nieuwenhuijsen et al. 2013).

Individual particles vary considerably in size, chemical composition, geometry, and physical properties (Lin et al. 2008). Atmospheric PM is a complex mixture of chemical components including metals, elemental carbon, other organic carbon, polycyclic aromatic hydrocarbons, sulfate and nitrate salts, and water. Several studies have shown that PAHs and metals are two main PM components that are associated with adverse health effects of PM (Kim et al. 2013; Zereini and Wiseman 2010).

Among air pollutants are trace elements associated with PM from a variety of pollution emission sources (Gao et al. 2002). For instance, fossil fuel combustion is the primary anthropogenic emission source of Co, Hg, Ni, Sb, Se, Cu, Mn, Zn, and V. Some quantities of Pb, Cu, Zn, Ni, and Cd are also imparted from vehicular exhausts (Allen et al. 2001). In addition, anthropogenic emissions of toxic trace metals (e.g., Pb, Cd, Zn, Ni, and Cu) have been reported to dominate natural processes (Wang et al. 2006). A strong correlation between the high elemental concentrations in aerosol particles and high mortality and morbidity has been found in several epidemiological studies (Dockery and Pope 1994; Wang et al. 2006).

For health reasons and to accurately characterize atmospheric PM, the chemical composition of PM must be determined. On the other hand, to improve air quality, it is necessary to differentiate elemental concentrations from various sources. Enrichment factor (EF) method proposed by Zoller et al. (1974) has been widely used as the first step to evaluate the potential strength of pollution-emitting sources (Gao et al. 2002; Zoller et al. 1974). To apportion the sources of aerosols, a factor analysis is usually required. The method has been used successfully by numerous researchers (Wang et al. 2006).

Several studies have focused on the mass concentrations, health impacts, chemical characterization, and source identification of PM in some cities of Iran (Givehchi et al. 2013; Hojati et al. 2012; Masoumi et al. 2012; Rashki et al. 2012). However, to the best knowledge of the present authors, there are limited published studies, which have dealt with the metal components of PM in Tabriz (Gholampour et al. 2014b; Sanobari and Banisaeid 2007).

Tabriz is the capital city of East Azerbaijan Province. It is one of the largest urban areas in Iran with the population of approximately 1.7 million in 2012 and total surface area of

320 km^2 (Yearbook 2013). There are some light and heavy industries in the northwest, west, and southwest of this city. Industries such as oil refinery, thermal power plant, and petrochemical complex are located in the southwest, while a cement factory is situated in the northwestern fringe of the city. In recent years, because of the development of industries and also increased number of vehicles in urban areas, Tabriz has been faced with serious air pollution problems, especially in winter (Gholampour et al. 2014b). In addition, the air pollution in Tabriz is mostly under the influence of atmospheric thermal inversion in the cold season; recently, the Middle East dust storm (originating from Iraq) in the warm season has exacerbated air pollution in this area (Sanobari and Banisaeid 2007).

The present study was therefore performed to determine the mass levels of total suspended particulate (TSP) and PM$_{10}$ (particles with the aerodynamic diameter of smaller than 10 μm) along with the variations of chemical characterization (metal components) associated with them in Tabriz. Finally, PM possible sources were identified by using the variations of metal components associated with TSP and PM$_{10}$.

Materials and methods

Sampling sites and schedule

Based on the different land use categories, two sites were selected (Fig. S1 in Supplementary Materials): (1) an urban site, located in the residential region (38° 3′ 18.08″ N, 46° 19′ 22.77″ E) with the distance of about 200 m from a major street and 1000 m from a main freeway (U.S. EPA 2013). The samplers were operated on the roof of a three-story building at the height of 15 m above the ground level. Six-day sampling was carried out throughout the sampling period from September 2012 to June 2013 (EPA 2015) and (2) an industrial suburban site situated out of the urban border, approximately 1000 m away from a major freeway and 500 m from the main street (38° 4′ 23.98″ N, 46° 9′ 35.55″ E). A petroleum refinery, a small industrial estate, a thermal powerhouse, and some other small industrial plants were located adjacent to the industrial sampling site. The samplers were operated on the height of 3 m above the ground level. About three to four samples were collected every month from November 2012 to May 2013 (EPA 2015). Location of the sampling stations is shown in Fig. S1 in Supplementary Materials.

PM measurement

TSP and PM$_{10}$ samples were collected by two high-volume samplers manufactured by Graseby–Andersen at flow rates of 1.13–1.41 m^3/min for 24 h. Both TSP and PM$_{10}$ were collected on a 20.3×25.4 cm Whatman glass micro-fiber filter.

Before and after the sampling, the filters were maintained first under 40 % relative humidity (RH) and 25 °C for over 48 h and later in room conditions for 2 h; then, they were weighed three times using an A&D electronic balance with the reading precision of 0.1 mg. After weighing, the filters were packed in aluminum foils and stored at −20 °C until extraction and chemical analysis.

Analysis of elements

For analyzing the elements, one quarter of each filter was digested at 170 °C for 4 h in a high-pressure Teflon digestion vessel with 10 mL HNO_3 (69 %), 3 mL HCLO4 (70 %), and 1 mL HF (48 %). After cooling, the solutions were dried and 1 mL concentrated HNO_3 was added. Then, it was diluted with 25 mL using distilled–deionized water. The obtained solutions were filtered through a micro-porous membrane with the pore size of 0.45 (Goudie and Middleton 2006; Ho et al. 2006).

All 31 elements (Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, La, Li, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, Te, Ti, Tl, Y, Zn, Zr, Pt, Rh, V, Si, and Hg) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, model ULTIMA, JOBIN-YVON Company, France). Method detection limits (MDLs) were determined by adding 3 standard deviations of the blank readings to the average 5 replicates of blank values. Efficiency of the recovery was measured by spiking one quarter of a particle-laden filter with the known amounts of elements. Detection limits, method detection limit, and efficiency of recovery for various elements are presented in Table S1 in Supplementary Materials.

For analyzing the elements in the crustal soil of the region, 1 g of the soil sample was digested using the previously mentioned method. Results of elemental measurements were used for calculating enrichment factor (EF).

Meteorological data

Wind speed, wind direction, ambient air temperature, atmospheric visibility, and RH at sampling stations were obtained from the National Climatic Data Center (NCDC) (NNDC 2015) and East Azerbaijan Meteorological Organization. The obtained data were examined for the missing values and outliers to input in WRPLOT View Freeware 7.0.0 to plot the wind rose and also in Microsoft Excel 2010 to plot the temporal trends for other parameters.

Data analysis

Data were analyzed in SPSS20 statistical software (SPSS Inc.) by means of data reduction (for the principal component analysis (PCA) of the elements), bivariate correlations (to quantify the relation between the elemental concentrations), and

multivariate test (to quantify significance differences between the concentrations of elements in the urban and suburban sampling sites). Differences and correlations were considered significant at 0.05 levels.

Results and discussion

PM mass concentrations

Variations of meteorological data, PM concentration, ratio of PM species, and ionic constituent of PM in the two sampling sites have been presented in our previous publications (Gholampour et al. 2014a, b). Briefly, in the studied region, January was the coldest month with the mean temperature of −3 °C, while July was the warmest month with the mean temperature of 38 °C. The prevailing wind blew from the northeast with the speed variation of 0.5 to 11.5 m/s, and the annual mean wind speed was 4.01 m/s (see Fig. S2 in Supplementary Materials).

In this study, 160 and 60 samples (24-h samples) were collected in the urban and in the industrial suburban sites, respectively. The annual average concentrations of TSP and PM_{10} in the urban sampling site were 142.2±76.3 and 85.3± 43.9 μg m^{-3}, respectively. In the industrial suburban site, the overall averages of TSP and PM_{10} mass concentrations were 178.7±52.7 and 109.9±30.2 μg m^{-3}, respectively. Percentage of the days on which 24-h mean concentrations of PM_{10} exceeded the WHO guideline (Europe and Organization 2006) and national standard level (50 μg m^{-3}) in the cold months was considerably higher than that of the warm months. The PM_{10}/TSP ratio for the whole studied period ranged between 0.35–0.91 and 0.32–0.79 in the urban and suburban sites, respectively.

Elemental constituents of PM

Mean and standard deviation contents of elements (TSP and PM_{10}) in the two sampling sites during the studied period (based on ng m^{-3} and mass percentage of PM) are summarized in Table 1. Sum of the concentrations of the analyzed elements in the urban sampling site ranged from 2566 to 14, 004 ng m^{-3} for TSP and 2141 to 8692 ng m^{-3} for PM_{10}; they accounted for about 2.2–6.8 % of TSP mass and 0.7–6.8 % of PM_{10} mass. The most abundant detected metals in the urban sampling sites were Al (217.5–4019.9 ng m^{-3}), Fe (272.5– 7658.0 ng m^{-3}), Pt (4.7–1994.4 ng m^{-3}), P (13.6– 2054.8 ng m^{-3}), Ti (10.8–960.4 ng m^{-3}), and Si (5.1– 2548.5 ng m^{-3}) for TSP and Al (217.6–3687.3 ng m^{-3}), Fe (197.1–3724.9 ng m^{-3}), Pt (65.9–2054.5 ng m^{-3}), P (11.0– 756.6 ng m^{-3}), Ti (14.1–541.3 ng m^{-3}), and Si (1.25– 488.0 ng m^{-3}) for PM_{10}. To compare our data with other studies, mean concentrations of some elements associated

Table 1 Mean concentration and standard deviation (SD) of the elements (ng m^{-3}) and contribution of PM mass (percentage) for TSP and PM$_{10}$ in the urban ($n=48$) and suburban ($n=30$) sites

| Elements | Urban sampling site | | | | Suburban sampling site | | | |
| | Concentration (ng m^{-3}) | | Contribute (%) | | Concentration (ng m^{-3}) | | Contribute (%) | |
	TSP	PM$_{10}$	TSP	PM$_{10}$	TSP	PM$_{10}$	TSP	PM$_{10}$
Al	2072±1260	2061±1080	1.64±1.28	2.6±1.69	3454±2272	1936±1561	2.044±1.168	2.149±1.660
As	4.5±4.2	4.8±5.0	0.004±0.004	0.007±0.011	5.7±4.4	7.1±7.3	0.005±0.005	0.009±0.010
Ba	141±166	29±30	0.082±0.105	0.035±0.047	270±204	246.6±207.6	0.215±0.275	0.260±0.235
Cd	3.0±3.0	3.8±4.9	0.002±0.002	0.005±0.008	5.2±8.0	3.5±4.4	0.003±0.003	0.004±0.005
Co	Nd	Nd	Nd	Nd	5.4±9.1	2.1±3.1	0.003±0.005	0.003±0.004
Cr	44.8±140.2	26.5±40.6	0.041±0.164	0.038±0.075	25.4±27.1	24.0±25.8	0.013±0.012	0.027±0.029
Cu	29.2±41.3	39.4±31.3	0.023±0.033	0.053±0.052	244.4±174.9	205.5±72.8	0.152±0.117	0.223±0.130
Fe	2039±1703	1165±826	1.116±0.479	1.219±0.717	2847±2072	993.3±631.2	1.411±0.714	1.027±0.723
Li	8.1±15.4	9.0±19.7	0.006±0.012	0.013±0.033	5.0±5.1	2.4±3.0	0.003±0.002	0.003±0.004
Mn	38.9±31.3	29.5±24.7	0.022±0.011	0.021±0.027	45.5±27.9	32.0±31.8	0.022±0.010	0.041±0.064
Mo	8.0±11.5	13.8±20.4	0.006±0.009	0.016±0.022	8.7±21.0	5.2±5.9	0.005±0.009	0.005±0.005
Ni	18.7±16.6	12.3±7.8	0.015±0.028	0.014±0.010	26.9±14.7	19.9±19.0	0.014±0.006	0.026±0.036
P	409±452	300±185	0.295±0.333	0.376±0.282	549.5±212.7	507.1±237.8	0.361±0.295	0.614±0.495
Pb	24.1±17.9	21.2±22.0	0.017±0.013	0.027±0.035	24.8±23.5	18.6±22.1	0.012±0.008	0.026±0.047
Se	0.69±0.31	0.35±0.25	0.0001±0.0002	0.0001±0.0002	0.36±0.26	0.22±0.17	0.000±0.000	0.000±0.000
Sr	112±170	46.9±63.5	0.075±0.134	0.062±0.093	31.2±22.4	28.7±31.7	0.016±0.009	0.028±0.042
Ti	263±206	170±113	0.155±0.069	0.188±0.095	362.9±206.7	183.4±194.4	0.195±0.060	0.180±0.227
V	16.1±17.4	12.1±12.3	0.010±0.009	0.013±0.012	25.2±12.0	17.4±15.5	0.015±0.006	0.023±0.031
Zn	12.5±11.3	19.1±24.3	0.009±0.009	0.023±0.026	15.8±20.9	14.6±23.4	0.008±0.008	0.014±0.026
Zr	191±257	183±254	0.119±0.161	0.199±0.275	146.5±193.1	83.5±93.5	0.079±0.104	0.083±0.073
Pt	708±705	687±633	0.414±0.413	0.737±0.652	188.2±135.6	Nd	0.088±0.212	Nd
Rh	22.2±34.4	22.4±34.4	0.013±0.022	0.020±0.035	Nd	Nd	Nd	Nd
Si	159.5±470	83.2±132.9	0.111±0.333	0.096±0.146	180.5±356.2	89.5±112.6	0.134±0.320	0.115±0.176
Sum	6349±5761	4958±3584	4.2±3.6	5.8±4.4	8490±6322	4431±3726	427.7±3.4	384.7±4.5

with TSP and PM$_{10}$ detected in other regions around the world are presented in Table 2.

Several studies have reported that the presence of Al, Fe, and Si is mainly the result of local and regional soil resuspension (Celo and Dabek-Zlotorzynska 2011; Hasheminassab et al. 2014). While some industrial sources could release elements such as Si, Fe, and Al, due to the lack of such industries in the studied region, these elements may be related to natural dust resuspension processes.

In the industrial suburban sampling site, sum of the concentrations of the analyzed elements ranged from 4043 to 13, 187 ng m^{-3} for TSP and 1793 to 7273 ng m^{-3} for PM$_{10}$. They accounted for about 3.2–7.1 % of TSP mass and 1.3–8.5 % of PM$_{10}$ mass. Based on the comparison of the two sampling sites, no appreciable difference in the mean concentration of most elements was observed between the two sampling sites ($p=0.27$). In the suburban sampling site, the most abundant detected metals were Al (2083.0–9664.0 ng m^{-3}), Fe (360.0–7221.5 ng m^{-3}), P (229.4–870.5 ng m^{-3}), Ti (137.3–

849.7 ng m^{-3}), Ba (5.3–581.2 ng m^{-3}), and Cu (100.0–610.9 ng m^{-3}) for TSP and Al (218.5–4179.6 ng m^{-3}), Fe (106.3–2005.1 ng m^{-3}), P (251.9–908.4 ng m^{-3}), Ba (10.6–584.9 ng m^{-3}), Cu (69.8–297.1 ng m^{-3}), and Ti (4.5–623.8 ng m^{-3}) for PM$_{10}$. Since Cu is from combustion sources, high levels of Cu in the PM samples could be caused by the combustion of coal and fossil fuels in the existing industries, especially coal burning in electricity generation plant near the sampling site. Percentage distribution of elemental constituents in PM in the two sampling sites is presented in Fig. 1.

IARC has classified Pb, Ni, As, and Cd as carcinogenic to humans (group 1) (WHO 2000). For ambient air, standard levels have been prescribed by the European Commission (EU) for Pb, Ni, As, and Cd as 500, 20, 6, and 5 ng m^{-3}, respectively (European Commission 2015).

As shown in Fig. 2, mean concentration of Ni, As, and Cd in the majority of urban samples did not exceed the EU's limits; but, in few cases, the average Ni, Cd, and As bound

Table 2 Elemental concentrations in TSP and PM₁₀ reported from other regions around the world

Area and place	Study period	PM	Al	As	Cd	Cu	Fe	Mn	MO	Ni	Pb	Zn	V	References
Izmir, Turkey	June 2004–May 2005	PM₁₀ (urban)	1311	–	1.5	44.6	921.2	29.2	–	15.8	140.6	288.6	14.4	(Yatkin and Bayram 2008)
Izmir, Turkey	June 2004–May 2006	PM₁₀ (suburban)	531	–	0.6	15.5	268.8	9.7	–	7.8	32.9	113.3	10.5	(Yatkin and Bayram 2008)
Kawasaki, Japan	1974–1996	TSP	–	–	–	100	1246	70.2	–	–	146.1	190	14.9	(Var et al. 2000)
Tokyo, Japan	1974–1996	TSP	–	–	–	30.2	676.9	40.1	–	–	124.7	298.7	8.9	(Var et al. 2000)
Kyoto, Japan	1974–1996	TSP	–	–	–	23	407.5	21	–	–	70.8	196.3	5.9	(Var et al. 2000)
Bern, Switzerland	1998–1999	PM₁₀	152	0.8	0.26	74	2048	25	4.46	3	49	–	1.4	(Hueglin et al. 2005)
Bern, Switzerland	1998–1999	TSP	130	0.42	0.08	68	1997	20	4.11	1.9	22	–	1	(Hueglin et al. 2005)
Zurich, Switzerland	1998–1999	PM₁₀	81	0.44	0.23	17	474	7.3	1.28	1.8	20	–	1	(Hueglin et al. 2005)
Zurich, Switzerland	1998–1999	TSP	37	0.1	0.03	12	414	5.1	0.93	0.11	5.9	–	0.3	(Hueglin et al. 2005)
Basel, Switzerland	1998–1999	PM₁₀	98	0.6	0.42	8.5	295	7.9	0.75	2.2	21	–	2.4	(Hueglin et al. 2005)
Basel, Switzerland	1998–1999	TSP	51	0.11	0.04	3.4	221	5.3	0.42	0.46	4.4	–	0.3	(Hueglin et al. 2005)
Daihai, China	2005–2006	TSP	–	10.3	–	8.5	1824	72	–	16.5	44.3	12.4	6.7	(Han et al. 2009)

to TSP exceeded the EU standards. Among the samples collected from the suburban site, the higher number of samples

(TSP and PM₁₀) than those of the urban site exceeded the EU's limits, which can be due to the existence of major
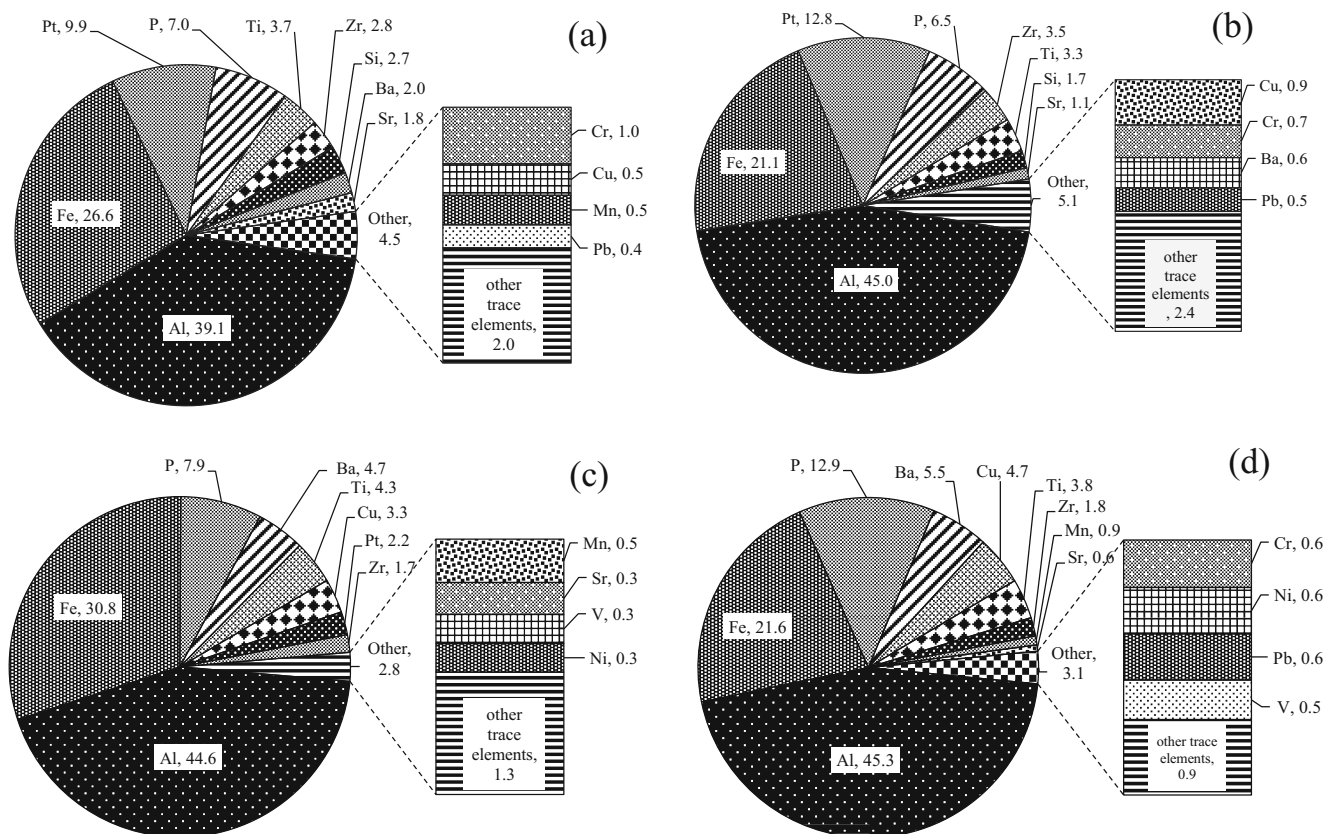

Fig. 1 Percentage distribution of elemental constituents in **a** TSP and **b** PM₁₀ in the urban sampling site and **c** TSP and **d** PM₁₀ in the suburban sampling site
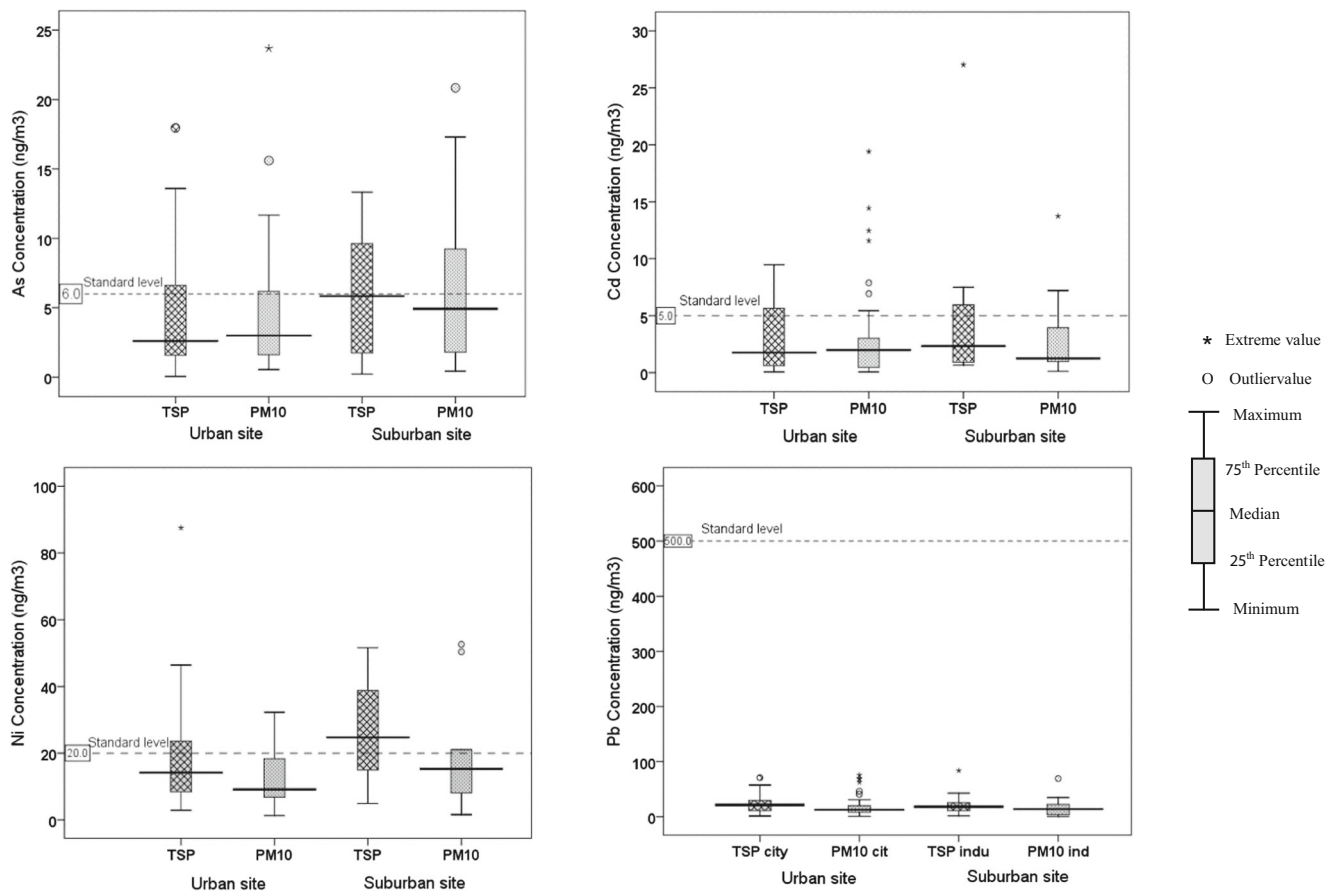
Fig. 2 Boxplots of the variation of selected trace element concentrations (ng m^{-3}) in TSP and PM$_{10}$ in the sampling sites; the *horizontal dash line* in the plots indicates the standard level of elements ($n=48$ for the urban sampling site and $n=30$ for the suburban sampling site)

anthropogenic sources in the suburban region contributing to the atmospheric loading of these elements including fossil fuel combustion, oil combustion, metal processing industry, and waste incineration by various industries. On the other hand, the dramatic changes in daily concentrations of elements could be affected by the variation of emission rates, wind speed and dynamics, precipitation episodes, etc.

During the studied period, in none of the analyzed samples, the average of Pb bound to PM exceeded the EU's standards, as the approved consumption of lead-free fuel by vehicles and various industries in both urban and suburban sites.

Chemical mass closure

Contribution of the analyzed chemical constituents to the mass concentrations of TSP and PM$_{10}$ for each sampling site is presented in Fig. 3. As can be observed, total of the analyzed constituents (ionic and elemental species along with PAH) in TSP and PM$_{10}$ accounted for about 20–25 % of TSP and 25–30 % of PM$_{10}$, leaving about 70–75 % unexplained. Based on the our previous published results, water-soluble ions are the major measured contributors (20 % for TSP and 25 % for PM$_{10}$) in the PM of each sampling site (Gholampour et al.
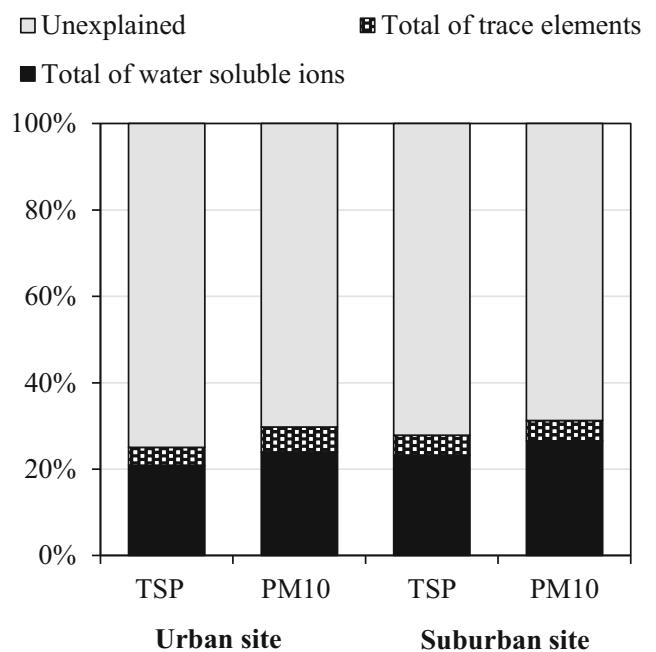

Fig. 3 Proportion of chemical constituents to the total mass in TSP and PM$_{10}$

2014b). Also, trace elements contribute to about 4–4.5 % of TSP and 4.5–5 % of PM$_{10}$.

Composition of the unexplained mass could not be determined based on the present study; but, it contained chemical species including elemental carbon, organic matters, hydrogen and oxygen associated with minerals and organic matter, water uptake by the filter substrates, and finally, mineral components such as carbonates (Viana et al. 2013).

Elemental constituents of the region's soil crust

For calculating the enrichment factor of elements in PM and also characterizing the elemental constituents of soil crust in the studied region, the amount of 35 elements in the soil was determined by ICP. Mean contents of the elements in the soil crust (based on ppm) and reference values (element/Al) together with the concentrations of elements in the soil, reported by Taylor (1964), are summarized in Table 3 (Taylor 1964). As can be observed, the most abundant detected elements in the region's soil crust were Al (60,088–60,694 ppm), Fe (19, 886–20,474 ppm), Ti (894–3481 ppm), Si (365–4246 ppm), P (472–1094 ppm), and Mn (450–1064 ppm). The measured concentrations of elements in this study were in agreement with the observed values by other previous study (Taghipour et al. 2013).

Sources identification

Enrichment factor

In order to evaluate the potential strength of pollution-emitting sources as the first step (Wang et al. 2006), assess the effect of anthropogenic activities on particulate metal, and also measure the extent of non-crustal contributions to the elemental concentration levels in the fine and coarse particle fractions, enrichment factor (EF) was calculated as follows (Yin et al. 2012):

$$\mathrm{EF} = \frac{\left({C_X}/{C_{Al}}\right)_{\text{particulate matter}}}{\left({C_X}/{C_{Al}}\right)_{\text{crust}}}$$

where C_X is the concentration of element X and C_{Al} is the concentration of Al as reference element. The subscripts of particulate matter and crust refer to PM samples and crustal materials, respectively. Al, Fe, or Si are usually used as the reference element; but, there is no generally accepted rule for its choice (Hassanvand et al. 2015). With respect to Table 2, since among the determined elements, Al had the highest concentration in the region's soil crust, the enrichment factors were calculated using Al as the reference element.

EF values of less than 1 indicated that the local crust was the main source of elements, EF between 1 and 5 meant that these elements were emitted from other sources beside crustal

soil, while EF of over 5 suggested that anthropogenic emission was predominant. Finally, if EF≥10, a significant fraction of the elements was contributed from non-crust sources (Yin et al. 2012).

The estimated enrichment factors for each element in the urban and suburban sampling sites are given in Figs. 4 and 5, respectively. It can be observed that EF for Si, Ti, Mn, Co, and Fe in the urban sampling site and Si, La, Mn, Be, Fe, and Ti in the suburban site (in both TSP and PM$_{10}$) was between 1 and 5; so, it could be concluded that the major fraction of these elements was originated from the region's crustal soil and resuspension of crustal materials. Wang el at. demonstrated that Si, Fe, Al, and Ti were related to construction and demolition activities and road dust (Wang et al. 2006). It was reported that some industrial sources could release elements of Si, Fe, and Al; but, due to the absence of such industries in the studied region, emission of these elements may be related to natural dust resuspension processes.

Increase of EF to more than 10 for other elements, especially Pt, Rh, Te, Cd, Cu, and Pb, could indicate that sources other than crustal soil had a major role in the emission of these elements. Higher EF for the mentioned elements represented that anthropogenic activities such as the combustion of fossil fuels in the existing residential areas and industries and also in the roads surrounding the sampling sites could contribute to a substantial fraction of these elements in the aerosols (Chen et al. 2009; Lin et al. 2008).

Platinum group elements (PGE), consisting of Pt, Rh, and Pd, are used in the automobile catalyst as active compounds to facilitate the oxidation of hydrocarbons and other incompletely oxidized components (Zereini and Wiseman 2010). PGEs are emitted together with alumina particles from the wash coat as a result of various chemical, physical, and thermal stresses such as mechanical abrasion and high temperatures (Palacios et al. 2000). It was shown that concentrations and EF of PGEs in this study were higher than other studies in developed countries, which can be due to the large number of old vehicles in the studied area and use of obsolete catalyst vehicles. Numerous studies have reported that traffic is responsible for the high levels of Ba, Cu, Cr, Mo, Pb, Sb, and Zn (Manno et al. 2006).

Observations of higher enhanced EF values for some elements in the urban sampling site than suburban site indicated that the contribution of anthropogenic activities in the enhancement of these elements in the PM of urban atmosphere was prominent. On the other hand, it was observed that, in both sampling sites, EF values for some elements during the cold season were higher than those in the warm season, which could indicate that the contribution of the region's crustal soil in the enhancement of these elements in PM increased by environmental temperature.

**Table 3** Mean concentration of trace elements (ppm) in the crustal soil of the studied region (*n*=25)

Element	Symbol	Concentration (ppm) Taylor study	Reference value (element/Al)	Concentration (ppm) Present study	Reference value (element/Al)
Aluminum	Al	82,300	1	60384.70	1
Arsenic	As	1.8	0.0000219	8.42	0.000139463
Barium	Ba	425	0.005164034	138.66	0.002296206
Beryllium	Be	2.8	3.40219E-05	1.47	2.44149E-05
Calcium	Ca	41,500	0.504252734	631.11	0.010451512
Cadmium	Cd	0.2	2.43013E-06	0.2	2.43013E-06
Cobalt	Co	25	0.000303767	12.02	0.000199104
Chromium	Cr	100	0.001215067	40.40	0.000668973
Copper	Cu	55	0.000668287	30.66	0.000507674
Iron	Fe	56,300	0.684082625	20162.25	0.333896666
Potassium	K	20,900	0.253948967	278.82	0.004617395
Lanthanum	La	30	0.00036452	4.80	7.9443E-05
Lithium	Li	20	0.000243013	11.67	0.000193261
Magnesium	Mg	23,300	0.283110571	285.11	0.00472156
Manganese	Mn	950	0.011543135	644.10	0.010666657
Molybdenum	Mo	1.5	1.8226E-05	0.45	7.52319E-06
Nickel	Ni	75	0.0009113	59.60	0.000986981
Phosphorus	P	1050	0.012758202	694.41	0.011499767
Lead	Pb	12.5	0.000151883	50.89	0.000842716
Antimony	Sb	0.2	2.43013E-06	0.15	2.50773E-06
Selenium	Se	0.05	6.07533E-07	0.05	8.28024E-07
Tin	Sn	2	2.43013E-05	2	3.3121E-05
Strontium	Sr	375	0.004556501	120.23	0.001991115
Tellurium	Te	0.005	6.07533E-08	Nd	Nd
Titanium	Ti	5700	0.069258809	2593.26	0.0429456
Thallium	Tl	0.45	5.4678E-06	1.34	2.21911E-05
Vanadium	V	135	0.00164034	45.51	0.00075362
Yttrium	Y	33	0.000400972	4.64	7.68643E-05
Zinc	Zn	70	0.000850547	4.84	8.02001E-05
Zirconium	Zr	165	0.00200486	51.79	0.000857691
Platinum	Pt	0.003	3.6452E-08	0.003	4.96815E-08
Rhodium	Rh	0.0002	2.43013E-09	1.08	1.78688E-05
Vanadium	V	135	0.00164034	55.15	0.000913311
Silicon [A]	Si	281,500	3.420413123	1615.79	0.02675823
Mercury	Hg	0.08	9.72053E-07	.316	5. 23568E-06

Principal components analysis

Principal component analysis (PCA) with varimax rotation (eigenvalues >3) was applied to the TSP and PM$_{10}$ data from the urban sampling site to obtain the groups containing species with a similar behavior and to identify their possible sources. Some elements were excluded from the PCA analysis because its extraction was less than 0.5. Table 4 displays the factor loadings with varimax rotation, extraction values of each elements, and the eigenvalues.

Three principal factors were obtained, which accounted for 63.02 and 67.62 % of the total variance for TSP and PM$_{10}$, respectively. For both TSP and PM$_{10}$, the first factor was characterized by Cd, Co, Mn, Mo, Sn, and Pb, reflecting the effect of traffic resuspension. Since Mn is generally thought to be a crustal component (Han et al. 2009), this source was interpreted as the resuspension of polluted soil from the road located about 500 m away from the sampling location. As seen in Table 3, factor 1 accounted for 28.72 % of TSP and 34.22 % of PM$_{10}$.

Fig. 4 Enrichment factors for elements in TSP and PM_{10} in the urban sampling site; *error bars* show standard deviations
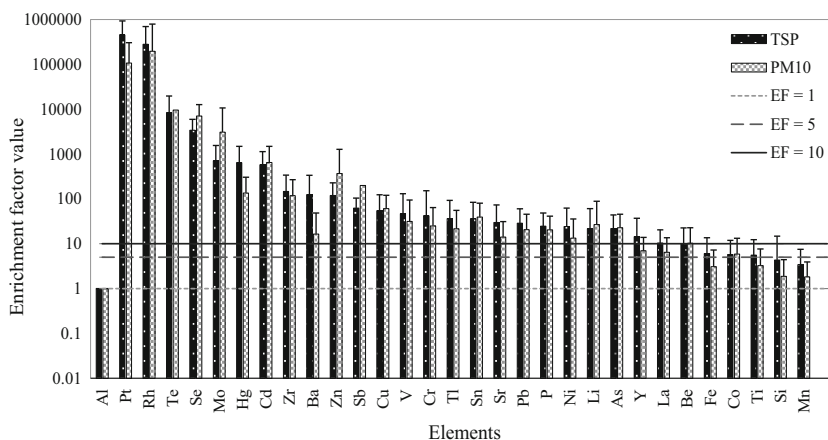
The second factor had high loadings of Al, As, Fe, and Ti accounting for 25.27 % of the total variance of TSP and 21.40 % of the total variance of PM_{10}. These elements are typically associated with soil particulates and crustal materials in windblown dust and resuspended dust from the urban and sampling sites around lands.

Finally, the third factor for TSP was loaded mainly by Ba, Pt, Rh, and V. As mentioned earlier, platinum group elements, consisting of Pt, Rh, and Pd, were used in the automobile catalyst. So, this factor represented the anthropogenic types of the pollution sources in the region, most likely PGE (Pt and Rh), waste and oil burning (V), and waste combustion (Ba) (Gao et al. 2002). These sources could contribute significantly to the loadings of the elements in the present studied region and account for 9.02 % of the total variance of TSP.

The third factor for PM_{10} was loaded mainly by Cu, Mn, Zr, Pt, Rh, and V and accounted for 12.01 % of the total variance of PM_{10}. It is clear that Cu was mainly derived from coal combustion and was highly correlated with traffic-related brake lining; on the other hand, Mn is a generally crustal

component. Therefore, since there were no industries in the studied region which used coal as fuel and with respect to the presence of other elements of factor 3, it can be concluded that vehicle exhaust and vehicle brake wear were the sources of factor 3.

Conclusion

In this study, the trace elements in TSP and PM_{10} were monitored in Tabriz urban and suburban regions and a portion of the anthropogenic emission sources of some elements in the PMs was determined.

The results showed that, in the urban sampling site, Al, Fe, Pt, P, and Ti were mainly concentrated in coarse particles and their EF values, other than Pt, in both TSP and PM_{10} particles were less than 10, suggesting that the coarse PMs in Tabriz were primarily derived from natural sources, especially crustal soil. This issue can be due to high construction activities in Tabriz and abundance of barren area around the urban region.

Fig. 5 Enrichment factors for elements in TSP and PM_{10} in the suburban sampling site; *error bars* show standard deviations
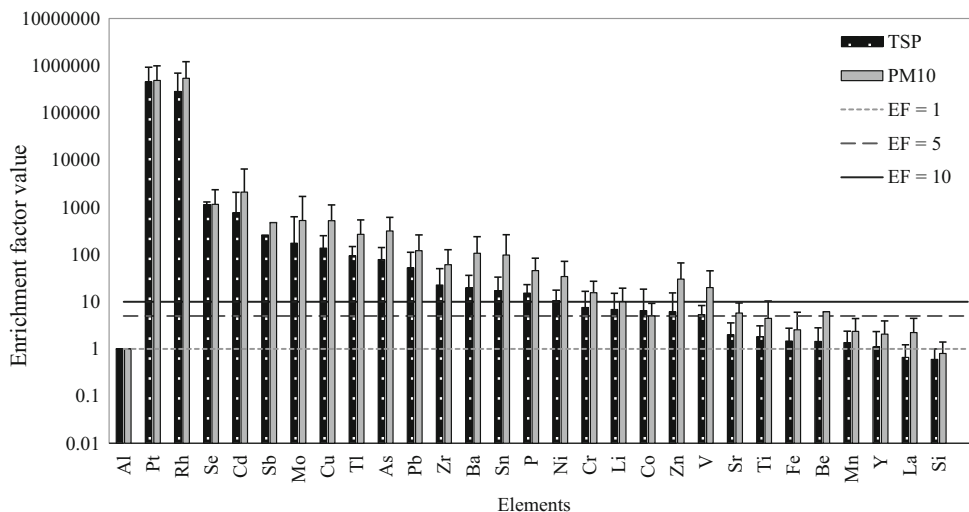
Table 4 Varimax-rotated PCA loadings for the elements of TSP and PM_{10} in the urban site

	TSP				PM_{10}			
	F1	F2	F3	Extraction	F1	F2	F3	Extraction
Al	0.223	*0.780*	−0.357	0.786	−0.057	*0.93*	0.152	0.891
As	−0.166	*0.739*	0.012	0.574	−0.416	*0.582*	−0.388	0.662
Ba	−0.255	−0.100	*0.664*	0.516				
Cd	*0.854*	−0.159	−0.258	0.821	*0.95*	0.023	0.029	0.904
Co	*0.662*	0.191	−0.091	0.583	*0.636*	0.161	−0.372	0.568
Cr					*0.908*	−0.075	0.126	0.845
Cu					0.245	0.044	*0.863*	0.806
Fe	0.487	*0.586*	0.519	0.851	0.154	*0.622*	0.481	0.618
La	*0.905*	−0.027	0.103	0.830	*0.89*	0.101	0.278	0.880
Li					*0.711*	−0.066	0.209	0.554
Mn	*0.643*	0.406	0.470	0.800	0.344	0.503	*0.619*	0.755
Mo	*0.856*	−0.325	−0.236	0.893	0.105	−0.918	0.04	0.855
Pb	*0.872*	−0.300	0.005	0.851	*0.942*	0.019	0.221	0.937
Sn	*0.710*	−0.176	0.181	0.567	*0.942*	0.097	0.109	0.909
Sr	*0.888*	−0.305	−0.265	0.952	*0.909*	0.039	0.309	0.924
Ti	0.465	*0.581*	0.515	0.819	−0.067	*0.677*	0.392	0.617
Y					*0.675*	0.291	*0.525*	0.816
Zn	*0.769*	−0.187	−0.270	0.699	−0.037	−0.934	0.005	0.873
Zr					0.43	0.443	*0.531*	0.663
Pt	−0.048	−0.702	*0.634*	0.897	−0.06	−0.925	*0.617*	0.873
Rh	−0.419	−0.579	*0.626*	0.902	−0.362	−0.84	*0.544*	0.858
V	−0.175	−0.191	*0.744*	0.620				
Eigenvalue	8.13	4.53	3.3		9.56	5.99	3.56	
% of variance	28.72	25.27	9.02		34.22	21.40	12.01	
Cumulative %	28.72	53.99	63.02		34.22	55.62	67.62	

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Eigenvalues >3. Rotation converged at seven iterations. PCA loadings >0.5 are shown in italics. Factor loadings >0.71 are typically regarded as excellent, and the values below 0.32 are very poor (Han et al. 2009)

In contrast, Pt, Rh, Te, Se, Zn, Ba, Cd, V, Pb, Cu, and many other elements that were associated with particles had high EF values, especially in the urban sampling site, which implied their anthropogenically dominant sources of origin.

Based on the results of the enrichment factor analysis, some dominant emission sources of the elements were identified using factor analysis. As a result of PCA analysis, three factors were revealed, which explained about 63.02 and 67.62 % of the elemental compositions of TSP and PM_{10} in the urban sampling site, respectively.

The results revealed that oil and fuel combustions by the vehicles and resuspension of particulate from the polluted soil around roads were the predominant source of these elements. On the other hand, platinum-group elements from vehicle exhaust along with vehicle brake wear and also waste combustion were other predominant sources of PM in the urban region. So, road traffic was found to be a significant source of a variety of trace elements.

The results of source apportionment indicated that crustal soil contributed to aerosol particle mass in the studied area with the greatest fraction. Finally, based on the results, it was concluded that the resuspension of large particles (road dust) from the major traffic road and construction dust from the nearby construction sites together with crustal soils were the main sources of PM in the urban region of Tabriz. The estimated concentrations of the highly enriched elements present in the aerosols were in agreement with the observed values. Results of this study elucidated the need for developing pollution control strategy, especially vehicle exhaust control, and creating green spaces around the city.

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