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RESEARCH ARTICLE

Concentration and potential source identification of trace elements in wet atmospheric precipitation of Shiraz, Iran

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Abstract

The aim of this study was to investigate the concentration of trace elements in wet atmospheric precipitation samples collected at six stations in Shiraz, southwest of Iran and identify their possible sources. In this study, 36 rainwater samples were collected from five urban stations and one suburban station during the rainy season spanning 2016 to 2017. Samples were analyzed for 19 trace elements using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Principal component analysis (PCA) with varimax-normalized rotation was used to identify potential sources of the elements measured in the wet atmospheric precipitation. Crustal enrichment factors (EFs) were also calculated, using Al as the reference element, to determine possible effects of human activities on element levels. Results showed that Al, with a mean concentration of 429.6 μg/l, had the highest measured concentration. The average concentrations of Fe, Zn, Mn, Ba, Cu, Pb and Ni were 305.7, 62.8, 23.9, 21.1, 14.4, 10.3 and 4.1 μg/l, respectively. The pH of the analyzed samples ranged from 4.5 to 6.9, with an average of 3.5. EF analyses showed that samples were not enriched with Fe, Ba, Li, Co, Cr or Mn but were fairly to extremely enriched with Zn, Cu, Pb and Ni. PCA resulted in four factors with eigenvalues greater than unity, which explained 78.8% of total variance.

Keywords Air pollution · Enrichment factor · Heavy metals · Rainwater · Trace elements · Wet precipitation

Introduction

Air pollution refers to specific concentrations of materials released from natural and human sources entering into the atmosphere such that their accumulation threatens human health and the integrity of the environment [1]. Industrial processes, combustion of fossil fuels, mining, waste incinerators, motor vehicles and other human activities release a large amount of pollutants to the atmosphere [2, 3]. Toxic elements such as Cr, Cu, Pb and Ni are released in the atmosphere as a result of agricultural and industrial activities, especially those with high combustion temperatures, such as non-ferrous metal melting industries [4]. Some trace elements, such as As, Zn, Cd, Cu, Sn and Pb, have primarily human origins, while some others, such as Fe, Mn and Al, originate from erosion of the earth's crust [5, 6]. Trace elements are of major concern because of their toxicity and carcinogenicity in the environment [7, 8]. Wet deposition is the most important natural pathway in removing these pollutants from the atmosphere. The concentration of trace elements in atmospheric precipitation depends on different factors, including proximity to emission sources, amount of precipitation and direction of air-mass movement [9]. Trace elements are readily dissolved in rainwater, particularly under low-pH conditions, causing rainwater contamination [10]. The chemical composition of atmospheric precipitation indicates the type and amount of contaminants released in an area [11]. Acid rain occurs due to the release of SO_2 and NO_X in the atmosphere, which are transformed to sulfuric acid (H_2SO_4) and nitric acid (HNO_3) when they interact with rainwater. On the other hand, the $CaCO_3$ present in local dust or ammonium released from both human activities as well as natural sources can neutralize the acidity of rain [12]. Thus depending upon the nature of air pollutants, rainwater may be

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acidic or basic. In areas where the biochemical cycle is disturbed by human activities, atmospheric precipitation becomes a significant source of toxic substances in the ecosystem [13]. Accordingly, monitoring of atmospheric pollutants through the measurement of pollutants in wet deposition has increased during recent decades and various studies have been conducted on the chemical properties of wet precipitation, with an emphasis on trace elements [14–16].

Due to the presence of industrial complexes such as cement factories as well as high traffic density in Shiraz, Iran, a large amount of pollutants that can contain trace elements are released and enter into the atmosphere. Middle East dust storms are another source of pollution in Shiraz. Given the low average precipitation level there, these trace elements accumulate in the atmosphere during dry seasons and are then removed from the atmosphere during rainy seasons by dissolving into rainwater and other atmospheric precipitation, thereby entering into ecosystems and the food chain. So, analyzing the wet precipitation is of great importance for illustrating the atmospheric pollution status in this urban area and can be used to determine the relative contribution of different sources of pollutants. Considering these facts and limited knowledge on rainwater quality due to lack of any quantitative study of wet deposition of air pollutants in Shiraz, this study aimed to identify the concentration of trace elements during wet seasons and the contribution of probable human activities on their concentrations for further research studies in the future.

Materials and methods

The study area

Shiraz, the capital of Fars province and one of the most crowded area in Iran, is located in a fairly restricted basin on the foothills of the Zagros Mountains (29° 37′ N and 52° 32′ E). The city has an area of 240 km^2 with 1.8 million habitants, which is the 5th most populous city in Iran [17]. The urban area is surrounded on the north, northwest, west, and southeast by high to medium height mountains and has an industrial town in the south and a cement factory in the west. Air circulation is therefore limited and pollutant accumulation makes the pollution situation worse. Annual average air temperature in the city is between 7.8 and 30.5 °C with the mean temperature of 19.1 °C. The annual average rainfall varies from 0.5 to 174.6 mm. The direction of the prevailing winds is from the northwest and the average wind speed is up to 12 m/s with a 250-degree direction [18].

Sampling location and sample collection

All samples were taken in a period of 5 months from December 2016 to April 2017. Samples were collected in five urban stations located in different geographical areas, namely the north, south, east, west and city center of Shiraz and the control sample was collected in a suburban station located in the town of Sepidan, outside the city of Shiraz in the uppermost direction of dominant winds. Characteristics of the sampling points are presented in Table 1. Sampling points in each area were selected based on parameters such as safety, minimization of sample contamination, ease of access and representativeness. Sampling location is shown in Fig. 1.

Given the occurrence of six precipitation events during the precipitation season spanning 2016 to 2017 and the six locations selected for sampling, a total of 36 rainwater samples were taken for analysis. Sampling equipment consisted of 250 ml polyethylene collecting flasks equipped with a high density polyethylene funnel [19]. The samplers were mounted approximately 9–12 m above ground level on the roofs of selected buildings. Sampling was carried out immediately after the start of precipitation and collected samples were sealed and transferred to the laboratory in a cool box [20].

Chemical analysis

The pH of collected samples was measured immediately prior to processing for further analyses by a MP-103 portable pH meter with the precision of 0.01. At the laboratory the volume of samples were determined. Samples were then filtered through membrane filters with 0.45-μm pore diameter. Immediately following filtration, diluted HNO_3 (Merck) was used to acidify the filtrates to a pH less than 2; they were kept in a refrigerator at 4 °C until chemical analysis. Samples were analyzed for 19trace elements using inductively coupled plasma-atomic emission spectrometry (ICP-AES) according to USEPA method 200.7 revision 4.4 [21]. The concentrations of nine elements, namely As, B, Be, Cd, Co Hg, Sb, Sn and V, were lower than their limit of detection (LOD). Therefore, only the concentrations of Al, Ba, Cr, Cu, Fe, Li, Mn, Ni, Pb and Zn are reported in this study.

Quality control

To avoid contamination of samples, all components of the sampler were acid cleaned by soaking overnight in a dilute HNO_3 solution bath and rinsed with distilled water. Quality control was conducted by preparing and analyzing blank (deionized water) samples. Analysis of blank samples passed through the sampler showed values for each target element that were significantly lower than those of rainwater samples. The LOD in μg/l was 0.7 for Al and Fe, 0.6 for As, 0.3 for B and Ba, 0.8 for Be, 0.08 for Cd, 0.4 for Co, 0.1 for Cu and below 0.1 for the remaining detectable elements. To determine the precision of the analysis, all of the samples and standard solutions were analyzed twice and the C.V of the repeated measurements for each heavy element was less than 5%.

Table 1 Characteristics of samplings points in the study area

Area number	Geographical locations	Specifications
1	City Center	High traffic density, the center for economic activities
2	North	Residential area
3	South	Residential area, Shiraz industrial town
4	East	Shiraz petrochemical industry
5	West	Ring road, residential area, Shiraz cement factory
6	Control area	Town of Sepidan (low pollution level)

Statistical analysis

Statistical analyses were performed using SPSS 21.0 package software (SPSS Inc. Chicago, IL). The Kolmogorov-Smirnov test was applied to check the normality of data. The spearman correlation analysis was used to investigate the degree of linear dependence between the different measured elements. Significance levels of 0.05 or less were referred to as significant. In order to identify the potential sources of the measured trace elements, principal component analysis (PCA) with varimax normalized rotation was used and components with eigenvalue >1 were selected [22, 23].

Enrichment factor

To assess trace elements contamination of wet deposition and recognize the intensity of anthropogenic sources relative to crustal sources of measured elements, the crustal enrichment factor (EFs) was used according to following equation:

$$\mathrm{EFs}=\frac{\left(\frac{Cx}{C\mathrm{Al}}\right)precipitatipn}{\left(\frac{Cx}{C\mathrm{Al}}\right)crust} \quad (1)$$

Where (C_x) Precipitation Sample is the concentration of the element in the wet precipitation sample, (C_x) Crust is the concentration of the same element in the earth's crust and (C_{Al}) is the concentration of Al, as the reference element, in the same sample and the crust [20, 24] .To estimate the impact of human sources on the contamination level, this factor was calculated for those elements that were present at concentrations above their crustal levels [25]. The factor indicates the degree of enrichment of a given element in comparison with the relative frequency of that element in the crust materials [26].

Fig. 1 Location of the study area to show the sampling sites

Results and discussion

Precipitation pH variation

The pH levels of collected samples were in the range of 4.5 to 7 with an average of 5.3 which is lower than the pH of natural rainwater (5.6). The frequency distribution of pH in atmospheric precipitation samples collected during the study is shown in Fig. 2. As shown in this figure, 43% of the samples had a pH less than 5.6. In general, the pH of the rainwater is 5.6 due to the equilibrium with the atmospheric CO_2 [27]. The acidity of rainwater is mainly caused by H_2SO_4 and HNO_3 while HCl, HF, and organic acids play a negligible role in comparison with these two acids [28]. SO_2 gas can easily be dissolved in rainwater droplets and affect the water's pH value [29]. The mean pH value of the samples collected in this study was in the acidic range. Low pH may reflect the significant effect of human activities in the studied area. In the study area, there is a large cement industry that uses oil and coal combustion, which, along with the high density of motor vehicles, can cause SO_2 and NO_x emissions, resulting in acidic wet precipitation. Another possible source of acidic gas can be the agricultural activities around Shiraz and its adjacent cities. These factors could be the reason for the reduced pH of wet precipitation in this area. The results of this study are consistent with the results obtained by Kamani, who reports that the majority of wet atmospheric samples collected in Tehran have pH values lower than the pH of normal rainwater [20]. In a study conducted in southern Brazil, the pH of the collected wet precipitation samples was mostly lower than 5.6 [30]. The low pH values are especially important from this point of view in that it has been reported that high acidity can increase the concentration of various trace elements in precipitation [31].

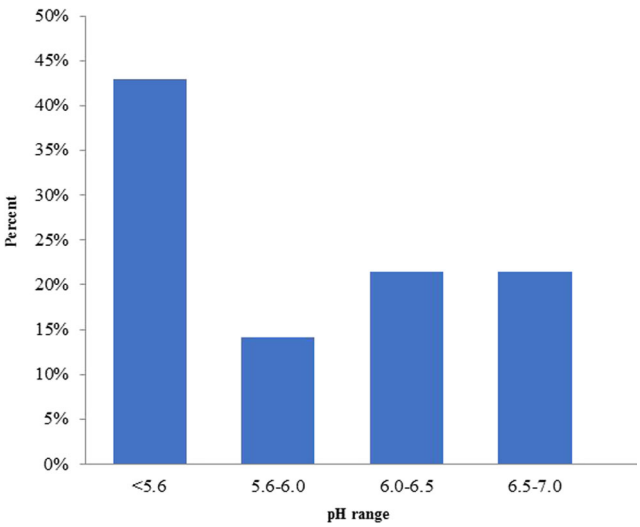

Fig. 2 The frequency distribution of pH in atmospheric precipitation in Shiraz

Trace element concentration in rainwater samples

According to the results of this study, the order of concentrations of elements in the rainwater samples from the studied area during the sampling period was, from highest to lowest, Al, Fe, Zn, Mn, Cu, Ba, Pb and Ni. Volume-weighted mean concentrations (VWMC) of trace elements in this study compared to other studies are presented in Table 2. As shown in Fig. 3 there was no significant difference in concentrations of measured elements in different sampling location in Shiraz (Kruskal-Wallis H test $p < 0.05$), however, a significant difference was observed between Shiraz and Sepidan town (Mann-Witney U test $p > 0.05$). Due to the diversity of human trace element sources, precipitation patterns and natural sources of these elements in different regions, values may be heterogeneous in terms of time and place [32]. Figure 4, shows the contribution of each measured element in the total collected samples. The concentration of trace elements in the wet precipitation of Shiraz could be affected by many sources in the study area. Shiraz Industrial Complex, a potential source of trace elements emissions, is located in the southern part of Shiraz. The industries in this complex include electronics, chemical, cellulosic, metal and food industries. The resulting pollutants that enter the environment primarily include CO_2, CO, SO_2, NO_x, trace elements and suspended particles. The metal industry releases high amounts of these elements into the environment due to the use of metals such as Ni, Cr, Cu, Ag and Au in the electroplating process [33]. Another possible source of air pollution in the study is the Shiraz Cement Factory, which is located in the western part of the city. Pollutants released from this industry include dust generated by grinding, gasses produced during the combustion of petroleum and coal, trace elements in calcareous materials, organic waste in the raw materials and some toxic elements and organic pollutants released during the burning of oil and organic waste in the raw materials [34]. The high traffic density in the centre of the city and the ring road, which extends all around the city, are other major sources of elements such as Cd, Pb and Cr, as reported in some studies [35, 36]. Based on the results of a similar study conducted in 2011 in Shiraz by Moore et al., it can be concluded that the concentrations of Zn and Cu have increased by 3.5 and 2.3 times (respectively) from 2011 until today. This increase can be attributed to an increase in motor vehicle use and industrial activities during these years [37, 38]. In contrast, the concentration of Pb in this study is slightly lower than those reported by Moore et al. This can be attributed to the improvement in the quality of gasoline and a ban the use of leaded gasoline in vehicles. The concentration of Pb in this study was significantly lower than in Tehran, the capital of Iran [20]. However, the concentration of Pb in this study was higher than those reported by Guo et al. in Hague, Tibet [32]. As reported in some previous studies, in addition to vehicles, some other activities and pollutant

Table 2 The average concentrations of trace elements in the atmospheric precipitations of Shiraz in comparison with previous studies

Metal	This study			China 2011	Shiraz 2011	Florida 2010	Jordan 2013	Tibet, Lhasa 2014
Zone	Minimum	Maximum	Mean					
Zn	4.00	220.00	62.82	65.2	18.25	2.19	30.5	14.21
Pb	4.00	22.00	10.35	9.6	13.97	306	40.8	1.59
Cu	7.70	19.6	13.4	3.8	4.16	4.61	31.2	1.71
Ni	2.00	6.00	4.125	1.0	–	0.374	–	0.58
Fe	38.4	786.7	305.75	15.3	–	26	90.4	221.4
Mn	2.3	62.10	23.90	6.2	–	1.13	21.85	7.7
Al	27.90	1115.20	429.61	37.4	–	53.4	115.2	130.5
Cr	1.00	4.00	1.57	0.04	–	0.09	–	0.43
Ba	4.00	25.00	12.21	6.1	–	1000	–	–
Li	00	2.00	0.4720	–	–	59.3	–	–

emitters such as waste incinerators, power plants and construction activities are involved in the release of Pb [24, 39]. Among the anthropogenic trace elements, Zn had the highest concentration in the wet precipitation samples, which is similar to other studies conducted around the world [16, 40]. In this study, Zn shows a higher value than that found in Florida [41], Jordan [42] and Tibet [32]. The concentrations of Cu, Ni, Fe, Mn, Al and Cr were higher in this study than those reported in studies conducted in Chenghu (China) [27], Florida [41], southern region of Jordan [42] and Tibet [32] whilst the concentrations of Ba and Li were lower than those reported in the study conducted in Florida [41]. According to the literature, there is a probability of a natural origin for Mn as well as Fe and Al [22, 43]. High levels of these elements can be attributed to Middle Eastern dust storms, which have increased dramatically in recent years and are caused by dried wetlands in Iraq and the western neighbours of Iran. The sources of Ni include combustion of fossil fuels and the oils used in cars [44]. In the same vein, due to the ever-increasing number of cars, which results in increased consumption of fossil fuels and an increase in other car-related factors, there is the probability of an increase in the emission of this pollutant.

Enrichment factor

Based on the hypothesis that the Earth's crust is the only source of Al, if the enrichment factor (EF) calculated for an element is close to 1, it shows that it is primarily produced from a crustal source. Elements with EF values between 1 and 10 are not considered enriched because of the differences

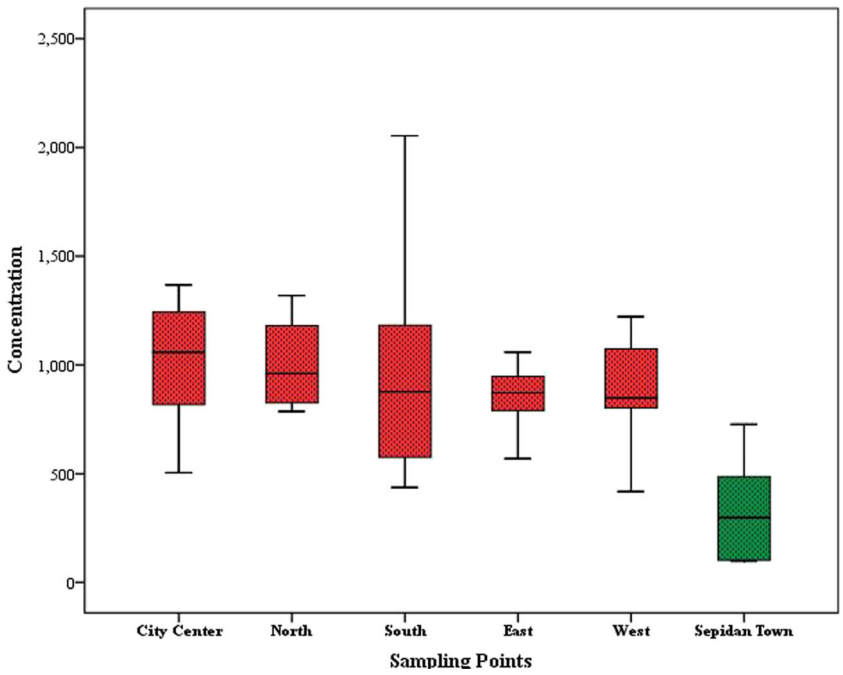

Fig. 3 Box plot of concentration of total trace elements (μg/l) at different sampling locations

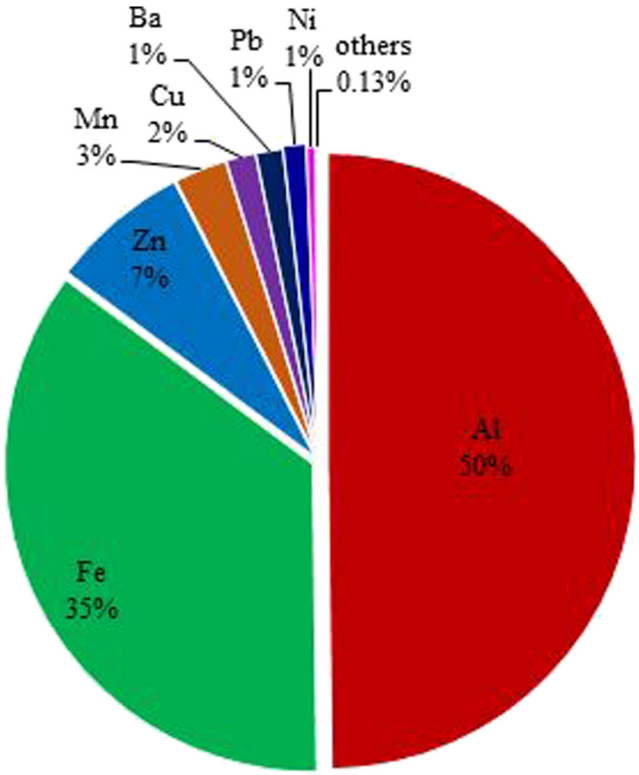

Fig. 4 The contribution of each element in the atmospheric precipitation of Shiraz

between the chemical composition of local soil and reference crustal composition. Elements with EFs between 10 and 100 are considered as moderately enriched, showing a higher-than-expected concentration of the particle elements in the rain in the crustal composition. Finally, EF values that are larger than 100 show high enrichment, indicating a high level of human pollution [45].

Figure 5, shows the calculated EFs values for elements found in rainwater samples of Shiraz. The EF values for Al, Fe, Ba, Li, Co, Cr and Mn were lower than 10, indicating that these elements were not enriched in the atmosphere and had a natural origin. The EF value for Ni fell in the 10–100 range, indicating that it was moderately enriched and its concentration was higher than what would be expected in crustal composition. Pb, Cu and Zn had EF values of more than 100, indicating the impact of human activities on the release of these elements and their intense enrichment in atmospheric precipitation. In a study conducted by Kang et al. in the central plateau of Tibetan, Zn had the highest EF value as in this study [46]. It has been reported that Zn and Pb had human sources and they are primarily produced and released into the atmosphere by vehicle traffic, industrial activities and combustion of fossil fuels [47, 48]. The combustion of fossil fuels, industrial metallurgical processes and waste incinerators are the major sources for Cu emission. Zn is also produced from similar activities [47]. Although Ni is one of the indicators for the release of pollutants from the combustion of fuel and traffic processes, petrochemical processes could also be possible sources of production and release of this element [20]. Since 1980, use of leaded gasoline has gradually decreased to reduce Pb pollution in the atmosphere. However, there is still a relatively high amount of Pb in the atmosphere due to combustion of other fuels in high-temperature processes like coal-fired power plants and re-suspension of dust and debris which is common in Shiraz due to wind blowing [49].

Factor analysis

The results of principal component analysis (PCA) are presented in Table 3. From the PCA results, four major components were identified that explained 78.8% of the total variance. To select the significant features for the interpretation of each component, factors loadings greater than 0.7 were considered in Table 3. The first component (factor 1), which is

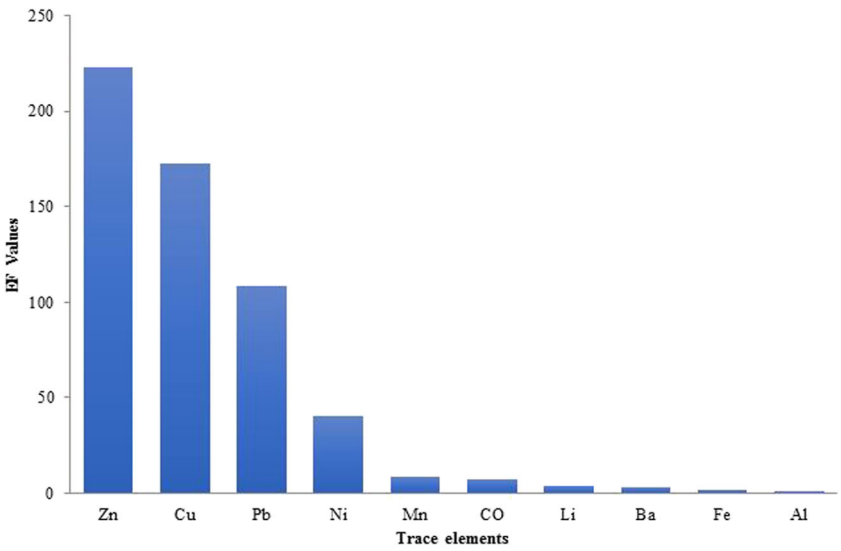

Fig. 5 Calculated EF values for trace elements in the atmospheric precipitations of Shiraz

Table 3 Factor analysis of trace element in wet precipitation

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Al	−0.121	0.225	−0.037	0.857
Ba	0.775	0.466	−0.061	0.096
Cr	0.946	−0.046	0.220	−0.150
Cu	−0.095	0.002	0.948	0.134
Fe	0.244	0.068	0.051	0.921
Li	0.864	−0.033	0.076	0280
Mn	0.237	0.911	−0.073	0.084
Ni	0.096	0.810	−0.017	0.214
Pb	−0.309	0.744	0.374	0.080
Zn	0.318	0.005	0.853	0.115
Total variance%	33.7 33.7	19.1 52.8	14.4 67.2	11.5 78.8

associated with Cr and Li, explained 33.7% of the total variance. Although Li and Cr can have an human origin, such as incineration, combustion of fossil fuels and some industrial activities [46], the EF values for these metals were lower than 10 and could be considered as having a crustal origin in this study. Additionally, studies of the coasts of Turkey showed that metals, such as Ni and Cr, were found in Eastern Mediterranean aerosols; this was attributed to the presence of soil enriched with these elements on the coasts [50, 51]. In this study, the presence of Ni and Cr in rainwater samples could be associated with airborne particles and, thus, this factor was attributed to natural crustal origin. The second component (factor 2), which is mainly associated with Mn, Ni and Pb, explained 19.1% of the total variance. Mn, originating primarily from the Earth's crust, has low solubility. It is emitted into the atmosphere by the windblown erosion of dusts and soils [30]. Regarding Mn enrichment, the leaching of this element before Al from crustal material during atmospheric precipitation contributes more to the emission of this pollutant than its man-made sources [43]. Conversely, Ni, which originates mainly from the production and recycling of Ni-Cd batteries [30, 39], and Pb, which is commonly emitted by fossil-fuel-burning plants, accumulate on atmospheric fine particulate matter (PM) during the evaporation-condensation mechanism. This might indicate that this component illustrates a combination of two natural and human sources for the presence of these elements in wet precipitation [30, 52]. The third component (factor 3), including Cu and Zn, explained 14.4% of the total variance. These elements are emitted into the atmospheric liquid phase from human sources, particularly industrial sources and traffic sources. They are enriched and placed on the surface of fine atmospheric particles, such as oxides, which are easily soluble when they are in contact with rainwater. Among the elements with human sources, Zn has a higher solubility. However, when rainwater creates absorbing locations on active surfaces, adsorption/desorption processes control these metals [30]. Elements, such as Cr, Ni, Cu, Pb and Zn, show different solubility levels, from medium to high, in the liquid phase. Some researchers have reported that variable conditions, such as the pH of the rainwater and the type of particles that carry these elements, are possible reasons for this occurrence [53]. As the emission of industrial pollutants and the combustion of fossil fuels from local sources are considered as a source of pollution, trace elements in the rain can be carried from regional distribution sources and through atmospheric rotations, from the adjacent areas to the target area [54]. Finally, the fourth component (factor 4), which is chiefly associated with Fe and Al, explains 11.5% of the total variance. Fe and Al are considered to derive from a natural source due to their high content in the Earth's crust. As observed, there was a strong correlation between the EF levels and the factor analysis for elements measured in this study. A correlation test was also used to determine the relationship between trace elements. Table 4, shows the calculated linear correlation coefficients for 36 samples of rainwater which confirmed the results of PCA.

Table 4 Spearman's rank correlation matrix for rainwater samples

	AL	Ba	Co	Cr	Cu	Fe	Li	Mn	Ni	Pb	Zn
AL	1										
Ba	0.019	1									
Co	0.309	0.447	1								
Cr	−0.122	0.311	0.006	1							
Cu	0.512	0.153	−0.009	0.016	1						
Fe	0.661*	0.091	0.030	0.130	0.418	1					
Li	0.344	0.363	−0.363	0.449*	0.021	0.370	1				
Mn	0.418*	0.347	−0.189	0.097	0.247	0.517*	0.104	1			
Ni	0.186	0.405	−0.205	−0.178	−0.075	0.114	0.265	0.609*	1		
Pb	0.329	0.110	−0.119	−0.130	0.478*	0.254	−0.134	0.430*	0.381	1	
Zn	0.105	0.133	−0.147	0.254	0.363*	0.235	0.252	0.190	0.015	0.175	**1**

* Correlation is significant at the 0.05 level (2-tailed)

Conclusion

Based on the results, a significant difference was not observed in the concentration of measured elements at different parts of urban stations. According to the average concentration of trace elements in the atmospheric precipitation in Shiraz, the highest concentrations belonged to Al and Fe, which mainly originated from the Earth's crust. Among the measured elements with an human origin, Zn had the highest concentration in wet precipitation samples. The pH levels of the samples collected from rainwater were in the range of 4.5–6.95, with an average value of 5.3 showing acidic condition. The values obtained from EF showed the high enrichment of Pb, Cu and Zn in atmospheric precipitation and in the high impact of traffic and industrial activities on the emission of these elements. Based on the PCA results, the trace elements present in the samples were classified into four groups according to their source. In the first component, Li and Cr had an EF less than 10, indicating that they were transported by crustal particles. In the second component, Mn with a crustal origin and Pb and Ni with human origins, had a combination of natural and human sources. Cu and Zn in the third component were elements of mainly industrial and traffic origin. Finally, in the fourth component, Al and Fe were metals of crustal origin. Comparison of the present study with a study conducted in Shiraz in 2011 showed that, in the present study, Zn and Cu had increased significantly. This change could be attributed to the increase in industrial activities and the number of vehicles in the study area. In contrast, Pb saw a slight decrease, which could be attributed to the improvement of the quality of fuels.

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Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

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