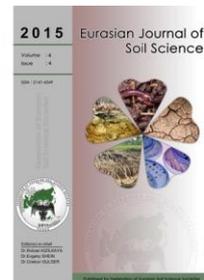




Eurasian Journal of Soil Science

Journal homepage : http://fesss.org/eurasian_journal_of_soil_science.asp



Source identification of heavy metals in atmospheric dust using *Platanus orientalis L.* leaves as bioindicator

Samira Norouzi *, Hossein Khademi

Isfahan University of Technology, Department of Soil Science, Isfahan, Iran

Abstract

Studies on atmospheric dust have been limited by the high cost of instrumental monitoring methods and also sampling difficulties. The use of organisms acting as bioaccumulators has recently been proposed. In this study, the leaves of *Platanus orientalis L.*, as a possible biomonitor of heavy metals in atmospheric dust, were evaluated to understand the likely source(s) of pollution in Isfahan, Iran. Concentration of Zn, Cu, Ni and Mn and Magnetic susceptibility (χ_{if}) were determined in washed (WL) and unwashed leaves (UL), monthly sampled from May to Nov., 2012. By subtracting the amount of metal concentrations and χ_{if} in UL and WL, the amount of these parameters in dust deposited on the leaves (UL-WL) were calculated. Enrichment factor analysis (EF), correlation coefficient, principal component analysis (PCA) and cluster analysis (CA) on the UL-WL data were employed to trace the heavy metals sources. Results showed that the metal concentration in UL and WL in primary sampling times was not statistically different. As time passed, this difference became more noticeable. Seasonal accumulation trends of elements concentration in UL-WL, referred to as accumulative biomonitors showing the accumulation of dust on the leaves are considerable and the contamination of plants by metal occurs mainly by retention of particulate matter. All the heavy metals are well correlated with χ_{if} , indicating the potential of magnetic measurement as an inexpensive and less laborious method to estimate heavy metals. Cu and Zn exhibited a very strong correlation with each other and the highest correlation with χ_{if} , suggesting an anthropogenic nature of these two metals. High EF of Cu and Zn showed that anthropogenic sources contribute a substantial amount of these metals to dust deposited on leaves. Whereas, less EF for Mn and Ni shows that natural source and local polluted soils might be the main origins of these metals. PCA results showed 2 principal components. Factor 1 with significant loading for Cu and Zn and factor 2 for Mn and Ni. In an agreement with the PCA and correlation results, CA showed strong clusters for Zn and Cu and also for Mn and Ni. Zn seems to originate from vehicular emissions, oil combustion and wear and tear of vehicle tires. Cu seems to originate from industrial processes, traffic and combustion of fossil fuels. Polluted soils in the area appear to be the main natural source for Mn and Ni in dust, while anthropogenic activities could be considered as the second origin

Article Info

Received : 01.07.2014

Accepted : 19.12.2014

Keywords: Tree leaves, Heavy metals, Magnetic susceptibility, Enrichment Factor, Multivariate statistics

© 2015 Federation of Eurasian Soil Science Societies. All rights reserved

Introduction

Atmospheric dust is one of the most important environmental pollutants. The dust may include a broad range of chemical species, ranging from elemental wastes to organic and inorganic compounds (Callén et al., 2009). The most important inorganic components are the trace metals which are emitted by various natural and anthropogenic sources, such as crustal materials, road dust, construction activities, motor vehicle

* Corresponding author.

Isfahan University of Technology, Department of Soil Science, Isfahan, 84156-83111 Iran

Tel.: +989103118356

e-ISSN: 2147-4249

E-mail address: samiranorouzi@yahoo.com

DOI: <http://dx.doi.org/10.18393/ejss.2015.3.144-152>

emissions, coal and oil combustion, incineration and other industrial emissions (Shah and Shaheen, 2010). The complexity of dust particles makes their characterization and source identification difficult. The source of dust particles has a particular importance for the evaluation of atmospheric pollution (Lu et al., 2008). Therefore, studies of dust are important for the determination of the origin, distribution, environmental damage and health effects of heavy metals (Lu et al., 2010).

Studies on atmospheric contamination have been limited by high cost of instrumental monitoring methods and difficulties in carrying out extensive sampling in time and space. That is why there has been an increasing interest in using indirect monitoring approaches based on a response of organisms that may act as bio accumulators (Anicic et al., 2011). Plants are particularly useful as biological indicators to evaluate air pollution because of their wide distribution (Kardel et al., 2010), and low sampling cost (Lehndorff and Schwark, 2010). Trees are very efficient in trapping atmospheric particles, mostly on their foliage (Qiu et al., 2009). Concentration of major and trace metals in plants depends on root uptake or accumulation of dry and wet deposition on outer plant organs such as foliage or bark (Lehndorff and Schwark, 2010). Elemental analysis of plant samples has for many years been an alternative, easy, and effective way of conducting ecological investigation in urban areas (Celik et al., 2005; Mingorance and Oliva, 2006).

Moreover, environmental magnetic methods based on the study of various parameters have been successfully used over several decades to characterize and quantify the degree of pollution of different environmental systems such as soil, sediments, air, water and snow. Several studies have shown significant correlation between the concentration of heavy metals and magnetic parameters (Lu et al., 2008; Salo et al., 2012). Recently, the applicability of magnetic biomonitoring has been increasingly applied in the evaluation of anthropogenic pollution. The analyses of magnetic particles and related trace elements in biological material such as tree leaves, needles, bark and ring cores are suggested as an alternative method in air pollution monitoring (Lehndorff et al., 2006; Zhang et al., 2008).

Magnetic properties of the leaf dust have been used for the identification of pollutants derived from vehicular or industrial emissions^[8]. Magnetic susceptibility provides a first indication of the concentration of ferrimagnetic minerals in dusts. Therefore, magnetic measurements on dust can serve as a complementary tool for the routinely used geochemical methods, which are known time-consuming, tedious and expensive (Lu et al., 2008).

Isfahan city as the capital of Isfahan Province, is frequently exposed to dust events during the year and has a high population with heavy traffic and many industrial complexes. Moreover, there is a good distribution of *Platanus orientalis* L. tree in Isfahan. Source identification of heavy metals in dust is very important for many aspects of economic, social and health management in the society. This paper presents data on magnetic susceptibility and heavy metal contents of dust absorbed on urban tree leaves to identify the sources of dust particles.

The main objectives of this study can be summarized as follows: (1) to verify the effectiveness of *Platanus orientalis* L. leaves as collectors of heavy metals and magnetic particulates; (2) to determine the relationships between magnetic susceptibility and heavy metal contamination in dust absorbed on the leaves; and (3) to evaluate the probable origins of heavy metals absorbed on the leaves employing multivariate statistical methods, enrichment factor and correlation coefficient.

Material and Methods

Study area

This study was conducted in Isfahan, the Iran's third largest city located in central Iran (51° 39' 40" E, 32° 38' 30" N). It covers an area of 482 km² and is the third populated city in Iran with a population of about 1,796,967. Its elevation is 1580 meter above the sea level. Isfahan city is characterized by a dry climate with hot summers. Existence of a desert area in eastern and northern part of the city seems to be the reason why the area is frequently exposed to dust events during the year. Moreover, Isfahan is the second industrial city in Iran with many different kinds of industries, including the biggest steel plant in the country, an Iron smelter, an oil refinery and a few petrochemical complexes. These industries in and around the city and also heavy traffic with the 24324 total number of registered public transport in 2011, have caused great atmospheric pollution in this city. In this study for leaves samples collection, 21 sites in different parts of the city were chosen to best cover the whole area (Figure 1).

Leaves sampling and analysis

Leaves were monthly sampled from Button wood (plane tree), *Platanus orientalis* L. (Platanaceae), a deciduous tree common in the area from the beginning to the end of the seasonal vegetation cycles (T₁: 19 May, T₂: 19 Jun, T₃: 19 Jul, T₄: 21 Aug, T₅: 19 Sep, T₆: 19 Oct, T₇: 18 Nov, 2012). In order to reduce age variation among tree samples, trees of approximately the same age were selected.

Leaves were cut off with stainless steel scissors from about 2-2.5 m height. 15-20 fully developed leaves were taken randomly from all sides of a crown in each site. After T₂ and T₆ sampling times, there was a heavy rain which could clean the leaves surfaces. Immediately after the sampling, the samples were placed in paper envelopes and transported to the laboratory.

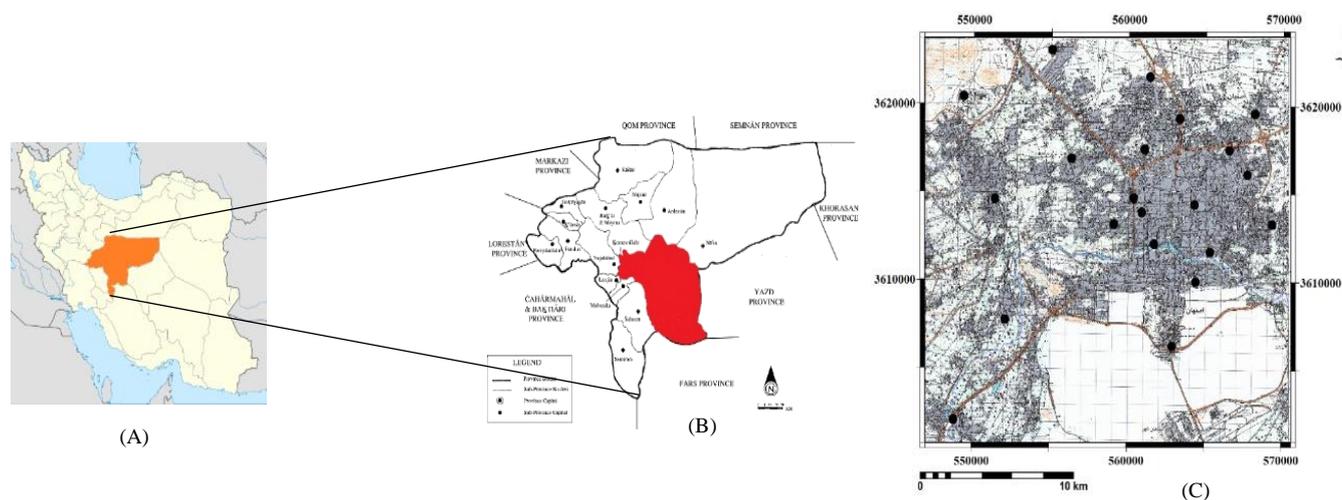


Figure 1. Map of Iran and Isfahan Province (A), Isfahan city (B) and the location of the atmospheric dust and leaves sampling sites (C).

The leaves samples of each site were divided into two subsamples. The first subsample, was thoroughly washed with running distilled water to remove dust particles and the other solid particles. While, the other half of the subsamples was left unwashed. Both types of samples were dried at 60°C for 48 hours and then pulverized to uniform size with a laboratory mill, then packed in plastic bags and kept under stable laboratory conditions prior to chemical analysis. The mill was thoroughly cleaned after each grinding to avoid any cross contamination (Celik et al., 2005).

0.4 g of leaves (dry weight) were placed in silicon vessels with 5ml of 70% HNO₃ (Merck), 2 ml of 30% H₂O₂ and 3 ml deionized water, and digested for 15 minutes in a microwave digester (MILE STONE GmbH), using a power program adapted as follows: 1 min at 1000 W, 75°C, 4 min at 1000 W, 180°C and 10 min 1000 W, 180°C, ramped down to 0W in 15 min (EPA, 1996). The digested samples were diluted with deionized water to a total volume of 25 ml. Final solutions were analyzed for the concentration of Cu, Mn, Ni and Zn using a Perkin Elmer 3030 atomic absorption spectrophotometer.

Magnetic susceptibility of unwashed (UL) and washed (WL) leaves was measured at low (0.46 kHz, χ_{lf}) and high frequency (4.6 kHz, χ_{hf}) using a Bartington MS2 dual frequency sensor.

Data analyses

Data handling included t-test and U-test for element concentrations and magnetic susceptibility parameters measured in washed (WL) and unwashed (UL) leaves samples for each sampling time. By subtracting the amount of metal concentrations and χ_{lf} in UL and WL, the amount of these parameters in dust absorbed on the leaves (UL-WL) were calculated. Nonparametric statics (Kruskal- Wallis H test) was used to assess the significance of differences ($p=0.05$) of element concentrations and χ_{lf} in different sampling times. To identify the relationship among heavy metals in dusts absorbed on leaves (UL-WL) and their relation with magnetic susceptibility, Spearman's correlation coefficient was used.

Enrichment factor (EF) analysis was used to differentiate the elements mainly originating from human activities and those of natural origin and to assess the degree of anthropogenic influence (Szczepaniak and Biziuk, 2003). EF represents the ratio of the element E and reference element R in the sample and in the crust or soil: $EF = (E/R)_{\text{sample}} / (E/R)_{\text{crust or soil}}$. In this study the enrichment factors (EFs) were calculated for the element concentrations in the UL-WL on the concentrations for all sites and sampling months. Fe was used as the reference element and the upper continental average crustal composition (Niencheski et al., 2002) and also, for comparative purposes, element concentrations in Isfahan city soil (Amiri, 2012) were used as crust/soil elements.

Spearman's correlation coefficient analysis and multivariate statistical analysis including principal component analysis (PCA) and cluster analysis (CA) were performed using the statistics software package SPSS. 16 to identify the heavy metals possible pathways and sources in dusts absorbed on the leaves. PCA was applied using varimax rotation with Kaiser Normalization. The metal concentrations on UL-WL data were standardized by means of z-scores before CA and Euclidean distances for similarities in the variables were calculated. Then, hierarchical clustering by applying Ward's method was performed on the standardized data set.

Results and Discussion

Heavy metals and magnetic susceptibility contents in unwashed (UL) and washed (WL) leaves

The mean concentrations of Cu, Mn, Ni, Zn and magnetic parameters (χ_{lf} and χ_{hf}), in unwashed and washed leaves of *Platanus orientalis* L. at different sampling times from all studied sites are presented in Table 1. In unwashed leaves (UL), there are an increasing trend in all element concentrations and in χ_{lf} and χ_{hf} contents from T₁ to T₆ sampling times, but because of the heavy rain after the T₆ sampling time, the element concentrations for T₇ is not cumulative and is less than those of the previous month.

In washed leaves (WL), monthly increasing trend was distinguished for Mn, but the concentrations of Cu and Zn showed a reducing trend from the beginning (May) to the end (Nov.) of the growing periods, while the Ni concentration in washed leaves remained at about the same level throughout the different sampling months. No systematic trend was observed for χ_{lf} and χ_{hf} during the sampling times. Seasonal discrepancy for the Cu and Zn concentrations was also noted previously (Anicic et al., 2011; Kim and Fergusson, 1994), pointing that these elements were the highest in the new leaves, and decreased along the growing season, possibly due to physiological role of these elements as essential constituents of plant tissue. It is considered that the Cu remobilization to non senescent parts occurs before the senescence, and leaf fall takes place.

For each sampling time, the mean values of metals and magnetic parameters in unwashed and washed leaves were compared by t-test or U-test. Results showed that rinsing with water could reduce the element concentrations and magnetic parameters in leaves samples. It is noted that there are considerable difference between the amounts of studied parameters in the unwashed and washed leaves in a specific sampling time. As shown in Table 1, the metal concentration and magnetic parameters differences between unwashed and washed leaves in primary sampling time (T₁) are not significant. But, as time passes and plant grows and the amount of dust absorbed on leaves surface increases, the cumulative metal concentration in unwashed leaves increases and the metal concentration and magnetic parameters differences between washed and unwashed leaves become significant.

Tomasevic et al. (2011), by comparison of the content of some trace elements (Al, As, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Pb) in leaves of four tree species common in the urban area of Belgrade (Serbia) concluded that a brief double rinsing with water (3–5 s) could reduce the concentration of Al, Fe and Pb ($p = 0.05$) in leaf samples of all investigated species.

Standard deviations for element concentrations especially for Cu and Zn and for magnetic parameters (χ_{lf} and χ_{hf}), were higher for the unwashed as compared to washed leaves samples at each sampling time. Rinsing the leaves samples prior to chemical analysis removed atmospheric dust absorbed on leaves surfaces and that, in turn, reduced the large variability of element concentration between leaves samples taken per each studied site in each sampling time. Moreover, some accidental impurities, large loosely adhered particles maybe easily lost from leaf surface by either wind or rain and different condition of environmental pollution per sampling site, caused the high standard deviation between element concentrations and magnetic parameters in unwashed leaves samples.

Table 1. Metal concentrations and magnetic parameters (χ_{lf} and χ_{hf}) (mean \pm S.D) in unwashed (UL) and washed (WL) leaves collected in different months in Isfahan city.

Sampling time	Elements					
	UL	WL	UL	WL	UL	WL
	Cu (mg/kg)		Mn (mg/kg)		Ni (mg/kg)	
T ₁	15.06 ^a (\pm 4.8)	14.64 ^a (\pm 4.6)	71.57 ^a (\pm 33.8)	66.75 ^a (\pm 31.8)	6.19 ^a (\pm 1.2)	6.13 ^a (\pm 1.2)
T ₂	15.12 ^a (\pm 5.9)	11.96 ^b (\pm 3.7)	84.02 ^a (\pm 44.6)	67.65 ^a (\pm 37.6)	7.41 ^a (\pm 1.1)	5.71 ^b (\pm 1.0)
T ₃	15.74 ^a (\pm 10.6)	11.80 ^b (\pm 3.9)	99.80 ^a (\pm 46.7)	77.95 ^a (\pm 42.4)	7.68 ^a (\pm 1.3)	5.83 ^b (\pm 1.1)
T ₄	20.0 ^a (\pm 15.1)	12.56 ^b (\pm 5.1)	135.77 ^a (\pm 73.9)	96.04 ^a (\pm 67.6)	9.31 ^a (\pm 1.5)	5.92 ^b (\pm 1.2)
T ₅	23.27 ^a (\pm 17.1)	12.30 ^b (\pm 5.4)	155.6 ^a (\pm 80.5)	100.68 ^b (\pm 76.8)	10.83 ^a (\pm 1.9)	6.01 ^b (\pm 1.0)
T ₆	26.96 ^a (\pm 20.4)	12.26 ^b (\pm 5.3)	176.22 ^a (\pm 86.9)	101.96 ^b (\pm 80.3)	12.74 ^a (\pm 2.3)	5.86 ^b (\pm 1.1)
T ₇	16.61 ^a (\pm 4.3)	11.30 ^b (\pm 3.8)	124.94 ^a (\pm 77.5)	100.48 ^a (\pm 76.5)	9.26 ^a (\pm 2.2)	5.83 ^b (\pm 1.1)
	Zn (mg/kg)		χ_{lf} ($10^{-8}m^3kg^{-1}$)		χ_{hf} ($10^{-8}m^3kg^{-1}$)	
T ₁	34.97 ^a (\pm 8.8)	32.64 ^a (\pm 8.3)	1.43 ^a (\pm 0.3)	0.78 ^a (\pm 0.64)	1.07 ^a (\pm 0.27)	0.27 ^a (\pm 0.27)
T ₂	40.95 ^a (\pm 14.4)	29.2 ^b (\pm 8.2)	3.72 ^a (\pm 2.2)	0.89 ^b (\pm 0.75)	2.64 ^a (\pm 1.6)	0.06 ^b (\pm 0.16)
T ₃	42.20 ^a (\pm 17.9)	30.45 ^b (\pm 8.7)	5.52 ^a (\pm 4.5)	0.6 ^b (\pm 0.74)	4.42 ^a (\pm 4.2)	0.0 ^b
T ₄	51.22 ^a (\pm 29.1)	29.55 ^b (\pm 8.8)	7.0 ^a (\pm 4.6)	0.8 ^b (\pm 1.3)	5.97 ^a (\pm 4.4)	0.42 ^b (\pm 0.95)
T ₅	59.76 ^a (\pm 41.5)	29.05 ^b (\pm 9.4)	12.4 ^a (\pm 11.9)	1.6 ^b (\pm 1.2)	11.13 ^a (\pm 12)	0.68 ^b (\pm 0.88)
T ₆	68.84 ^a (\pm 52.1)	28.18 ^b (\pm 9.2)	11.58 ^a (\pm 5.1)	1.89 ^b (\pm 0.73)	10.72 ^a (\pm 5.03)	0.67 ^b (\pm 0.07)
T ₇	40.56 ^a (\pm 13.1)	27.95 ^b (\pm 8.5)	5.48 ^a (\pm 2.9)	1.85 ^b (\pm 1.3)	4.54 ^a (\pm 2.4)	0.79 ^b (\pm 0.9)

t-test or U-test between metal concentration in UL and WL in each sampling time. Means with same letters are not statistically significant in $p < 0.05$.

Spearman correlation between χ_{lf} and χ_{hf} in unwashed and also in washed leaves were 0.98 and 0.68, respectively (statistically significant at $p < 0.01$). That is why only χ_{lf} values will be discussed.

Seasonal accumulation trends of element concentrations in leaves, often referred to as accumulative biomonitors, have been reported for many plant species (Kim and Fergusson, 1994; Piczak et al., 2003). It shows that the accumulation of dust and aerosols on the leaves are considerable and the contamination of plants by metal occurs mainly by retention of particulate matter (Al-Khashman et al., 2011). It has been widely accepted that most of these elements have been emitted to the plants from anthropogenic sources and traffic has a major influence on these accumulation (Tomasevic et al., 2011).

Metal concentrations and magnetic susceptibility contents in dust absorbed on the leaves (UL-WL)

The ability to distinguish between airborne and soil contamination was assessed by washing the leaves (Al-Khashman et al., 2011). By subtracting the amount of metal concentrations and χ_{lf} in unwashed (UL) and washed leaves (WL), the amount of these parameters in dusts absorbed on the leaves (UL-WL) were calculated.

The seasonal trend of metal concentrations and χ_{lf} in (UL-WL) by sampling time is shown in Figure 2. There are cumulative trend with time of sampling from the beginning (T₂) to the end of vegetation period (T₆) in UL-WL for all elements and χ_{lf} . It means that each specific month, distinctive amounts of atmospheric particulate matter from different origins were added to leaves surface and will remain unless the rain occurs.

Correlation coefficient analysis

The Spearman's correlation coefficients for heavy metals and χ_{lf} in the dust absorbed on plant leaves (UL-WL) in all sampling times and sites, are presented in Table 2. Almost all the heavy metals have good correlation ($p < 0.01$) with each other as well as with the magnetic susceptibility (χ_{lf}) values.

Among metals, Cu and Zn exhibited very strong correlation with each other ($r > 0.79$), and a strong correlation was observed between Mn and Ni ($r > 0.74$). These indicate that Zn and Cu were likely derived from a similar source, while the source of Ni and Mn is the same but different from that of Cu and Zn.

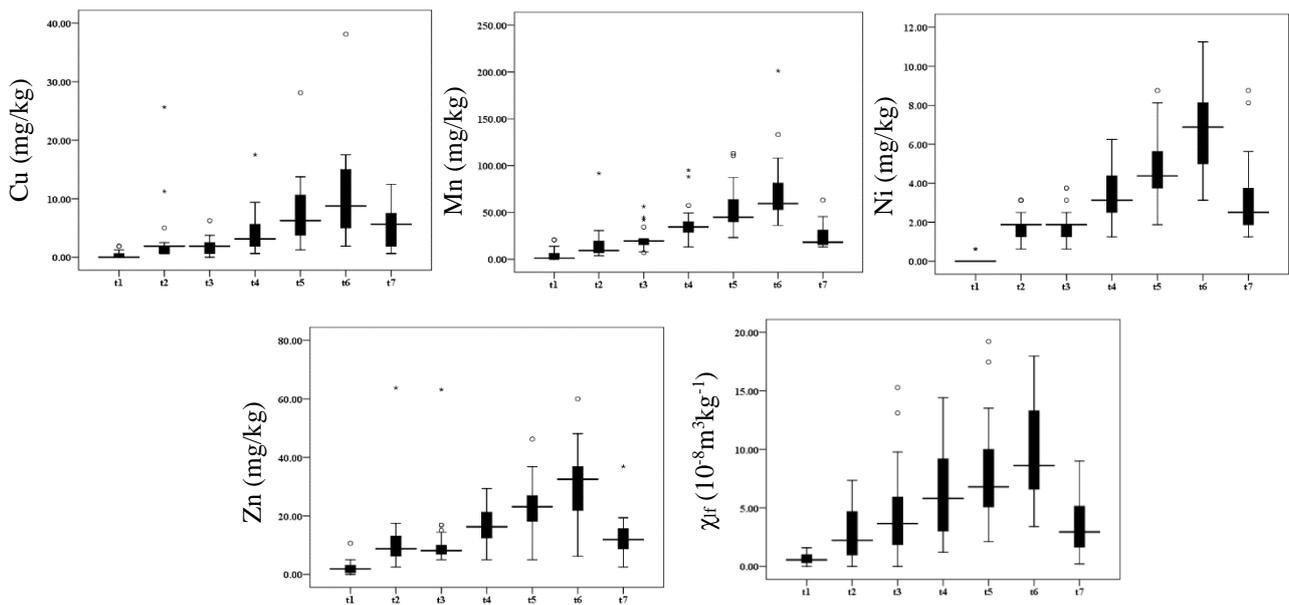


Figure 2. Seasonal trend of metal concentrations and χ_{lf} in dust absorbed on the leaves (UL-WL).

Among four studied metals, Zn and Cu exhibited strong correlation with the magnetic parameter (χ_{lf}), followed by Mn and Ni. The significant correlation between magnetic susceptibility and contents of heavy metals suggests an anthropogenic nature of the magnetic carrier, indicating that magnetic particles and heavy metals coexist in the dusts. This relationship could also be due to the fact that heavy metals are incorporated into the lattice structure of the ferromagnetic particles during combustion processes or are adsorbed onto the surface of pre-present ferromagnetic minerals in the environments (Lu et al., 2008; Salo et al., 2012). Coexistence of the heavy metals and magnetic particles was found in many case studies (Davila et al., 2006; Lu et al., 2008; Salo et al., 2012).

The strong correlation between magnetic parameters and heavy metal concentrations in the dusts absorbed on leaves can be used to rapidly assess the concentration and distribution of heavy metals. Compared with the conventionally chemical analysis, the magnetic measurement technique provides an inexpensive and less laborious method for the measurement of heavy metals in the dusts (Lu et al., 2008; Salo et al., 2012). Results of this study indicate that the magnetic measurement can be used as a proxy for evaluation of heavy metal pollution and contamination in dusts absorbed on the leaves.

Table 2. The Spearman correlation coefficient between metals and magnetic susceptibility (χ_{lf}) in dust absorbed on leaves (UL-WL).

	Cu	Mn	Ni	Zn	χ_{lf}
	(mg/kg)				($10^{-8}m^3kg^{-1}$)
Cu	1				
Mn	0.56**	1			
Ni	0.63**	0.74**	1		
Zn	0.79**	0.64**	0.71**	1	
χ_{lf}	0.55**	0.53**	0.51**	0.58**	1

** : Correlation is significant at the 0.01 level.

Enrichment Factor (EF) analysis

In general, the enrichment of elements in dusts as compared to the upper continental crust composition or soil is an indication of emissions from anthropogenic sources. If EF approaches unity, the Earth's crust is the predominant source. If $EF > 10$, a significant fraction of the element is contributed from non-crustal and anthropogenic sources (Gao et al., 2002).

Figure 3 provides the EF values analyzed for the dusts absorbed on the leaves (UL-WL) for all sampling times and sites. EFs of Cu and Zn are relatively higher than those of Ni and Mn. EFs of Mn and Ni, calculated

based on the element contents of both city soil and crust, were more than unity but below 10, suggesting that the crustal source is dominant and a fraction of these elements may originate from anthropogenic activities. Cu and Zn values are greater than 10 for both studied cases (city soil and crust), indicating the significant contribution of non-crustal and anthropogenic sources for these elements.

For all the studied elements, EF values calculated based on the crust element concentrations, is greater than those values calculated based on city soils elemental concentrations. It means that, urban soils are polluted in comparison with the crust. Dusts are originated from polluted soils in Isfahan city and that is why the heavy metals in dust have less EFs values.

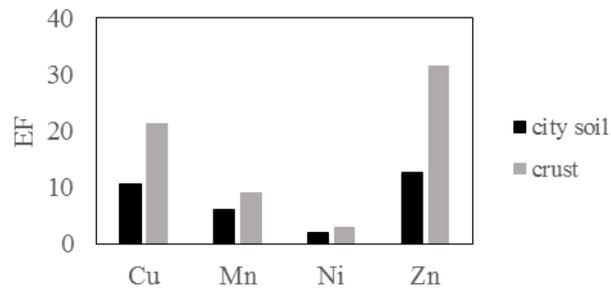


Figure 3. Enrichment factor of metal concentrations in dust absorbed on leaves (UL-WL).

Multivariate statistical analysis (PCA, CA)

Table 3 shows the factor loadings with a varimax rotation and eigenvalues resulting in principal component analysis (PCA) for the elements in dust absorbed on the leaves (UL-WL) for all studied sampling times and sites. Results indicate that there are 2 eigenvalues higher than one and these two factors explain 89.40% of the total variance.

The first factor (PC1), explain 47.53% of the total variance and loads heavily on Cu and Zn. Factor 2 (PC2), dominated by Mn and Ni, accounts for 41.86% of the total variance.

Table 3. Principal component analysis after varimax rotation for metals in dust absorbed on leaves (UL-WL).

	Rotated Component Matrix ^a	
	PC1	PC2
Eigenvalue	1.91	1.67
% Total variance	47.53	41.86
% Cumulative variance	47.53	89.40
Cu	0.97	0.096
Mn	0.129	0.904
Ni	0.140	0.899
Zn	0.957	0.197

Extraction method: principal component analysis. Rotation method: Varimax with Kaiser Normalization. ^a Rotation converged in three iterations. (PCA loadings > 0.8 are shown in bold).

The cluster analysis (CA) results for the heavy metals in dust absorbed on leaves (UL-WL) are shown in Figure 4. Two very strong clusters are observed. The first one with pair of Cu-Zn and the other with pair of Mn-Ni, in full agreement with the PCA and EF results.

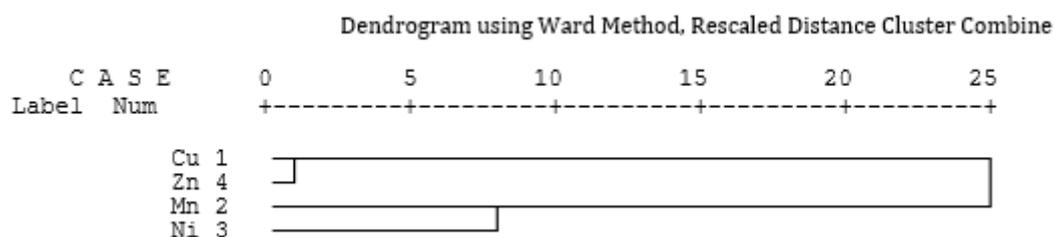


Figure 4. Dendrogram results from Ward method of hierarchical cluster analysis for metals in dust absorbed on leaves (UL-WL).

Heavy metal source identification

The EF values suggest an anthropogenic source including industries and traffic for Zn and Cu, while EF values for Mn and Ni indicates that they mainly originate from a natural source (local soil), but also influenced by anthropogenic activities. The correlation coefficient analysis indicates that Cu and Zn have a common source, while Ni and Mn have another common source. PCA and CA results are consistent with these interpretations.

Zn in dust can originate from the wear and tear of vulcanized vehicle tires and corrosion of galvanized automobile parts (Al-Khashman, 2007; Nazir et al., 2011). Zn has been suggested as a good marker of gasoline engine emissions (Basha et al., 2010). Cu is often used in car lubricants (Al-Khashman, 2007). Cu can be released to the urban environments as a result of wear of the automobile's oil pump or corrosion of metal parts which come into contact with the oil. Another possible source of Cu is the corrosion of metallic parts of cars and engine wear (Al-Khashman, 2007; Basha et al., 2010; Nazir et al., 2011).

Considering Isfahan city as the third large and populated city in Iran, with heavy traffic and many industrial complexes, the existence of Cu and Zn in the dust absorbed on urban tree leaves is mainly attributed to the industrial and traffic sources.

Lu et al (2010), reported that maximum concentration of Cu and Zn was found in street dust samples from location corresponding to heavy traffic and industry, while their minimum values were detected in dust from residential sites of low traffic density.

Many studies reported the natural source for Mn and Ni in dusts (Lu et al., 2010). Nazir et al., (2011) reported that Mn is mainly derived from Earth's crust and resuspension of soil dust. In present study, polluted local soils appear to be the main natural source for these elements in dust absorbed on leaves. Mn and Ni seem to be enriched by anthropogenic activities. Basha et al., (2010), reported that Ni was contributed by oil combustion. Because of chemical complexes located in Isfahan city, oil is used for both heating and industrial purposes. So, local soils as a natural and main source and anthropogenic sources as the second origin are identified for these metals.

Conclusion

Platanus orientalis L. leaves were studied for magnetic parameters and heavy metal concentrations in dust absorbed on the leaves, since they effectively accumulate the atmospheric pollution and can be used as a biomonitor, instead of high cost instrumental pollution monitoring methods. The strong correlation between magnetic susceptibility and heavy metals in dust absorbed on the leaves offers a rapid and time-efficient approach for assessment of the level of heavy metal pollutions. Based on the comparison of heavy metals concentrations of dust absorbed on the leaves by crust and soil values of heavy metals, and according to PCA and CA, coupled with correlation coefficient analysis, the heavy metals were classified into two main groups based on their sources: natural (local soil) and anthropogenic. Results indicated that traffic and industry activities are significant emission sources of Zn and Cu, while, Ni and Mn are nearly similar to local polluted soils enriched by anthropogenic activities.

References

- Al-Khashman, O.A., 2007. Determination of metal accumulation in deposited street dusts in Amman Jordan. *Environmental Geochemistry and Health* 29: 1-10.
- Al-Khashman, O.A., Al-Muhtaseb, A.H., Ibrahim, K.A., 2011. Date palm (*Phoenix dactylifera L.*) leaves as biomonitors of atmospheric metal pollution in arid and semi-arid environments. *Environmental Pollution* 159: 1635-1640.
- Amiri, S., 2012. Effects of land use and parent material on the spatial distribution of topsoil magnetic susceptibility in eastern Isfahan. A thesis for the degree of Master of Science. Isfahan University of Technology, pp.132. (In Persian).
- Anicic, M., Spasic, T., Tomasevic, M., Rajsic, S., Tasic, M., 2011. Trace elements accumulation and temporal trends in leaves of urban deciduous trees (*Aesculus hippocastanum* and *Tilia spp.*). *Ecological Indicators* 11: 824-830.
- Basha, S., Jhala, J., Thorat, R., Goel, S., Trivedi, R., Shah, K., Menon, G., Gaur, P., Mody, K. H., Jha, B., 2010. Assessment of heavy metal content in suspended particulate matter of coastal industrial town, Mithapur, Gujarat, India. *Atmospheric Research* 97: 257-265.
- Callén, M.S., de la Cruz, M.T., López, J.M., Navarro, M.V., Mastral, A.M., 2009. Comparison of receptor models for source apportionment of the PM10 in Zaragoza (Spain). *Chemosphere* 76: 1120-1129.
- Celik, A., Kartal, A.A., Akdogan, A., Kaska, Y., 2005. Determining the heavy metal pollution in Denizli (Turkey) by using *Robinio pseudo-acacia L.* *Environment International* 31: 105-112.

- Davila, A.F., Rey, D., Mohamed, K., Rubio, B., Guerra, A.P., 2006. Mapping the sources of urban dust in a coastal environment by measuring magnetic parameters of *Platanus hispania* leaves. *Environmental Science and Technology* 40: 3922–3928.
- EPA, 1996. Environmental Protection Agency, Method 3052, SW-846.
- Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on PM 2.5 particulate matter over the New York–New Jersey harbor estuary. *Atmospheric Environment* 36: 1077–1086.
- Kardel, F., Wuyts, K., Babanezhad, M., Vitharana, U.W.A., Wuytack, T., Potters, G., Samson, R., 2010. Assessing urban habitat quality based on specific leaf area and stomatal characteristics of *Plantago lanceolata* L. *Environmental Pollution* 158: 788–794.
- Kim, N.D., Fergusson, J.E., 1994. Seasonal variations in the concentrations of cadmium, copper, lead and zinc in leaves of the horse chesnut (*Aesculus hippocastanum* L.). *Environmental Pollution* 86: 89–97.
- Lehndorff, E., Schwark, L., 2010. Biomonitoring of air quality in the Cologne Conurbation using pine needles as a passive sampler, Part III: Major and trace elements. *Atmospheric Environment* 44: 2822–2829.
- Lehndorff, E., Urbat, M., Schwark, L., 2006. Accumulation histories of magnetic particles on pine needles as function of air quality. *Atmospheric Environment* 40: 7082–7096.
- Lu, S.G., Zheng Y.W, Bai, S.Q., 2008. A HRTEM/EDX approach to identification of the source of dust particles on urban tree leaves. *Atmospheric Environment* 42: 6431–6441.
- Lu, X., Wang, L., Li, L.Y., Lei, K., Huang, L., Kang, D., 2010. Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. *Journal of Hazardous Materials* 173: 744–749.
- Mingorance, M.D., Oliva, S.R., 2006. Heavy metals content in *N. oleander* leaves as urban pollution assessment. *Environmental Monitoring and Assessment* 119: 57–68.
- Niencheski, L.F.H., Baraj, B., Garcia Franca, R., Mirlean, N., 2002. Lithium as a normalizer for the assessment of anthropogenic metal contamination of sediments of the southern area of Patos Lagoon. *Aquatic Ecosystem Health and Management* 5 (4): 473–483.
- Piczak, K., Lesniewicz, A., Zyrnicki, A., 2003. Metal concentrations in deciduous tree leaves from urban areas in Poland. *Environmental Monitoring and Assessment* 86: 273–287.
- Qiu, Y., Guan, D., Song, W., Huang, K., 2009. Capture of heavy metals and sulfur by foliar dust in urban Huizhou. *Chemosphere* 75: 447–452.
- Nazir, R., Shaheen, N., Shah, M.H., 2011. Indoor/outdoor relationship of trace metals in the atmospheric particulate matter of an industrial area. *Atmospheric Environment* 101: 765–772.
- Salo, H., Bucko, M.S., Vaahtovuori, E., Limo, J., Makinen, J., Pesonen, L.J., 2012. Biomonitoring of air pollution in SW Finland by magnetic and chemical measurements of moss bags and lichens. *Journal of Geochemical Exploration* 115: 69–81.
- Shah, M.H., Shaheen, N., 2010. Seasonal behaviours in elemental composition of atmospheric aerosols collected in Islamabad, Pakistan. *Atmospheric Research* 95: 210–223.
- Szczepaniak, K., Biziuk, M., 2003. Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. *Environmental Research* 93: 221–230.
- Tomasevic, M., Anicic, M., Jovanovic, L., Peric-Grujic, A., Ristic, M., 2011. Deciduous tree leaves in trace elements biomonitoring: A contribution to methodology. *Ecological Indicators* 11: 1689–1695.
- Zhang, C., Huang, B., Piper, J.D.A., Luo, R., 2008. Biomonitoring of atmospheric particulate matter using magnetic properties of *Salix matsudana* tree ring cores. *Science of the Total Environment* 39(3): 177–190.