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Biomonitoring of atmospheric particulate pollution via chemical composition and magnetic properties of roadside tree leaves

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Abstract

Particulate matter (PM) is a main atmospheric pollution which threats human health and well-being. In this research, we chemically and magnetically analysed roadside tree leaves, collected from three tree species in two main roads (from two different cities) and a reference area, for 28 elements and the saturation isothermal remanent magnetisation. Comparison of unwashed and washed leaves revealed that deposited particles on the leaf surface contain various elements including Al, Ca, Fe, Mg, Mn, Na, Si, Ti, Ba, Co, Cr, Cu, Ni, Rb, V, Zn, and Zr. Moreover, there was no significant difference between washed/unwashed leaves in Cl, K, P, S, As, Cd, Cs, Pb, Sn and Sr concentrations, which indicates tree leaves may not be a suitable biomonitor for these elements. Our results showed that site and tree species are important factors which affect atmospheric elements deposition. Among the three considered tree species, *Chamaecyparis lawsoniana* showed the highest potential for atmospheric particle accumulation. The PCA results revealed that Al, Fe, Ti, Co, Cr, Cu, Ni, Rb, Si, V, Zn, and Zr indicated emissions from road traffic activities and soil dust, and Ca, Mg and Na from sea salts, and Mn and Sb from industrial activity. The biplot results showed that the site effect was much stronger than the species effect for all elements and SIRM values. Moreover, elements from traffic, industrial activity and soil dust are significantly correlated with leaf SIRM indicating that leaf SIRM can be a suitable bioindicator of exposure to traffic–derived particles and soil dust, and not from sea salts. It is concluded that chemical composition and SIRM of urban tree leaves can serve as a good indicator of atmospheric PM pollution in Iran, and anywhere else where the studied trees grow.

Key words: chemical composition; atmospheric deposition; biomagnetic; biomonitoring; tree leaves; species specific

1 Introduction

Particulate matter (PM) with aerodynamic diameter below 2.5 and 10 µm ($PM_{2.5}$ and PM_{10}) are pollutants which can seriously harm human health and wellbeing in urbanized and industrialized areas. The main sources of urban atmospheric particulates are road activity, industrial activity, domestic heating and construction activity. Among varies sources of PM, road traffic induced particles are known as a main source of suspended particles in many urban atmospheres (Vu et al. 2015); they include exhausted emissions, wear and tear fractions, and resuspended roadside dust due to vehicles movements and wind. Chemical composition of traffic–derived particles contain a number of trace metals including Fe, Mn, Cu, Ni, Zn, Ba, Cd, Pb, Cr, Ti and V (Huhn et al. 1995; Harrison and Jones 1995; Gunawardena et al. 2012) of which some have magnetic properties (Maher et al. 2008). Metals can be inhaled by humans and cause inflammatory reactions or may adhere to suspended atmospheric particles and deposit on different surfaces. These metals are mainly toxic and persistent, and can be taken up by different plants and animals and transferred through the food-chain to humans.

Many researchers formerly used biological material for monitoring of air quality, in particular PM pollution (Conti and Cecchetti 2001; Kardel et al. 2010; Kardel et al. 2011; Vuković et al. 2015), as the measurement of PM concentration directly in the atmosphere is expensive and practically impossible at high spatial resolution. Among different biological material, plants - specifically trees - provide some services such as increasing carbon storage, mitigating the heat-island effect and wind storms, decreasing sound pollution, improving air quality in an urban environment (Rai 2016) and protection of cultural heritage (Kocić et al. 2014).

Urban trees, with dense twigs and leaves and complex leaf surface morphology, as natural receptors can effectively capture and reduce atmospheric particles (Jamil et al. 2009; Fantozzi et al. 2013; Nowak et al. 2006; Wang et al. 2006).

Different methods can be applied for the monitoring of deposited atmospheric particles on leaf surfaces. Due to the strong correlation between atmospheric PM and NOx concentrations and heavy metal concentrations on the one hand and magnetic properties of leaves on the other hand (Hofman et al. 2017; Maher et al. 2008), magnetic measurements of leaves demonstrated to be a good proxy for estimating the atmospheric, traffic and industrial particle pollution (Hofman et al. 2014 and 2017; Kardel et al. 2011 and 2012; Lu et al. 2008; Maher et al. 2008; Mitchell et al. 2010). Saturation isothermal remanent magnetisation (SIRM) is one of the magnetic variables with high sensitivity for materials which are weak in magnetic properties (Mitchell et al. 2010). Despite the large amount of studies already performed on SIRM of different tree species in different urban environments (Hofman et al. 2014; Kardel et al. 2011 and 2012; Maher et al. 2008; Mitchell et al. 2010; Sant’Ovaia et al. 2012), there is still not enough information on SIRM and large number of metal concentrations of deposited particles on tree species (with different leaf surface morphology) in sites with different climates and traffic densities. Also, it is not fully clear which one of the two, site or species, effects the accumulation of particles on the leaf's surface more and which elements can differentiate one site from another the most.

In Iran, due to high air pollution problems in mega cities, the monitoring of air quality for other cities is largely ignored. The aim of this study was (i) to determine and identify the elements deposited on the leaf surface of three tree species in three different road sites in different climates and traffic densities; (ii) to assess the effect of species and sites on the deposited elements; and (iii) to evaluate the relationship between large number of metal concentrations of leaves and leaf saturation isothermal remanent magnetization (SIRM).

2 Materials and methods

2.1 Study area and sampling

In each of the cities Babolsar (36° 32′ 1.80″ N, 52° 38′ 56.23″E), Babol (36° 41′ 52.22″ N, 52° 35′ 36.12″ E) and Boumehen (35° 43′ 55.40″ N, 51° 52′ 6.65″E) in Iran (Fig. 1), we selected a study site in order to compare the chemical composition of leaf deposited atmospheric particulate matter. The city of Boumehen is approximately 1960 m above sea level, Babolsar 21 m, and Babol city is 2 m below the sea level. Babol city is located 20 km from Babolsar city and 164 km from Boumehen. The prevailing wind direction in the year of sampling was northeast, west and northeast, and sum of precipitation was 1110, 764, 631mm in the cities of Babolsar, Babol and Boumehen, respectively, as measured in the nearest weather stations (data obtained from I.R. of Iran Meteorological Organisation, http://www.irimo.ir). The mean temperature in the cool season (winter time) was 8, 7 and 6.5°C, and in the hot season (summer time) it was 26, 26 and 30°C in the cities of Babolsar, Babol and Boumehen, respectively.

The road from Babol city was a boulevard with a width of around 30 m and high traffic density (more than 20000 vehicles each day in this road). In the city of Boumehen, at 30 km to the capital city Tehran, a road with high traffic density was selected. The city has different industrial activities (e.g., cement production, silica sand mining, hard rock, sand and gypsum mining, ceramic factory) at different distances (25-60 km) to the city centre. A local road from the sub-urban area of Babolsar city was selected as a reference location, with a distance of about 100-250 m to the southern Caspian Sea. In Iran, vehicles use different types of fuel, i.e. petrol, gasoline, compressed natural gas (CNG) and liquid petroleum gas (LPG).

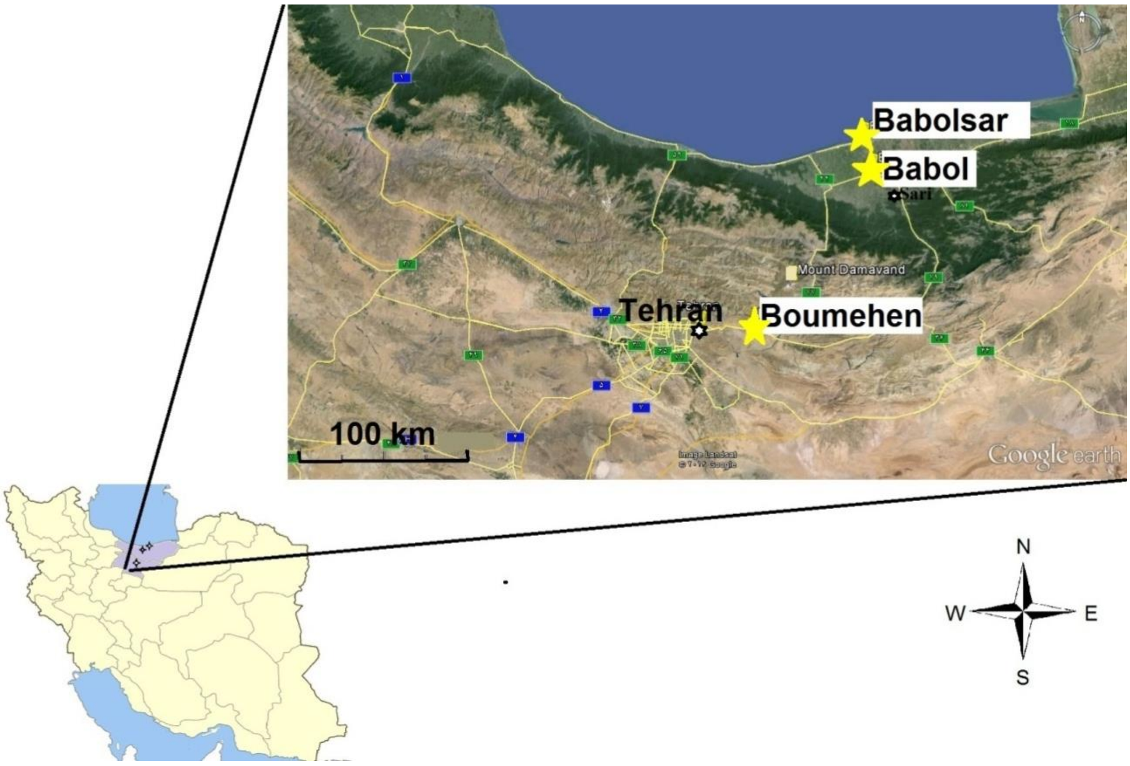

Fig. 1: study area indicating the three sampling sites (Babolsar, Babol and Boumehen) in the northern part of Iran (source: Google Maps)

Three evergreen species were selected, i.e. *Chamaecyparis lawsoniana* (English name: Lawson falcy) with scale-like leaves, *Ligustrum japonicum* (English name: wax-leaf privet) with broad leaves, and *Pinus brutia* subsp. *eldarica* (Medw) Silba

(English name: Eldar pine) with needles based on their availability near the selected roads.

In Babolsar, *P. brutia* subsp. *eldarica* trees were located at a distance of 150-250 m to the beach, while the *C. lawsoniana* trees were at 100-150 m to beach.

L. japonicum was sampled only in Babol. *C. lawsoniana* was sampled from the same site as *L. japonicum* in Babol and in Babolsar. *Pinus brutia* subsp. *eldarica* was sampled in the cities of Babolsar and Boumehen. Leaf samples were collected from 46 trees (10 trees from each species in the city of Babol and Boumehen, and 8 trees from each species in the city of Babolsar) at a height of 1.5-2 m from ground level on 2 and 3 July 2012. There was no rain at least for 10-15 days before sampling. Leaf samples from each tree were stored in a paper envelope and transferred to the laboratory for chemical and magnetic analyses.

2.2 Sample preparation and XRF analysis

In the lab, the samples were divided into two subsamples: one subsample was washed with 20 ml of deionised water in a glass beaker and gently rubbed for one minute with the fingers covered by gloves (for each leaf separately) to remove particles deposited on the leaf surface, and the other subsample remained unwashed. A subsample contained 1-2 leafy branchlets of *C. lawsoniana*, 5-6 leaves of *L. japonicum* or 6-8 needles of *Pinus brutia* subsp. *eldarica*. By comparison of the washed and unwashed subsamples, we can identify the elements that belong to deposited particles on the leaf surface, not to the leaf itself. Both washed and unwashed leaves were dried in an oven for 7 days at 45 °C. Then, the subsamples were powdered using a mortar and pestle. Subsequently, the weights of the subsamples were determined by an electronic balance with an accuracy of 0.0001 g.

For making a pellet, around 0.6 g glucose was pressed with 5 ton for 30 s. Then, 0.48 g sieved leaf powder was gently mixed with 0.08 g glucose and added to the glucose pellet surface. Thereafter, these double layer samples were pressed with

8 ton for 30 s. Samples were covered with microfilm and analyzed using energy dispersive X-ray Fluorescence (PANalytical, Epsilon 5) for the concentration of 28 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Sb, Cs, Ba and Pb).

2.3 Sample preparation and SIRM analysis

Between 4 to 8 leaves, branchlets or needles were tightly packed by cling film into a 10cc plastic container for magnetic measurement. The containers with the samples were magnetized with a pulsed DC magnetic field of 1 Tesla using a Molspin pulse magnetiser (Molspin Ltd, UK) as described by Matzka and Maher (1999). Subsequently, the saturation isothermal remanent magnetisation (SIRM) was measured using a Molspin Minispin magnetometer with high sensitivity ($\sim 10^{-9}$ A m^2). The instrument was calibrated after every ten measurements by means of a magnetically-stable rock specimen, as described by Kardel et al. (2011, 2012). The SIRM value was normalised to leaf dry weight (10^{-5} A m^2 kg^{-1}) and each SIRM value was the average of two measurements on the same sample.

2.4 Statistical analysis

First, the normality of the data was tested for all considered variables by Kolmogorov-Smirnov tests, and the data that did not meet normality were normalised by logarithmic transformations.

Significant differences in elemental concentration between unwashed and washed leaves were tested for each species and each polluted site (Boumehen and Babol) separately by t-tests.

Significant differences in elemental concentration between washed leaves (*C. lawsoniana* and *P. brutia* subsp. *eldarica*) for polluted sites and unwashed leaves for the reference site (Babolsar) were tested separately by t-tests.

Differences in concentrations of unwashed leaves and also in leaf SIRM values were tested between species and sites by using a two-way analysis of variance (ANOVA) procedure and a Tukey-HSD test.

Pearson's correlation analysis was performed to evaluate the relationship between SIRM values of unwashed leaves and all element concentrations of unwashed and washed leaves.

A Principal Component Analysis (PCA) using varimax orthogonal rotation with Kaiser normalization was applied on the elemental concentrations of unwashed and washed leaves, and also on the elemental concentrations of the unwashed leaves, to 'cluster' the sites and species, to estimate the potential common sources and to reduce multicollinearity. Before the PCA, Kaiser-Meyer-Olkin (KMO) measurement of sampling adequacy and Bartlett's test of sphericity were used to test for data suitability. Statistical analysis was carried out using R version 3.4.2 software (R Development Core Team 2017). The Fcatoextra and ggplot2 Package (Wickham, 2009) and FactoMineR package (Le et al. 2008; Husson et al. 2017) were used for PCA analysis and making PCA biplots.

3 Results

3.1 Chemical composition of unwashed leaves vs washed leaves

The concentrations of macro-elements in the unwashed leaves amounted up to 76 mg/g dry weight, and 239 µg/g dry weight for micro-elements (Table 1). In the washed leaves, the macro-elements had concentrations of up to 62 mg/g and the micro-elements up to 150 µg/g. The highest concentrations were found for Ca and K. In the washed leaves of one or more species, the concentrations of Si, Cr and Co were below the detection limit. The Pb concentrations were below detection limit in all washed and unwashed samples.

The order of abundance of deposited macro-elements on the leaf surface, based on the difference between the unwashed and washed leaves, was Ca> Si> Fe> Al> Mg> Ti> Na> Mn, and for micro-elements was Zn> Cr> Ba> Ni> Cu> Sb>

Zr> V> Rb> Co. The unwashed leaves of *P. brutia* subsp. *eldarica* in the city of Boumehen had significantly higher concentrations of Al, Ca, Fe, Mg, Mn, Na, Si, Ti, Ba, Co, Cr, Cu, Ni, Rb, V, Zn, and Zr elements compared to its washed leaves ($p<0.05$) (Table 1). The unwashed leaves of *C. lawsoniana* from Babol city had significantly higher concentrations of Al, Fe, Ca, Mn, Si, Ti, Ba, Co, Cr, Cu, Ni, Rb, Sb, V, Zn and Zr elements compared to the washed leaves of this tree species ($p<0.05$) (Table 1). The unwashed leaves of *L. japonicum* in the city of Babol had, compared to the washed leaves, significantly higher concentrations of Al, Ca, Fe, Mg, Si, Ti, Co, Cu, Ni, V, and Zr elements ($p<0.05$) (Table 1). For Cl, K, P, S, As, Cd, Cs, Pb, Sn, and Sr elements, there was no significant difference between washed and unwashed leaves of any of these species. So for further analysis, these elements are not considered.

Moreover, the PCA biplot on all chemical elements of unwashed and washed leaves showed higher values of all considered elements that relate to the first axis for unwashed leaves compared to the washed leaves (Fig. 2). The elements that relate to the first axis were Al, Fe, Ca, Si, Ti, Co, Cr, Cu, Ni, Rb, V, Zn and Zr.

Table 1: Mean (± standard deviation) of elemental concentrations (in mg/g dry weight or µg/g dry weight) in unwashed and washed leaves of *L. japonicum, C. lawsoniana* and *P. brutia* subsp. *eldarica* (Medw) Silba, from Boumehen and Babol. Significant differences ($p<0.05$) between unwashed and washed leaves are shown in bold.

	P. brutia subsp. *eldarica*		*C. lawsoniana*		*L. japonicum*	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed
Macro-elements (mg/g)						
Al	**3.28±0.71**	1.70±0.18	**5.48±1.04**	4.21±0.38	**5.01±0.62**	3.91±0.44
Ca	**23.75±3.63**	15.02±2.09	**52.74±5.90**	41.06±4.21	**76.33±9.89**	62.27±9.95
Cl	3.45±1.77	3.50±1.30	2.11±0.95	2.52±0.97	1.70±0.32	1.92±0.59
Fe	**6.21±1.52**	2.31±0.33	**8.90±1.96**	4.15±0.62	**3.13±0.53**	1.41±0.04

K	26.34±4.06	26.80±1.88	40.55±7.36	32.68±8.27	16.98±2.84	19.97±3.02
Mg	**1.93±0.39**	1.10±0.18	3.67±0.82	3.32±0.46	**3.90±0.47**	3.15±0.42
Mn	**0.19±0.02**	0.14±0.02	**0.14±0.03**	0.11±0.01	0.23±0.05	0.29±0.11
Na	**1.29±0.08**	1.14±0.03	1.70±0.19	1.69±0.13	1.82±0.11	1.65±0.11
P	3.09±0.25	2.79±0.18	2.91±0.57	3.32±0.58	3.02±0.21	2.77±0.46
S	3.85±0.87	2.38±0.68	4.76±0.63	3.60±1.19	5.66±0.65	4.61±1.49
Si	**2.36±2.41**	DL	**8.10±3.17**	0.40±0.27	**5.41±2.54**	2.27±0.89
Ti	**0.40±0.09**	0.13±0.02	**0.81±0.19**	0.35±0.08	**0.25±0.06**	0.09±0.00
Micro-elements (µg/g)						
As	11.50±0.51	11.50±0.57	9.80±1.52	9.60±0.00	10.20±0.45	10.25±0.50
Ba	**80.50±32.56**	22.75±8.18	**80.20±25.96**	32.50±7.85	143.60±33.90	150.75±24.05
Cd	2.00±0.00	2.00±0.00	2.00±0.00	2.00±0.00	2.00±0.00	2.00±0.00
Co	**2.10±0.64**	0.75±0.50	**3.20±0.84**	1.00±0.00	**0.80±0.45**	DL
Cr	**53.10±20.51**	DL	**165.80±45.80**	21.25±13.15	**17.40±19.02**	DL
Cs	5.15±0.59	4.50±0.57	4.00±1.22	3.75±0.50	4.60±0.55	4.75±0.50
Cu	**61.25±21.02**	19.25±6.94	**38.40±14.65**	15.50±4.43	**8.60±3.78**	1.50±1.91
Ni	**33.55±7.36**	12.00±2.16	**64.00±15.05**	19.75±4.11	**18.40±5.18**	7.50±1.00
Pb	DL	DL	DL	DL	DL	DL
Rb	**4.85±1.66**	1.25±0.50	**5.60±1.52**	1.00±0.00	2.20±0.84	1.75±1.26
Sb	40.05±11.56	29.75±13.32	**19.40±11.57**	3.75±2.63	36.80±8.90	35.75±8.42
Sn	1.10±0.31	1.00±0.00	1.20±0.45	1.25±0.50	1.00±0.00	1.00±0.00
Sr	93.65±13.73	81.50±14.05	161.80±23.40	168.75±47.38	147.2±22.55	144.50±38.56
V	**10.00±3.01**	2.00±0.82	**17.20±3.42**	8.00±0.00	**6.00±1.58**	3.25±0.50
Zn	**116.05±31.70**	37.25±14.59	**239.80±79.05**	69.00±17.00	**85.40±53.40**	56.25±49.54
Zr	**8.75±2.57**	2.50±0.58	**16.00±4.06**	4.75±1.71	**4.60±1.82**	2.00±0.00

DL: below detection limit

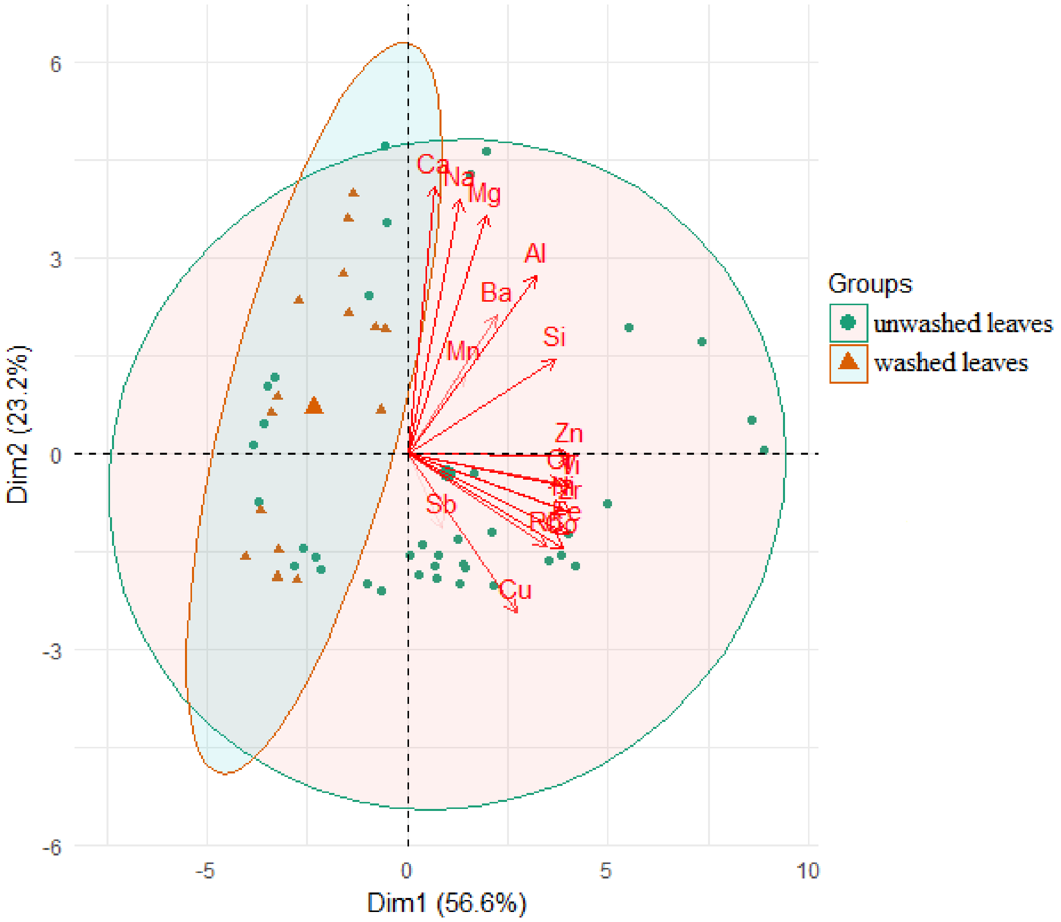

Fig. 2: PCA biplot for elements of unwashed and washed leaves in Boumehen and Babol sites.

3.2 Chemical compositions of roadside tree leaves in different sites

The statistical results for unwashed leaves revealed that species had a significant effect on the accumulation of the chemical elements. The unwashed leaves of *C. lawsoniana* had significantly ($p<0.05$) higher concentrations of Fe, Ti, Co, Cr, Cu, Ni, Rb, Zn, Zr, V and lower concentrations of Ca, Mn, Ba, Sb compared to unwashed leaves of *L. japonicum* in the same site (Babol; Table 2). The unwashed leaves of *C. lawsoniana* had significantly higher concentrations of Al, Ca, Mg, Na and lower concentrations of Fe, Ti, Cr, Ni, Sb compared to unwashed leaves of *P. brutia* subsp. *eldarica* in the same site (Babolsar; $p<0.05$; Table 2).

Moreover, the statistical results revealed that chemical compositions of unwashed leaves and their concentration highly depended on site ($p<0.05$). The Boumehen and Babol sites had significantly higher concentration of all considered elements compared to the reference site in Babolsar, except for Ca, Rb and Sb in Boumehen, and Na in Babol, for the same species ($p<0.05$) (Table 2).

The statistical results showed there was no significant difference between elements for washed leaves of *P. brutia* subsp. *eldarica* in Boumehen site compared to unwashed leaves of this species in the reference site at Babolsar except for Al, while the concentration of Al, Fe, Ti, Mn, Ni and Zn elements for washed leaves of *C. lawsoniana* were significantly ($p<0.05$) higher in Babol site compared to unwashed leaves of this species in the reference site Babolsar (data are shown in Table 1 and 2).

Table 2: Chemical composition (mean±standard deviation) of unwashed leaves of *L. japonicum, C. lawsoniana* and *P. brutia* subsp. *eldarica* from different sites. Significant differences between sites for each species at p=0.001 '***', p= 0.01 '**', p= 0.05 '*'. Significant differences between co-located species are shown in bold.

	P. brutia subsp. *eldarica*		*C. lawsoniana*		*L. japonicum*
	Boumehen	Babolsar	Babol	Babolsar	Babol
Macro-elements (mg/g)					
Al	3.28±0.72***	2.06±0.12	5.48±1.04**	**2.76±0.25**	5.01±0.62
Ca	23.74±3.63	26.17±7.42	52.74±5.91*	**39.81±7.26**	**76.33±9.89**
Fe	6.21±1.52***	**2.36±0.40**	**8.89±1.96*** **	1.53±0.19	3.13±0.52
Mg	1.93±0.39**	1.47±0.14	3.67±0.82*	**2.34±0.27**	3.90±0.47
Mn	0.19±0.02**	0.08±0.03	0.14±0.03**	0.06±0.02	**0.23±0.05**
Na	1.29±0.08*	1.21±0.05	1.70±0.19	**1.50±0.08**	1.82±0.11
Si	2.36±2.41***	DL	8.10±3.18**	DL	5.41±2.54
Ti	0.40±0.09***	**0.18±0.04**	**0.81±0.19** **	0.10±0.02	0.25±0.06
Micro-elements (µg/g)					

Ba	80.50±32.56***	12.75±4.11	80.20±25.96***	17.75±3.09	**143.60±33.90**
Co	2.10±0.64**	0.75±0.50	**3.20±0.84****	DL	0.80±0.45
Cr	53.10±20.51***	**17.00±9.09**	**165.80±45.81****	1.00±2.00	17.40±19.02
Cu	61.25±21.02***	12.50±9.25	**38.40±14.65****	10.75±3.50	8.60±3.78
Ni	33.55±7.36***	**18.75±3.50**	**64.00±15.05****	12.00±2.16	18.40±5.18
Rb	4.85±1.66	1.75±2.22	**5.60±1.52*****	0.75±0.96	2.20±0.84
Sb	40.05±11.56	**34.50±7.23**	19.40±11.57*	3.25±3.95	**36.80±8.90**
V	10.00±3.01***	4.75±1.90	**17.20±3.42*****	2.25±1.26	6.00±1.58
Zn	116.05±31.70***	1.75±3.50	**239.80±79.06****	DL	85.40±53.46
Zr	8.75±2.57***	3.50±1.00	**16.00±4.06****	2.00±0.00	4.60±1.82

3.3 Leaf SIRM of roadside tree leaves in different sites

The leaf SIRM values of all species and sites varied between 0.03 and 893.49 x 10^{-5} A m^2 kg^{-1} (Table 3). Both *C. lawsoniana* and *P. brutia* had significantly ($p<0.0001$) higher leaf SIRM values in Babol and Boumehen than in reference site Babolsar.

In Babol, leaves of *C. lawsoniana* had significantly higher SIRM values compared to *L. japonicum* ($p<0.05$), but there was no significant difference between leaf SIRM values of co-located species (*C. lawsoniana* and *P. brutia*) in Babolsar.

Table 3: Mean (± SD) SIRM (x10^{-5} A m^2 kg^{-1}) for unwashed leaves of *L. japonicum, C. lawsoniana* and *P. brutia* subsp. *eldarica* from Boumehen, Babol and the reference site Babolsar. Significant differences ($p<0.05$) are shown with different letters.

Species	Site	SIRM x10^{-5} A m^2 kg^{-1}
P. brutia subsp. eldarica	Boumehen	696.89 ± 83.66^{c}
	Babolsar	0.06 ± 0.01^{a}
C. lawsoniana	Babol	783.97 ± 92.73^{d}

	Babolsar	0.05±0.02^{a}
L. japonicum	Babol	629.69±44.09^{b}

3.4 Correlation between leaf SIRM and deposited elements on leaf surface

There was a strong, positive and significant correlation between Fe, Ti, Co, Cr, Cu, Ni, Rb, V, Zn, and Zr elements and between Al, Ca, Mg, Na, Si, and Ba elements in unwashed roadside leaves (Table 4a), and the same correlations persisted for washed leaves except for Rb (Table 4b). In unwashed leaves, a positive and significant correlation were observed between Si,and Al, Ca, Fe, Mg, Na, Ba, Co, Cr, Ni, Rb, V, Zn, Zr, SIRM, while in washed leaves, a significant and positive correlation persisted between Si and Al, Ca, Mg, Mn, Na, Ba, Zn. Moreover, a positive and significant correlation was observed between leaf SIRM and Al, Fe, Mn, Si, Ti, Ba, Co, Cu, V, Zn, Zr elements of unwashed roadside leaves, while for washed leaves were observed a positive and significant correlation between SIRM and Fe, Co, Ni, Zn elements (Table 4).

3.5 PCA analysis on elemental concentrations and SIRM of unwashed leaves

First, the result of Bartlett test was significant ($p < 0.05$) and the criterion of Kaiser Meyer-Olkin (KMO) obtained 0.79 which confirms the suitability of the data for further analysis using PCA on the unwashed leaves. The components with eigenvalues greater than one were considered for varimax rotation to obtain the final matrix. Also factor loadings greater than 0.50 were considered significant. The first component of the PCA for unwashed leaves explained 55.58 % of the total variance and showed strong positive loadings for Fe, Ti, Co, Cr, Ni, V, Zn and Zr, and moderate positive loadings for Al, Si, Cu, Rb and SIRM. The second factor explained 23.37 % of the total variance with high positive loadings of Ca, Mg, Na and Ba. The third factor explained 12.02 % of total variance with positive loadings Mn and Sb.

The biplot for unwashed leaves (Fig. 3) revealed that the first component differentiated the roadside leaves (Boumehen and Babol) from the leaves at the reference site (Babolsar), and it also differentiated between *C. Lawsoniana* and *L. Japonicum* in Babol. The second component differentiated between species (Fig. 3). Moreover, the biplot showed that SIRM differentiated between sites and species in the same way as the derived chemical elements from traffic and soil dust (Fig. 3).

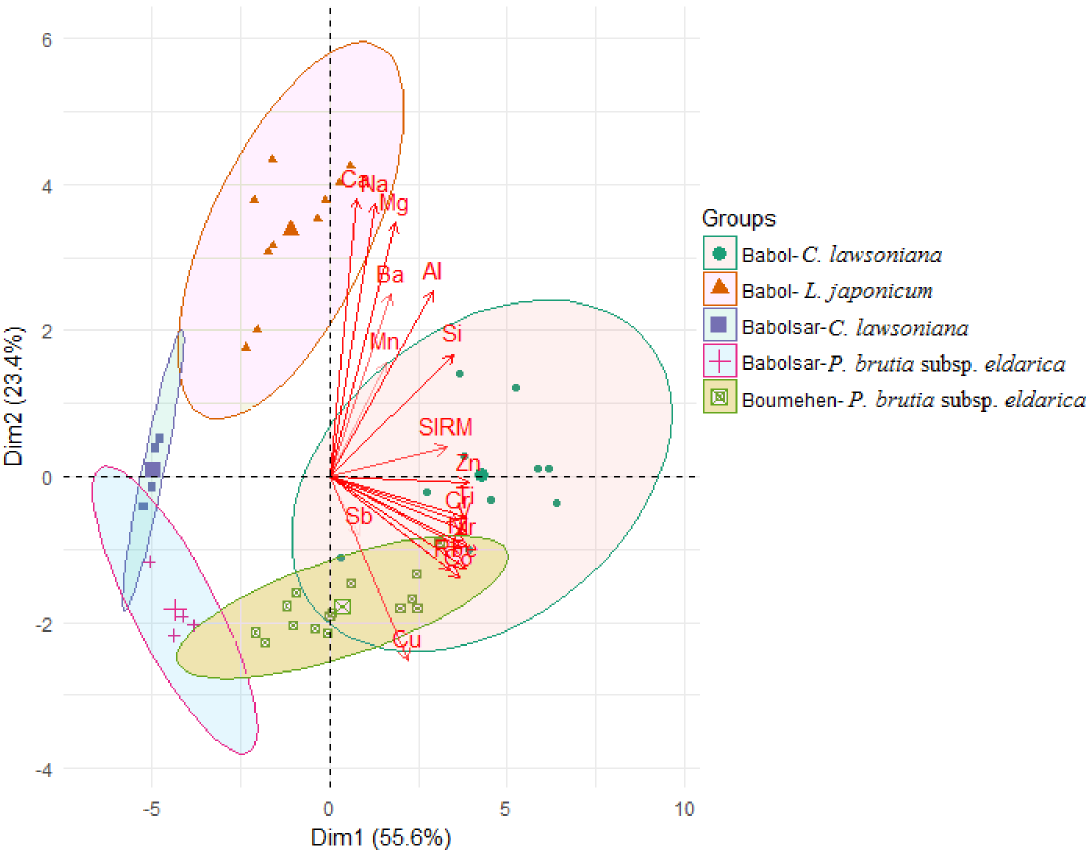

Fig. 3: PCA biplot for elements and SIRM value of unwashed leaves in different sites and species

4 Discussion

4.1 Chemical compositions of leaves

When using heavy metal concentration of plant leaves for biomonitoring of atmospheric pollution, it is often difficult to distinguish the atmosphere (deposition) from the soil (root uptake) as sources of the observed metal concentration in the leaf sample. Leaf washing is a solution to overcome this problem (Al-Alawi and Mandiwana 2007). The differences in element concentrations between washed and unwashed leaves revealed that deposited particles on the leaf surface in the studied sites may contain various elements including Mg, Al, Si, P, S, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Zr, Sb and Ba. Our results confirm that the atmospheric deposited particles contain various metals which are in line with finding of other studies. Al-Alawi and Mandiwana (2007) used the washing technique for the leaves of *Pinus halepensis* L. and reported that the unwashed leaves had significantly higher content of Pb, Cu, Zn and Cd compared to the washed leaves, confirming that atmospheric deposition contains metals in different sites of Amman City, Jordan. Oliva and Espinosa (2007) investigated metal concentration in soil, plant leaves and the atmosphere, and they reported no clear correlation between soil and plant leaves. They stated that their results indicate that the considered metal concentration in plant leaves mostly related to atmospheric metal concentration.

The results of leaf washing in our study showed that there was no significant difference between washed and unwashed leaves for Cl, K, P, S, As, Cd, Cs, Pb, Sn, and Sr elements. These results indicate that tree leaves may not be a suitable biomonitor for these elements or request other methodology for the detection of these elements. The possible reasons are: a) these elements are just not present in the atmosphere at high concentrations and so deposition is low (e.g. P, Pb, Sn and Cd) or b) some of these elements are present in such high concentration in the leaf, that low deposition of these elements (such as K) on the leaves are not sufficient to considerably increase the total element concentrations of the unwashed leaves, and c) elements such as K leach in huge amounts from the leaves when immersed in the water, which could have increased the K concentration in the washing solution very fast and therefore the remaining drops of washing solution on the leaves may have still contributed a lot to the concentrations of the washed leaves. Further research is needed on soil, atmospheric dust and tree leaves to identify the source of these elements (Cl, K, P, S, As, Cd, Cs, Pb, Sn, and Sr) in the atmospheric deposited particles. Our results on concentrations of water soluble ions in the washing solution in the same samples revealed significantly high concentration of SO_4^{2-} in polluted sites (Boumehen and Babol) compared to Babolsar and coming from atmosphere (data not published), while in the present study there was no significant difference in S concentration between unwashed/washed leaves in polluted sites, probably because these SO_4^{2-} ions in the washing solution were coming from leaching out of the interior of the leaf. However, its concentration was significantly higher in Boumehen and Babol sites compared to Babolsar site (data not shown).

Serbula et al. (2012) assessed heavy metal concentrations in different organs of *Robinia pseudoacacia* L. and topsoil in an industrial area in Bor (Eastern Serbia). They reported that *R. pseudoacacia* is not a suitable indicator of air and soil As pollution as the As concentration was high in air and topsoil but not in the plant organs. Moreover, in agreement with our results, Norouzi et al. (2015) investigated the concentrations of Cu, Fe, Mn, Ni, Pb, and Zn elements of *Platanus orientalis* L. tree leaves in Isfahan, Iran. They reported *P. orientalis* tree leaves as a suitable bioindicator for atmospheric pollution for all considered heavy metals except Pb.

In comparison with other studies, our results for roadside trees showed elevated values for most considered element concentrations, and leaf SIRM. For instance, all considered tree species in Babol and Boumehen sites in our study showed a higher value for Ba, Cd, Cr, Cu, Fe, and Zn elements in leaves comparing to leaves of *Quercus ilex* L. (also an evergreen species) in Florence, Italy, except for Mn and Pb (Ugolini et al. 2013). Moreover, the concentration of Al, Ba, Cd, Co, Cr, Cu, Fe, Ni, Sr, V, and Zn elements and the SIRM value for all considered species on our roadside sites (Babol and Boumehen) were much higher compared to two moss species (*Sphagnum girgensohnii* and *Hypnum cupressiforme*) exposed over the city of Belgrade for short time exposure (during summer) except for Pb (Vuković et al. 2015), as Pb was not detected in our study.

4.2 Effect of sites and species on leaf elements and SIRM

Our results showed a significant effect of site and species on the leaf elemental concentrations and the leaf SIRM, and the effect of site is more pronounced than the effect of species in the variation of chemical composition.

The results of chemical composition of the leaf showed that the concentration of many heavy metals is different for the different sites and species, and the PCA biplot confirms these results accordingly (Fig 3). For instance, the high concentration of Cu and Sb elements for tree leaves of *Pine* sp. in the Boumehen compared to the Babolsar indicates that the source of pollution in Boumehen site is different from that in the Babolsar site or the same source but further away from the sampled trees. As the differences between the roadside leaves and the reference site leaves mainly occurred along the first axis of the PCA, the roadside and reference sites thus mainly differed in element concentrations that showed high factor loadings with this axis, i.e. Fe, Ti, Co, Cr, Ni, V, Zn, Zr and to a lesser extent Al, Si, Cu, Rb and SIRM. Likewise, differences in elemental concentrations between species at the same site were most pronounced in the concentrations of elements that had high factor loadings with the second axis of the PCA, i.e. Ca, Na, Mg, Ba and Cu. We can conclude that the presence of road traffic mainly leads to an increase in metals such as Fe, Ti, Co, Cr, Ni, V, Zn and Zr, and that differences between species are most pronounced in elements like Ca, Na and Mg which are mainly deposited as larger particles.

Significant differences in the metal concentration of leaves for the co-located species in Babol are related to the plant structure and the leaf surface characteristics. Our results showed that *C. lawsoniana* with micro-roughness leaf surface had significantly higher metal concentrations and SIRM values compared to *L. japonicum* with smooth and waxy leaf surface in Babol. These results confirm a higher ability of *C. lawsoniana* to accumulate atmospheric particles in comparison with *L. Japonicum.* In the Babolsar site, *P. brutia* subsp. *eldarica* had significantly higher concentration of metals with atmospheric sources and lower soil dust and sea salt sources compared to *C. lawsoniana*. The reason could be that the trees were at a close distance from the road for *P. brutia* subsp. *eldarica*, while the *C. lawsoniana* trees were closer to the beach. The effect of distance of tree leaves from the roads has been reported by other studies too (e.g., Matzka and Maher 1999; Szönyi et al. 2008; Kardel et al. 2012).

Our results are in agreement with those of Moreno et al. (2003) who first pointed out the effect of species and Freer-Smith et al. (2005), who reported an effect of species and site on atmospheric-particle accumulation on tree leaves. An effect of species on atmospheric-particle accumulation has been reported by other studies too (Amato-Lourenco et al. 2016; Jamil et al. 2009; Sæbø et al. 2012; Song et al. 2015).

Wang et al. (2006) observed plant with a large micro-roughness leaf surface accumulates a large amount of dust particles. Wang et al. (2015) observed epicuticular wax ultrastructures significantly contributing to particle accumulation on leaf surfaces. Simon et al. (2014) reported no significant difference in the amount of deposited particles along an urbanization gradient due to metrological conditions and topography, but deposited particles depended on species characteristics (e.g. trichomes density on leaf surface). A study by Sæbø et al. (2012) on 47 tree and shrub species identified hair density, wax quantity and specific leaf area (leaf area to leaf dry weight ratio) as leaf surface traits that affect PM accumulation. Our observations of the differences in species are in line with the relationship of higher SLA with higher particle deposition as observed by Sæbø et al. (2012) and Wang et al. (2006). Next to that, also leaf longevity and related time exposure play an important role in the species effect on accumulation of particles on leaves (Lehndorff et al. 2006). An effect of leaf surface characteristics and exposure time on magnetic particles accumulation has been reported by other studies too (Hofman et al. 2014; Kardel et al. 2011; Mitchell et al. 2010).

4.3 Deposited metals: sources and their relation to leaf SIRM

The link between Co, Cr, Cu, Fe, Ni, Ti, V, Zn, Zr metals and motorised road traffic is known from literature and these metals occur in the unwashed leaves, so the presence of these metals in the leaves of Boumehan and Babol strongly indicate that road traffic is an important contributor to the atmospheric pollution in these sites. In the first component of the PCA for unwashed leaves, moderate loadings of Al, Cu and Si indicate that these elements co-occurred with elements derived from traffic and have other sources too. Moreover, the good correlation of Al, Cu, Rb and Si with leaf SIRM for unwashed leaves indicates that leaf SIRM is a suitable indicator of these elements. The second component has high positive loadings of Ca, Mg, Na, and Ba, which are considered as crustal and sea salt elements, indicating that soil dust and sea salt could be another important source of deposited particles. Moreover, elements from sea salt and marine spray were not significantly correlated with leaf SIRM values since they are diamagnetic (Sagnotti et al. 2006), so that leaf SIRM could not serve as a proxy for these elements. The third component has positive loadings of Mn and Sb, indicating that these elements have another source comparing to the two first components, which could be industrial activities. Moreover, leaf SIRM also can be used for monitoring of industrial activities when the activities produce magnetic particles (Hanesch et al. 2003; Schädlich et al. 1995).

The leaf SIRM correlated significantly and positively with the elemental concentrations of unwashed leaves except for Na, Mg, Ca, Sb and Rb, while most relationships weakened or even disappeared when the leaves were washed. These findings suggest that leaf SIRM is mainly related to the metals deposited on the leaf surface and are in agreement with other studies. For example, Lu et al. 2008 report a high correlation between magnetic properties and heavy metal content (mainly Fe, Mn, and Cu) of deposited dust on leaf surface in China. Also, Wang (2016) found high correlation of Cu and Ba with SIRM in street dust in Xuzhou, China. Castanheiro et al. (2016) were able to relate leaf SIRM with the Fe, Zn and Pb content of particles deposited on *Hedera* sp. leaves in an urban environment in Belgium, but also significant relationships with the metals Cd and Mn were found. Several former studies introduced leaf SIRM as good proxy of atmospheric pollution, traffic–derived or industry–derived particles and dust pollution (Hansard et al. 2011; Hofman et al. 2014; Kardel et al. 2012; Maher et al. 2008), which is confirmed in this study.

5 Conclusions

Our results revealed that the leaves of roadside trees are able to accumulate on their surface various elements including Al, Fe, Ca, Mg, Mn, P, S, Si, Ti, Ba, Co, Cr, Cu, Ni, Sb, Rb, V, Zn, Zr. Thus, it can be concluded that leaves can be a suitable monitor for these deposited elements. While leaf surface may not be a good indicator for deposition of some metals such as K, Cl, P, S, As, Cd, Cs, Pb, Sn and Sr elements.

From the chemical composition and SIRM value of the three considered species, it can be concluded that *Chamaecyparis lawsoniana* has the highest potential to accumulate atmospheric particles for monitoring purposes in Iran as well as for other places where this species is available.

Fe, Ti, Co, Cr, Ni, Rb, V, Zn, and Zr elements were abundantly observed on leaves in two sites and these elements are known in literature to originate from motorized road traffic, which indicates the main source of pollution in Babol and Boumehen is nearby road traffic rather than other, more distant sources. The most abundant traffic–derived metals showed to be strongly correlated with leaf SIRM. The leaf SIRM and the concentration of traffic-derived metals clearly depend on sites and species with the effect of site being much stronger than the effect of species. Overall, it can be concluded that leaf SIRM is a good proxy for anthropogenic particles e.g. derived from traffic and/or industrial activity, but is not a suitable indicator for sea salt elements.

This study, by indicating suitable trees and appropriate analytical methods for air pollution monitoring, provides valuable information for further urban managements and planning, and biomonitoring of atmospheric PM pollution in Iran and anywhere else where the studied trees occur.

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Table 4: Correlation matrix for the SIRM of unwashed leaves and the concentrations of macro and micro elements (µg/g) of a) unwashed leaves and b) washed leaves. Significant correlations are shown in bold (p<0.05).

a)

	Macro elements							Micro elements										Magnetic parameter
	Ca	Fe	Mg	Mn	Na	Si	Ti	Ba	Co	Cr	Cu	Ni	Sb	Rb	V	Zn	Zr	SIRM
Al	**0.70**	**0.57**	**0.93**	0.45	**0.85**	**0.94**	**0.69**	**0.74**	**0.53**	**0.63**	0.09	**0.60**	0.05	0.46	**0.66**	**0.74**	**0.64**	**0.56**
Ca		-0.11	**0.89**	0.26	**0.93**	**0.53**	0.10	**0.50**	-0.15	0.11	-0.49	0.02	-0.22	-0.19	0.03	0.17	0.01	0.08
Fe			0.25	0.41	0.09	**0.68**	**0.94**	0.46	**0.97**	**0.84**	**0.75**	**0.89**	0.28	**0.88**	**0.95**	**0.91**	**0.97**	**0.76**
Mg				0.31	**0.98**	**0.80**	0.44	**0.63**	0.21	0.42	-0.21	0.35	-0.13	0.15	0.38	0.49	0.35	0.32
Mn					0.22	0.43	0.28	**0.80**	0.35	0.13	0.44	0.20	**0.56**	0.43	0.33	0.48	0.32	**0.76**
Na						**0.69**	0.31	**0.54**	0.05	0.30	-0.34	0.21	-0.23	0.00	0.22	0.35	0.20	0.18
Si							**0.79**	**0.71**	**0.65**	**0.71**	0.20	**0.70**	0.16	**0.59**	**0.76**	**0.83**	**0.75**	**0.55**
Ti								0.40	**0.92**	**0.95**	0.49	**0.96**	0.12	**0.76**	**0.96**	**0.94**	**0.98**	**0.67**
Ba									0.42	0.23	0.32	0.29	0.46	**0.52**	0.44	**0.55**	0.44	**0.64**
Co										**0.81**	**0.72**	**0.87**	0.32	**0.88**	**0.93**	**0.88**	**0.95**	**0.73**
Cr											0.34	**0.99**	-0.01	**0.63**	**0.91**	**0.86**	**0.89**	**0.55**
Cu												0.45	0.42	**0.75**	**0.55**	**0.53**	**0.61**	**0.63**
Ni													0.09	**0.72**	**0.95**	**0.89**	**0.93**	**0.60**
Sb														0.45	0.21	0.25	0.21	0.39
Rb															**0.82**	**0.77**	**0.85**	0.40
V																**0.89**	**0.95**	**0.68**
Zn																	**0.95**	**0.77**
Zr																		**0.77**

b)

	Macro elements							Micro elements										Magnetic parameter
	Ca	Fe	Mg	Mn	Na	Si	Ti	Ba	Co	Cr	Cu	Ni	Sb	Rb	V	Zn	Zr	SIRM
Al	**0.91**	0.31	**0.99**	0.26	**0.98**	**0.57**	0.40	**0.52**	0.08	**0.51**	-0.35	0.33	-0.43	-0.21	**0.66**	**0.50**	0.30	0.29
Ca		-0.01	**0.93**	0.42	**0.92**	**0.73**	0.00	**0.74**	-0.24	0.23	**-0.63**	-0.01	-0.15	-0.03	0.42	0.34	0.04	0.08
Fe			0.22	-0.32	0.19	-0.28	**0.98**	-0.40	**0.83**	**0.81**	**0.54**	**0.92**	**-0.76**	-0.36	**0.85**	**0.50**	**0.91**	**0.54**
Mg				0.22	**0.99**	**0.54**	0.31	**0.53**	-0.00	0.44	-0.39	0.25	-0.37	-0.16	**0.60**	0.40	0.20	0.18
Mn					0.20	**0.84**	-0.33	**0.71**	-0.25	-0.23	**-0.53**	-0.35	0.18	0.01	-0.17	**0.61**	-0.30	0.35
Na						**0.51**	0.28	**0.51**	-0.02	0.43	-0.39	0.24	-0.36	-0.15	**0.57**	0.37	0.17	0.16
Si							-0.22	**0.91**	-0.38	-0.09	**-0.64**	-0.28	0.15	0.07	0.00	**0.51**	-0.17	0.24
Ti								-0.34	**0.73**	**0.84**	0.43	**0.88**	**-0.77**	-0.32	**0.89**	0.47	**0.93**	0.43
Ba									-0.44	-0.21	**-0.68**	-0.41	0.29	0.02	-0.08	0.25	-0.28	0.16
Co										**0.56**	**0.70**	**0.80**	**-0.56**	-0.43	**0.60**	0.43	**0.63**	**0.63**
Cr											0.31	**0.91**	**-0.70**	-0.31	**0.81**	0.48	**0.84**	0.41
Cu												**0.60**	0.15	-0.02	0.12	0.07	0.47	0.25
Ni													**-0.70**	-0.35	**0.78**	0.47	**0.85**	**0.52**
Sb														**0.69**	**-0.73**	0.48	**-0.62**	**-0.51**
Rb															-0.33	0.48	-0.19	**-0.56**
V																0.48	**0.75**	0.43
Zn																	0.47	**0.70**
Zr																		0.38