Wavelength dispersive X–ray fluorescence spectrometry as a tool for trace element determination in Pistacia vera L. leaves and soils

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Research Article

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Abstract

Pistachio (*Pistacia vera* L.) is known as important nut crop in the world with high nutritional and commercial relevance. In the present study, the concentrations of selected major and trace elements (Br, Ca, Cu, Fe, K, Mg, Mn, P, Sr, and Zn) in *P. vera* samples as well as theirs ambient soils from two geographical Algerian sites (Djelfa and Laghouat districts) were measured. The analytical measurements were performed by means of a wavelength dispersive X–ray fluorescence spectrometer (WDXRF). Results showed that highest contents of Br, Ca, Fe, and Mg were reported in samples collected from *Sidi Makhlouf* (Laghouat) orchard. However, Cu concentration is higher in *P. vera* from *Ain El Ibel* (Djelfa) province. For the remaining elements namely K, Mn, P, Sr and Zn, the values are comparable between both provinces. The maximum soil contents of Cu, K, and Mn were found in *Sidi Makhlouf* grove. However, the highest amount of Br was detected in soil samples collected from *Ain Ibel* orchard. No significant difference for Ca, Fe, Mg, P, Sr, and Zn concentrations was found between both soil orchards. These data must be taken into account during fertilization of pistachio orchards, in order to prevent nutritional disorders and to enhance productivity and kernel quality.

1. Introduction

The wavelength dispersive X–ray fluorescence spectrometry (WDXRF) is a non–destructive instrument for fast quantitative measurement of macro– and microelements in a wide range of sample kinds (mining, environmental, geological, biological, pharmaceutical samples). This procedure permits multi-elemental analysis in short time and high precision compared to other traditional analytical methods (Zawisza et al., 2012; Smoliński et al., 2016).

Pistachio (*Pistacia vera* L.) is an important rustic nut tree in the Asian and Mediterranean areas (Turkey, Syria, Italy and Greece) where it can survive in stony poor calcareous (alkaline) soils (Fig. 1). For longtime, fertilization programs for pistachio groves have largely ignored, due to its low nutrient needs and high rusticity to harsh conditions (Demirkiran and Cengiz, 2010.).

For human health, it is well known that intake of pistachio nuts considerably decreases the oxidative stress and LDL cholesterol, enhances antioxidant capacity and prevents damages produced by free radicals (reactive oxygen species), due to its high total polyphenol content (Arcan and Yemenicioglu, 2009; Fabani et al., 2013).

The most works performed so far pistachio leaves were carried out with its organic constituents such as flavonoids, anthocyanins and phenolic contents (Hosseinzadeh et al., 2012; Elakremi et al., 2022). However, to our knowledge, this nut tree has still not received enough interest toward their composition in mineral and trace elements.

It is known that macro– and microelement composition of plant tissues are in distorted relation with the mineral pool existed in the rooting zone of the plant. The bioaccumulation of chemical elements differs with plants, trace element kinds, and soil, in which the plants were grown (Anderson and Smith, 2005).

The Mediterranean arid soils are characterized by a high alkalinity ($pH > 7$) and elevated carbonate concentrations ($CaCO_3$), which may led to low bioavailability of some essential trace elements for arboriculture (Halitim, 1988). The acidification and application of microelement amendments to arid calcareous soils may improve the tree growth and increases their productivity (Domínguez et al. 2008).

In this investigation we sought to: (1) explore the differences between the bioaccumulation abilities of trace elements across the two *P. vera* orchards, (2) evaluate the effect of geographical province on the elemental levels, (3) elucidate relationships that exist between major and trace elements in leaves tissues and adjacent soil which pistachios were grown (4) and finally to compared the results with reported literature data.

2. Material and Methods

2.1. Pistachio grove description

The study was conducted in two productive *P. vera* orchards grafted on *P. Atlantica* rootstock and planted with density of 200 trees/ha in the Djelfa and Laghouat provinces, southern Algeria. The first orchard was located in *Ain El Ibel* site (Djelfa province–Figure 2) (34° 21' 17" North latitude, 3° 13' 22" East longitude, and 1036 m elevation) on a typical calcimagnisic soil with silty–sand texture. The second orchard was located in *Sidi Makhlouf* (Laghouat province–Figure 2)) (34° 7' 60" North latitude, 3° 1' 0" East longitude, and 900 m elevation) on a typical xerocalcimagnisic soil with silty–sand texture. The climates of the areas are respectively semi–arid and hyper–arid Mediterranean with an annual rainfall around 250 mm/year for *Ain El Ibel*, and do not exceed 170 mm/year for *Sidi Makhlouf*. The two orchards were 9 year–old, watered using flood irrigation (2–3 times / week) and have a mean nut production of 5–7 kg tree^{-1}.

2.2. Sampling methodology

In each orchard, tree parallel transects were traced. In each replicate transect at a regular interval (10 m), ten uniform size *P. vera* trees were selected. Ten mature leaves per tree were randomly harvested from the middle 1–year–old branches. To ensure the homogeneity, from each transect, subsamples are combined into a single composite sample (Nedjimi, 2020). In laboratory, leaf samples were rinsed carefully with deionized H_2O, oven-dried at 65 ^{o}C for 48h and milled to fine particles (200µm) in an agate mortar and pestle.

From a depth of 0.60 m, adjacent soil samples were randomly collected in each orchard using a pedologic auger (Searles et al., 2009). For each soil sample, ten subsamples were mixed to form one composite sample/transect. In laboratory, these samples were air dried and subsequently sieved through a 2 mm mesh to eliminate stones and debris prior to chemical analysis.

2.3. Physicochemical characteristics of orchard soils

The physicochemical proprieties of soils were characterized using universal standard analyses (Pansu and Gautheyrou, 2006). Soil particle fractions were determined using the Robinson pipette. The soil texture triangle was used to determine soil textural categories. Soil pH (1:5 w/v) and electrical conductivity (EC) were determined using pH meter and conductivity meter respectively. Organic matter (OM) was determined by $K_2Cr_2O_7$ oxidation and titration with Mohr salt [$(NH_4)_2$ Fe $(SO_4)_2.6H_2O$]. Carbonate content ($CaCO_3$) was assessed by the Bernard calcimeter.

2.2. Element quantification by wavelength dispersive X–ray fluorescence

Triplicate for each sample (vegetal and soil) were pressed on a hydraulic press machine (150 ton) to make pressed powder pellets of 30 mm ø. A RIGAKU ZSX PRIMUS II Wavelength dispersive X–ray fluorescence spectrometry (WDXRF) with rhodium target X–ray tube was applied for the analytical determination. The X–ray tube was operated at 50kV and 40mA. A diffraction crystal LiF200 and scintillation counter as a detector were used. The measurements were carried out in the vacuum with counting time of 250 s. A two certified reference materials namely SRM–NIST 1573a (Tomato Leaves) and CRM–IAEA–SOIL 7 were analyzed for XRF quality control using the same methodology.

2.4. Calculation and statistical analysis

The macro– and microelement concentrations (µg g^{-1}) were quantified using the following equation (Gama et al., 2017):

$$\rho_{samp} = \rho_{stand}\left[\frac{i_{samp}.\, w_{samp}}{i_{stand}.\, w_{stand}}\right]$$

Where ρ_{samp} and ρ_{stand} denote the element concentrations in the pistachio sample and standard, i_{samp} and i_{stand} denote the net intensities of elements in the pistachio sample and standard, and w_{samp} and w_{stand} were the sample and standard weights respectively.
The performance of WDXRF measurement and the meaning of the experimental results were carried out by using the statistical parameter A_{score}. This coefficient was measured as follows (Waheed and Fatima, 2013):

$$|A_{score}|\,(\%) = \frac{(x_{lab} - x_{ref})}{x_{ref}} \times 100$$

where x_{lab} and x_{ref} are respectively the measured and certified data of the SRM−NIST 1573a or CRM−IAEA−SOIL 7. The exactitude of WDXRF measurement is satisfactory if the relative error was < 10%.

Bioaccumulation index (Bi_x) is a ratio of concentration of a given element in the *P. vera* leave versus the concentration of this element in the adjacent soil. This coefficient was measured using the following equation (Nedjimi, 2018):

$$Bi_x = \frac{\rho_{tissue}}{\rho_{soil}}$$

Where ρ_{tissue} and ρ_{soil} denote the concentration of the element in the pistachio and subsoil samples respectively.

Principal component analysis (PCA) was used to examine the interrelationships between the macro– and microelement contents in *P. vera* leaves and their corresponding soils. Pearson correlation coefficient (r) was performed between chemical element concentrations in pistachio plant and soil. The differences between the element concentrations were assessed by *Tukey*'s–multiple test ($P < 0.05$). Data were analyzed by using the statistical package of SPSS version 10.1.

3. Result and discussion

3.1. Quality control of WDXRF technique

The estimation of precision and accuracy of WDXRF technique was based on the analysis of two certified reference materials i.e. SRM−NIST 1573a (Tomato Leaves) and CRM−IAEA−SOIL 7. Table 1 represents the data obtained for the elemental concentrations in the two standards. For all chemical elements, the A_{score} was generally less than 10%, and no discrepancy were observed between the measured and certified values, confirming the accuracy of the results obtained by this analytical methodology.

Table 1
Quality control of the XRF measurement based on comparison of measured and certified values ($\mu g\ g^{-1}$) of SRM–NIST 1573a (Tomato Leaves) and CRM–IAEA–SOIL 7. Values represent mean ± standard error of mean ($n = 3$).

Elements	SRM–NIST 1573a (Tomato Leaves)			CRM–IAEA–SOIL 7		
	Certified value	Measured value	$\lvert A_{score} \rvert$	Certified value	Measured value	$\lvert A_{score} \rvert$
Br	1300	1270 ± 177	2.31	7	6.89 ± 0.85	0.61
Ca	50450 ± 550	50211 ± 320	0.47	163000	162000 ± 690	1.27
Cu	4.70 ± 0.14	4.48 ± 0.13	4.68	11	10.86 ± 1.14	0.12
Fe	367.50 ± 4.30	363 ± 12.52	1.22	25700	25669 ± 192	0.37
K	26760 ± 480	26256 ± 429	1.88	12100	12055 ± 188	0.44
Mg	12000	11900 ± 249	0.83	11300	11250 ± 122	2.06
Mn	246.3 ± 7.1	238.98 ± 7.4	2.97	631	618 ± 14	1.30
P	2161 ± 28	2098 ± 89	2.92	460	454 ± 18	1.85
Sr	58	57 ± 2.54	1.72	108	110 ± 2.52	1.01
Zn	30.94 ± 0.55	30.58 ± 1.83	1.16	104	102.95 ± 11.42	0.61

3.2. Physicochemical characteristics of the soil samples

Physicochemical proprieties of sampling soil such as texture, pH, $CaCO_3$, organic matter, and electrical conductivity were measured following standard techniques, and are shown in Table 2. The soils can texturally be classified as silty–sand in nature for both pistachio orchards. The contents of OM are less than 2%, ranging from 1.2 to 1.7% in *Ain El Ibel* and *Sid Makhlouf* soils respectively. These values correspond to typical level of OM found in Algerian arid soils (Halitim, 1988). Soils of both orchards are neutral with pH value of 7.8. The available carbonate ($CaCO_3$) content in the soils is very high, ranging from 22% (*Ain El Ibel*) to 38% (*Sid Makhlouf*). Soils were generally no saline and the electrical conductivity varied between 1.2 and 1.5 dS m^{-1}.

Table 2
Physicochemical proprieties of soils below sampled *P. vera* trees

Site	Granulometry %					pH	$CaCO_3$ (%)	OM (%)	EC (dS m^{-1})	pF	Texture
	Clay	Fine silt	Coarse silt	Fine sand	Coarse sand						
Ain El Ibel	13	16	15	36	19	7.8	22	1.70	1.5	9.8	Silty–sand
Sidi Makhlouf	15	19	13	24	28	7.8	38	1.20	1.2	7.7	Silty–sand

3.3. Macro– and microelement contents

Ten macro– and microelements namely Br, Ca, Cu, Fe, K, Mg, Mn, P, Sr and Zn from two studied pistachio orchards and their related soils were quantified. Table 3 shows the average contents of chemical elements in soils where the investigated pistachios were grown. The DWXRF analysis displays that Ca was the most abundant major element, followed by Fe, K and Mg in both soils. The average contents of chemical elements in *Ain Ibel* soil were in the following order: Ca (94800 µg g^{-1}) > Fe (8750 µg g^{-1}) > Mg (8200 µg g^{-1}) > K (7480 µg g^{-1}) > P (477 µg g^{-1}) > Sr (107 µg g^{-1}) > Zn (16.40 µg g^{-1}) > Br (16.20 µg g^{-1}) > Mn (12.30 µg g^{-1}) > Cu (5.40 µg g^{-1}). However, for *Sid Makhlouf* soil, these chemical elements follow the concentration pattern as: Ca (80200 µg g^{-1}) > K (9390 µg g^{-1}) > Mg (8380 µg g^{-1}) > Fe (7330 µg g^{-1}) > P (390 µg g^{-1}) > Sr (119 µg g^{-1}) > Mn (112 µg g^{-1}) > Zn (18.90 µg g^{-1}) > Cu (14.60 µg g^{-1}) > Br (8.10 µg g^{-1}).

Table 3
Mean values of chemical elements (µg g^{-1}) determined in *Ain El Ibel* and *Sidi Makhlouf* soils where *P. vera* were grown. Values represent mean ± SE (n = 3).

Elements	***Ain El Ibel***	***Sidi Makhlouf***
Br	16.20 ± 2.40 (a)	8.10 ± 0.60 (b)
Ca	94800 ± 125 (a)	80200 ± 298 (ab)
Cu	5.40 ± 1.01 (b)	14.60 ± 1.2 (a)
Fe	8750 ± 54 (a)	7330 ± 322 (ab)
K	7480 ± 157 (b)	9390 ± 167 (a)
Mg	8200 ± 241 (a)	8380 ± 89 (a)
Mn	12.30 ± 2.0 (b)	112 ± 11 (a)
P	477 ± 17 (a)	390 ± 23 (ab)
Sr	107 ± 12 (a)	119 ± 16 (a)
Zn	16.40 ± 3.20 (a)	18.90 ± 1.50 (a)

Values across rows followed by different letters indicate significant difference at $P < 0.05$ according to the *Tukey´s* multiple range test.

The mean values of major and trace element concentrations in different pistachio orchards are shown in Table 4. Results demonstrated that concentrations of all elements did not vary significantly between groves, except for Br, Ca, Fe and Mg where their concentrations were higher in *Sidi Makhlouf* province. The chemical elements in *Sidi Makhlouf* orchard were present in the descending content pattern as: Ca (9070 µg g^{-1}) > K (5580 µg g^{-1}) > Mg (3380 µg g^{-1}) > P (337 µg g^{-1}) > Fe (66 µg g^{-1}) > Br (13.70 µg g^{-1}) > Sr (9.0 µg g^{-1}) > Mn (7.80 µg g^{-1}) > Zn (3.10 µg g^{-1}) > Cu (2.70 µg g^{-1}). Conversely the average contents of these elements in *Ain Ibel* grove decrease as follow: Ca (7720 µg g^{-1}) > K (4910 µg g^{-1}) > Mg (2490 µg g^{-1}) > P (365 µg g^{-1}) > Fe (40.10 µg g^{-1}) > Mn (8.60 µg g^{-1}) > Sr (8.0 µg g^{-1}) > Br (5.30 µg g^{-1}) > Cu (4.70 µg g^{-1}) > Zn (4.40 µg g^{-1}).

Table 4

Mean values of chemical elements (μg g^{-1}) determined in *P. vera* leaves from *Ain El Ibel* and *Sidi Makhlouf* provinces. Values represent mean ± SE (*n* = 3).

Elements	***Ain El Ibel***	***Sidi Makhlouf***
Br	5.30 ± 1.20 (b)	13.70 ± 2.20 (a)
Ca	7720 ± 162 (b)	9070 ± 165 (a)
Cu	4.70 ± 0.50 (a)	2.70 ± 0.30 (b)
Fe	40.10 ± 4.30 (b)	66 ± 8 (a)
K	4910 ± 102 (ab)	5580 ± 252 (b)
Mg	2490 ± 114 (b)	3380 ± 191 (a)
Mn	8.60 ± 1.20 (a)	7.80 ± 1.20 (a)
P	365 ± 32 (a)	337 ± 53 (a)
Sr	8.0 ± 1.60 (a)	9.0 ± 1.40 (a)
Zn	4.40 ± 1.60 (a)	3.10 ± 0.80 (a)
Values across rows followed by different letters indicate significant difference at P < 0.05 according to the *Tukey´s* multiple range test.		

Calcium (Ca)

The amount of Ca in both studied pistachios ranged from 7720 ± 162 to 9070 ± 165 μg g^{-1}, noticing that maximum concentration was detected in *Sidi Makhlouf* orchard (Table 4). Calcium is an essential macronutrient required for plant growth. It acts as an essential factor for cell wall rigidity, and is considered as a second messenger in many biochemical processes and signal transduction (Thor, 2019). Its shortage leads to meristem degeneration, and increases the plant senescence (Saure, 2005).

Potassium (K)

The concentration of K was found ranging between 7480 ± 157 and 9390 ± 167 μg g^{-1}, where, *Sidi Makhlouf* province contained much K amount than *Ain El Ibel* province (Table 4). Potassium is an essential macro component in many biochemical activities such as protein metabolism, ion homeostasis, photosynthesis, starches synthesis, and enzyme activation (Ragel et al., 2019). In water and salt stresses, this element helps plants to cell turgor, stomatal conductance and osmoregulation (Hasanuzzaman et al., 2018). The leave chlorosis with dwarf internodes was the main symptoms of K deficiency (Kathpalia and Bhatla, 2018).

Phosphorus (P)

Phosphorus showed closed concentration values for both studied pistachios (390 ± 23 and 477 ± 17 μg g^{-1} respectively for *Sidi Makhlouf* and *Ain El Ibel* province) (Table 4). Phosphorus is a principal macro–element in nucleic acid structure, membrane lipid composition (phospholipids), and energy metabolism (ATP and ADP) (Schachtman et al., 1998). Some soil microbial communities such as arbuscular mycorrhizal fungi (AMF) and plant growth promoting bacteria (PGPB) have been reported to enhance the P uptake by the roots through exudate secretion and/or soil acidification (Richardson et al., 2009). The most common deficiency symptoms of P are purple stems, stunted growth, and delayed maturity (Kathpalia and Bhatla, 2018).

Iron (Fe)

Iron is one of the essential trace elements for plant growth and development (Rout and Sahoo, 2015). It contributes in many biological activities such as photosynthesis, Krebs cycle, hormone synthesis, and nitrogen fixation. It acts as co–factor of many key enzymes like cytochromes of the electron transfer chain (Kobayashi and Nishizawa, 2012), however its shortage leads to interveinal leave chlorosis and decreases the biomass productivity (López-Millán et al., 2013). There were no significant difference in Fe accumulation between both pistachio groves, where the amount of Fe started from 337 ± 53 $\mu g\ g^{-1}$ (*Sidi Makhlouf*) up to 365 ± 32 $\mu g\ g^{-1}$ (*Ain El Ibel*) (Table 4).

Magnesium (Mg)

No significant difference for Mg concentration was detected between both pistachios (8200 ± 241 and 8380 ± 89 $\mu g\ g^{-1}$ respectively for *Ain El Ibel* and *Sidi Makhlouf* grove) (Table 4). Magnesium is a very important macro–element to fruit–tree growth, thus this element is the major constituent of the chloroplast formation and contributes in the chlorophyll synthesis and light energy transfer (PSII activity). Additionally it acts as activator of many enzymes such as polymerases, ATPase and kinases (Shaul, 2002). Mg deficiency can induces a decrease of carboxylation efficiency, chlorophyll pigment content (Chl *a* and *b*) and the leaves become yellow (Guo et al., 2016).

Manganese (Mn)

Manganese is an indispensable trace element involves in photosynthetic machinery, carbohydrates formation, and acts as activator of pyruvate carboxylase (PC). However, its deficiency causes leave necrosis and inhibits plant development (Alejandro et al., 2020). A significant difference of Mn concentration has been noticed between both pistachio leaves, where the concentration of Mn in *Sidi Makhlouf* province was very high (112 ± 11 $\mu g\ g^{-1}$) compared to *Ain El Ibel* province (12.30 ± 2.0 $\mu g\ g^{-1}$) (Table 4).

Copper (Cu)

Copper is another important trace element for plant growth. It involved in a large number of metabolic activities like respiration, photophosphorylation, and electron transport. Is an essential element in multiple enzymes, including ascorbate peroxidase (APX), cytochrome oxidase (COX) and Cu/Zn superoxide dismutase (SOD1) (Mir et al., 2021). The necrosis and chlorosis were the major symptoms of Cu deficiency (Kumar et al., 2021). The concentration of Cu determined in both orchards showed that *Sidi Makhlouf* pistachio (14.60 ± 1.2 $\mu g\ g^{-1}$) have more Cu content than *Ain El Ibel* province (5.40 ± 1.01 $\mu g\ g^{-1}$) (Table 4).

Zinc (Zn)

Zinc is also an important micronutrient for plant nutrition. It acts as catalytic component of numerous enzymes such as alkaline phosphatase (ALP), alcohol dehydrogenase (ADH), and superoxide dismutase (SOD) (Balafrej et al., 2020). Its deficiency causes the leave chlorosis, and necrotic spot development (Sadeghzadeh, 2013). The concentrations of Zn in both *P. vera* groves were found almost comparable (16.40 ± 3.20 $\mu g\ g^{-1}$ in *Ain El Ibel* and 18.90 ± 1.50 $\mu g\ g^{-1}$ in *Sidi Makhlouf*) (Table 4).

Bromine (Br)

Bromine is a trace compound without nutritional functions for vegetables. Generally Br concentrations in plant species were less than 50 $\mu g\ g^{-1}$, however higher content of this component were found in contaminated soils (Kabata-Pendias, 2011). Yellow and necrotic leaves were the main symptom of Br toxicity (Djingova et al., 2013). Our results displayed that Br content in *Ain El Ibel* orchard was nearly twice that in *Sidi Makhlouf* province (8.10 ± 0.60 and 16.20 ± 2.40 $\mu g\ g^{-1}$ respectively) (Table 4).

Strontium (Sr)

Strontium is not indispensible for plant nutrition, but is easily uptake by root system (Kabata-Pendias, 2011). Present study shows that Sr displayed a similar concentration for both *Pistacia vera* trees (107 ± 12 in *Ain El Ibel* and 119 ± 16 µg g^{-1} *Sidi Makhlouf*) (Table 4).

3.4. Bioaccumulation index (Bi_x)

The results of bioaccumulation index (Bi_x) for the examined pistachios were shown in Fig. 3. For Ca, Fe, Mg, Sr and Zn, Bi_x were low (< 0.4) and there were no significant differences ($P > 0.05$) between the two orchards. In contrast, Br, Cu and Mn had the highest Bi_x, and there were greater differences ($P < 0.05$) between the two orchards. The Bi_x of P and K were similar for both groves. A higher value was reported for Br in Pistachio of *Sidi Makhlouf* (Bi_x = 1.63). Conversely, *Ain El Ibel* pistachio showed higher values for Mn and Cu (0.67 and 0.80 respectively). Despite the relatively high levels of Ca, Fe and Zn in soil, their transfer into the pistachio trees was limited. Soil Alkalinity (high pH) is the main determinant factor of cationic trace elements bioavailability. Thus, negative correlations between pH and Bi_x can occur for the almost trace elements, which are more immobile at higher pH (Adriano, 2001). Maintaining acid soil pH should be an integral part of any fertilization program that involves the rates of trace element bioavailability.

3.5. The principal component analysis (PCA)

The principal component analysis (CPA) performed with all chemical elements for two *P. vera* groves, showed that 89.04% of the total variation could be explained by the two first principal components (Fig. 4). PC 1 explained 77.01% of the variation and separated *Sidi Makhlouf* from *Ain El Ibel* orchard. The eigenvalues of PC 1 and PC2 were 7.70 and 1.20 respectively (Table 5). The projection of variables on the factor plane indicated that *Sidi Makhlouf* orchard were negatively associated with high contents of Br, Ca, Fe, K, Mg, and Sr (loading values ranging between 0.92–0.99). However *Ain El Ibel* soil was negatively related to high concentrations of Cu, Mn, P and Zn with loading values between 0.24–0.84.

Table 5
Principal component analysis (PCA) results (factor loadings) of chemical elements determined in *P. vera* leaves.

Elements	**Principal components**			
	PC1	**PC2**	**PC3**	**PC4**
Br	-0.98	-0.07	-0.16	-0.06
Ca	-0.99	-0.00	-0.05	-0.06
Cu	0.76	0.03	-0.63	-0.07
Fe	-0.92	0.25	-0.28	-0.09
K	-0.99	-0.09	-0.08	-0.06
Mg	-0.98	-0.03	-0.14	-0.10
Mn	0.84	0.40	-0.34	-0.03
P	0.81	-0.39	0.35	-0.26
Sr	-0.97	-0.21	0.10	0.09
Zn	0.24	-0.88	-0.41	0.07
Eigenvalues	7.70	1.20	0.93	0.11
Cumulative eigenvalues	7.70	8.90	9.84	9.95
Cumulative %	77.01	89.04	98.38	99.50
% Variance	77.01	12.03	9.34	1.12
Significant correlations at $P < 0.05$.				

3.6. Relationships between element contents

Tables 5 depict the Pearson's correlations (*r*) in terms of the detected chemical elements in both pistachios and their related soils. The very strong positive correlation exists when $r = 0.80$ or higher, the strong positive correlation exists when *r* varies from 0.69 to 0.79, and the positive correlation is given when *r* varies from 0.59 to 0.50 (Table 6). The availability and uptake of trace elements by root system is restricted by competition/antagonism mechanism and by the level of carbonates in the soil (Bravo et al., 2017). As a consequence of high pH, alkaline soils are habitually associated to trace element deficiencies such as Fe and Cu due to high precipitation of these elements in sol solution. The interactions between chemical elements are also a significant aspect to be taken into account. [see Kabata-Pendias (2011) for more discussion of this topic].

Table 6
Pearson correlation coefficient (*r*) of chemical elements in *P. vera* and its related soils.

Ain El Ibel Pistacia	**Br**	**Ca**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**P**	**Sr**	**Zn**
Br	1.00									
Ca	0.51*	1.00								
Cu	0.98***	0.34 ns	1.00							
Fe	0.95***	0.22 ns	0.99***	1.00						
K	0.71**	0.97***	0.57*	0.47 ns	1.00					
Mg	0.98***	0.65*	0.93***	0.89***	0.82***	1.00				
Mn	0.50*	-0.49 ns	0.65*	0.74**	-0.25 ns	0.34 ns	1.00			
P	-0.56*	0.43 ns	-0.71**	-0.79**	0.18 ns	-0.41 ns	-1.00***	1.00		
Sr	-0.50*	0.49 ns	-0.65*	-0.74**	0.25 ns	-0.34 ns	-1.00***	1.00***	1.00	
Zn	1.00***	0.51*	0.98***	0.95***	0.71**	0.98***	0.50*	-0.56*	-0.50*	1.00
Ain El Ibel Soil	Br	Ca	Cu	Fe	K	Mg	Mn	P	Sr	Zn
Br	1.00									
Ca	0.94***	1.00								
Cu	0.50*	0.16 ns	1.00							
Fe	0.39 ns	0.69**	-0.60*	1.00						
K	-0.99***	-0.87***	-0.63*	-0.24 ns	1.00					
Mg	0.99***	0.87***	0.62*	0.25 ns	-1.00***	1.00				
Mn	1.00***	0.94***	0.50*	0.39 ns	-0.99***	0.99***	1.00			
P	0.96***	1.00***	0.24 ns	0.63*	-0.90***	0.91***	0.96***	1.00		
Sr	0.43 ns	0.72**	-0.57*	1.00***	-0.28 ns	0.29 ns	0.43 ns	0.66*	1.00	
Zn	0.98***	0.85***	0.65*	0.21 ns	-1.00***	1.00***	0.98***	0.89**	0.25 ns	1.00
Sidi Makhlouf Pistacia	Br	Ca	Cu	Fe	K	Mg	Mn	P	Sr	Zn
Br	1.00									
Ca	0.99***	1.00								
Cu	-0.87***	-0.93***	1.00							
Fe	-1.00***	-1.00***	0.90***	1.00						
K	1.00***	0.99***	-0.88***	-1.00***	1.00					
Mg	0.92***	0.97***	-0.99***	-0.95***	0.94***	1.00				

Significance of correlations: *: $P < 0.05$; **: $P < 0.01$; ***: $P < 0.001$, ns: non-significant.

Ain El Ibel Pistacia	Br	Ca	Cu	Fe	K	Mg	Mn	P	Sr	Zn
Mn	-1.00***	-0.99***	0.87***	1.00***	-1.00***	-0.92***	1.00			
P	0.67*	0.78**	-0.95***	-0.72**	0.69**	0.90***	-0.67*	1.00		
Sr	0.95***	0.89***	-0.67*	-0.93***	0.94***	0.76**	-0.95***	0.41 ns	1.00	
Zn	0.98***	0.94***	-0.76**	-0.97***	0.98***	0.84***	-0.98***	0.52*	0.99***	1.00
Sidi Makhlouf Soil	Br	Ca	Cu	Fe	K	Mg	Mn	P	Sr	Zn
Br	1.00									
Ca	0.93***	1.00								
Cu	0.99***	0.88***	1.00							
Fe	0.98***	0.82**	1.00***	1.00						
K	-0.95***	-1.00***	-0.90***	-0.86***	1.00					
Mg	0.96***	0.77**	0.98***	1.00***	-0.81**	1.00				
Mn	0.95***	0.76**	0.98***	0.99***	-0.80**	1.00***	1.00			
P	-0.78**	-0.96***	-0.70**	-0.63*	0.94***	-0.56*	-0.54*	1.00		
Sr	0.94***	0.75**	0.98***	0.99***	-0.79**	1.00***	1.00***	-0.53*	1.00	
Zn	-0.98***	-0.84**	-1.00***	-1.00***	0.87***	-0.99***	-0.99***	0.64*	-0.99***	1.00
Significance of correlations: *: $P < 0.05$; **: $P < 0.01$; ***: $P < 0.001$, ns: non-significant.										

3.7. Comparison with others pistachio species

Table 7 demonstrated a comparison of our results with those existing in the literature in different *Pistacia* species. The concentrations of Ca found during this work were similar than those reported in *P. vera* from *Turkey* (Demirkiran and Cengiz, 2010; Ak and Fidan, 2016). However, high concentrations of Ca were reported by Hamlat et al., (2019) in *P. terebinthus* and *P. lentiscus* from Algeria. Leaves of *P. vera* from Turkey are rich in P (600 µg g^{-1}), compared to the contents of this element in Algerian pistachios. Current results about K are in agreement with values reported by Ak and Fidan (2016) for Turkey pistachio. Conversely, *P. terebinthus* and *P. lentiscus* showed higher values than those found in this work (Hamlat et al., 2019). The concentrations of Cu in Algerian pistachios are lower than those reported in pistachio leaves from Turkey (Demirkiran and Cengiz, 2010; Ak and Fidan, 2016). The Turkish pistachio had Mn concentrations 3–5 higher than Algerian pistachios. Regarding Zn contents, Ak and Fidan (2016) reported similar values for *Pistachia vera* from Turkey. The content of Mg in Turkish pistachio (Demirkiran and Cengiz, 2010) is relatively high compared to Algerian pistachios, but no significant difference for Mg contents was found between the other provenances. Additionally, Algerian pistachio showed low Fe concentrations respect to other Pistachios reported by Ak and Fidan (2016) from Turkey, and Hamlat et al., (2019) from Algeria. The significant differences between elemental profiles from different provinces could be attributed to the selectivity process of element bioaccumulation, climate and soil origins (Anderson and Smith, 2005).

Table 7

Comparison of some macro– and microelements contents (μg g^{-1}) in *P. vera* from different regions of the world.

Species	***P. vera***	***P. vera***	***P. vera***	***P. vera***	***P. terebinthus***	***P. lentiscus***
Country	Algeria (This study)	Algeria (This study)	Turkey (Demirkiran and Cengiz, 2010)	Turkey (Ak and Fidan, 2016)	Algeria (Hamlat et al., 2019)	Algeria (Hamlat et al., 2019)
Ca	7 720 (b)	9070 (b)	604.14 (b)	10600 (b)	20148 (a)	17883 (a)
Cu	4.70 (b)	2.70 (b)	21.79 (a)	15.04 (a)	–	–
Fe	40.10 (d)	66 (d)	19.34 (e)	174.12 (c)	843 (a)	452 (b)
K	4 910 (a)	5580 (a)	12.75 (b)	5200 (a)	8740 (a)	8199 (a)
Mg	2 490 (b)	3380 (b)	245.74 (b)	4 900 (a)	–	–
Mn	8.60 (c)	7.80 (c)	24.82 (b)	50.19 (a)	–	–
P	365 (b)	337 (b)	135.51 (c)	600 (b)	–	–
Zn	4.40 (b)	3.10 (b)	16.29 (a)	5.25 (b)	26.3 (a)	16.6 (a)

4. Conclusion

Collectively, our study demonstrated that highest contents of Br, Ca, Fe, and Mg were reported in pistachio leaves collected from *Sidi Makhlouf* (Laghouat) orchard. However, Cu concentration is higher in *P. vera* from *Ain El Ibel* (Djelfa) orchard. The Bioaccumulation indexes of P and K were similar for both groves. However, *Ain El Ibel* pistachio showed higher values of Mn and Cu. Present data would be helpful in the pistachio fertilization under semi- and hyper-arid climates. Future work could focus on the effect of trace element amendments to enhance *P. vera* productivity and nut quality.

Declarations

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Ethical Approval: Not applicable.

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Availability of data and materials: All data generated or analyzed during this study are included in this published article.

Conflict of interest

No potential conflict of interest was reported by the author.

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Figures

Figure 1

Pistacia vera L. (Djelfa province): Tree (A), Leaves (B), Fruits (C), and Nuts (kernels) (D).

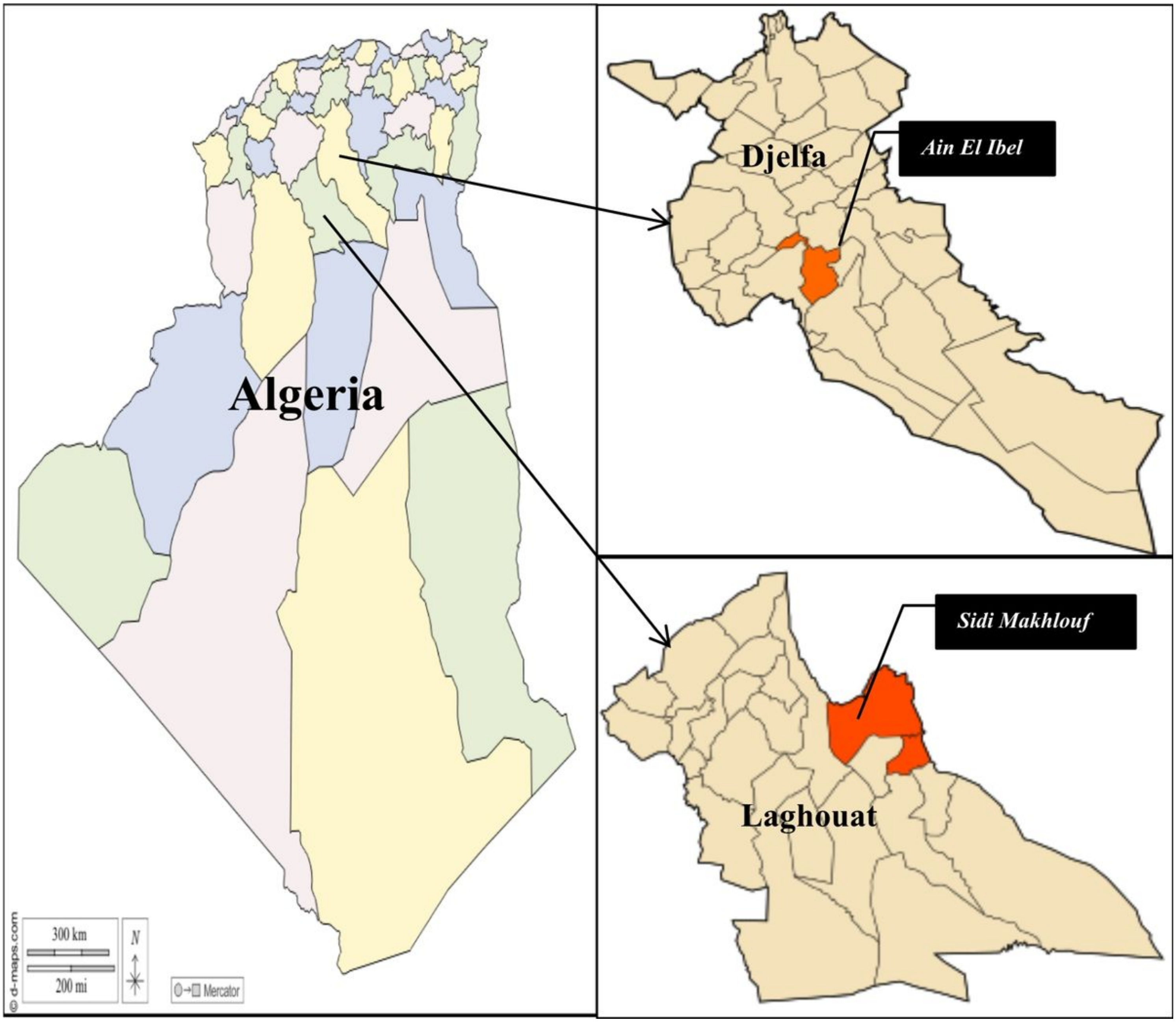

Figure 2

Location of the sampling orchards.

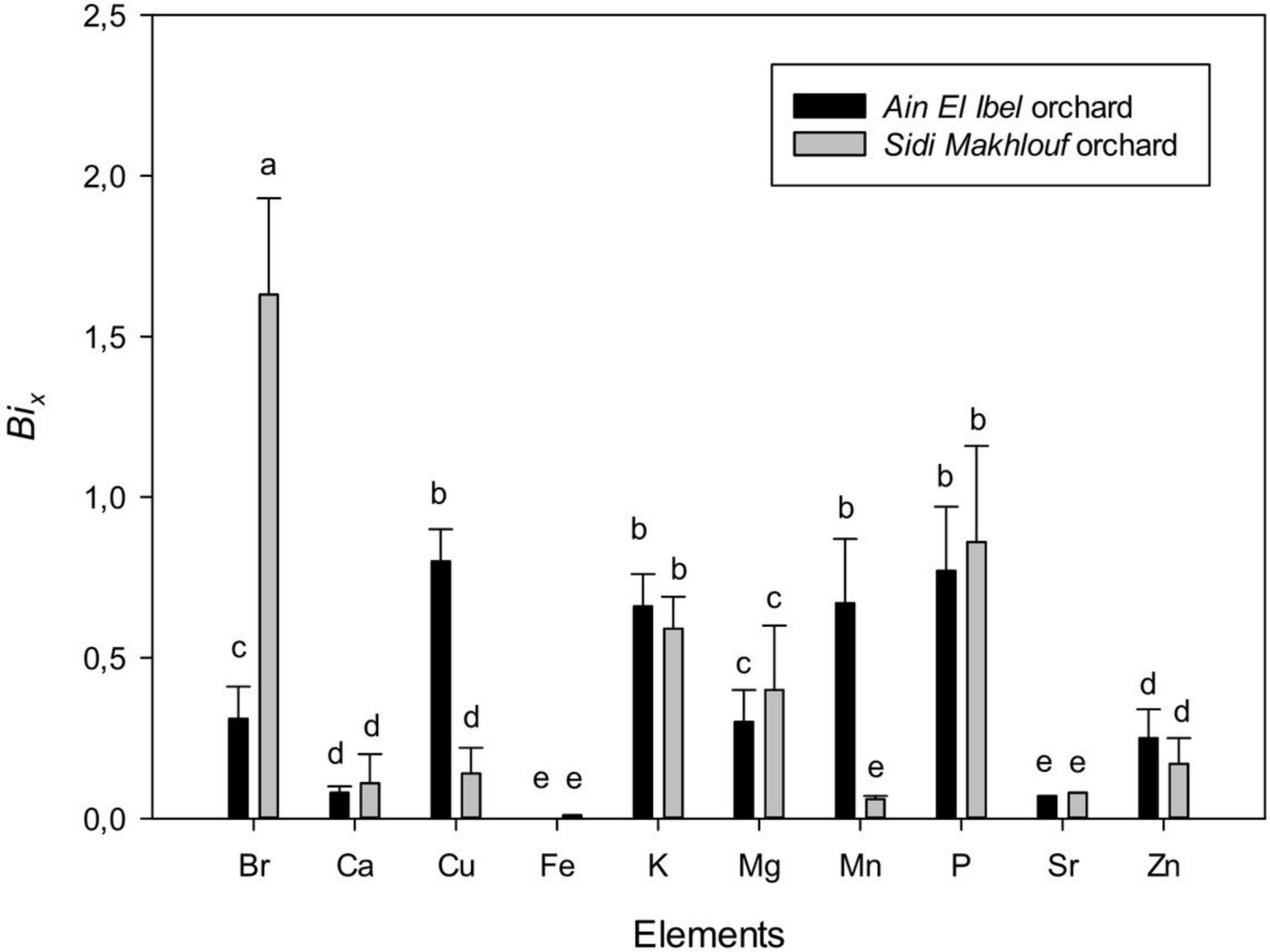

Figure 3

Bioaccumulation index (Bi_x) of chemical element from soil to *P. vera* leaves. Values represent means ± standard deviation (*n*=3). Different letters above bars indicate significant difference at $P < 0.05$ according to the *Tukey*'s multiple range test.

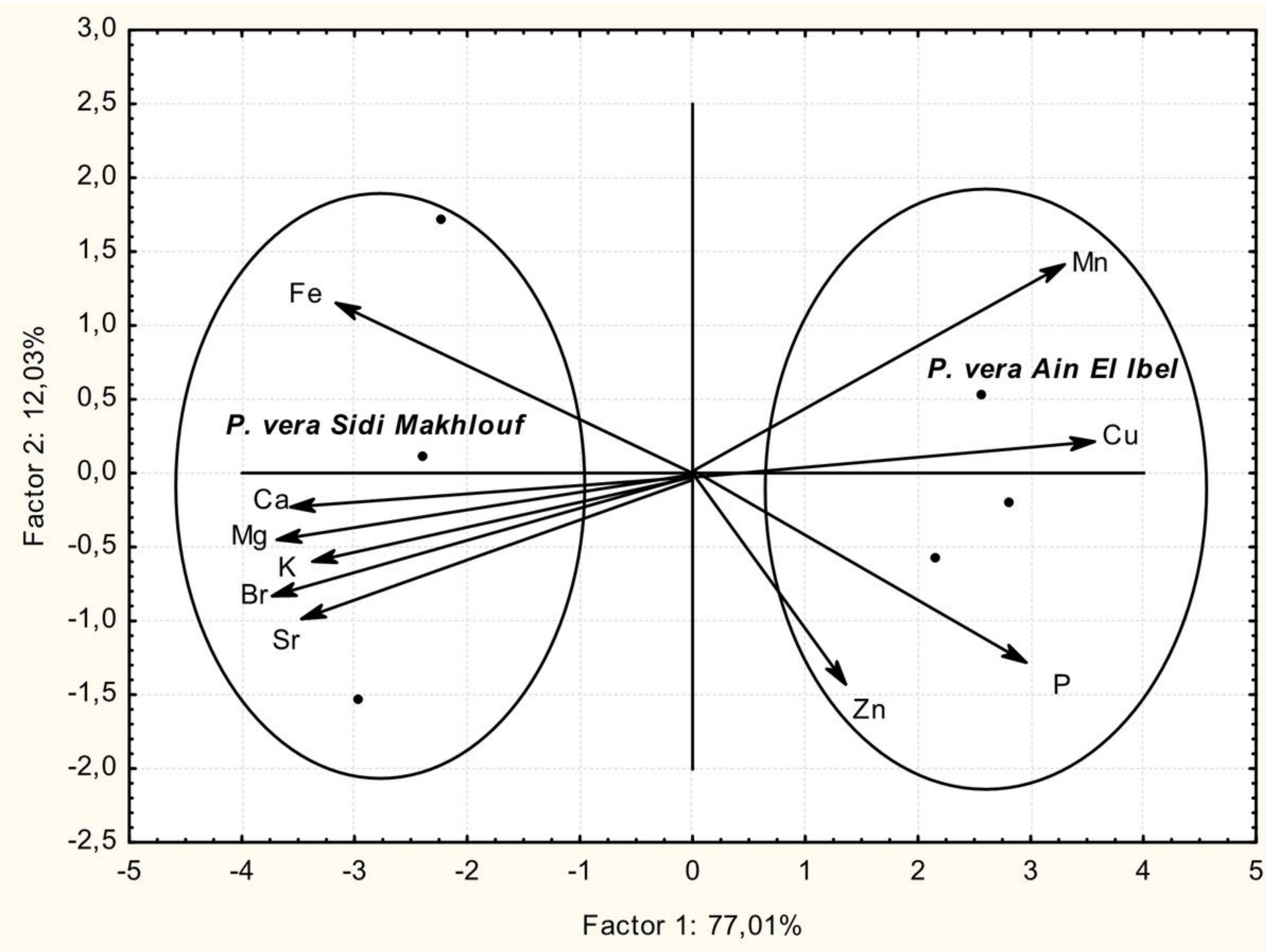

Figure 4

Principal component analysis (PCA) ordination diagram of *P. vera* leaves and their ambient soils correlated to chemical element contents.