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Metal contents and chemometric evaluation of some medicinal plant species growing in different soil structures

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ABSTRACT: Properties of the soil, state of the particules, class of the soil and air, water and the chemicals (calcium cations, humus, colloidal iron, aluminum, nitrogen, various polysaccharides etc.) that soil contains are the most important factors on formation and development of the plants. Trace elements play an important role in the active chemical formation in medicinal plants and are responsible for the toxicity of medicinal plants. In this study, 5 medicinal plants (*Sorghum halepense* (L.) Pers., *Convolvulus arvensis* L., *Physalis angulate* L., *Cynodon dactylon* (L.) Pers. and *Portulaca oleracea* L.) collected from 3 different soil structures and the metal content of these soil samples (Total 18 samples) (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, and Sr) determined by using Inductively coupled plasma–mass spectrometry (ICP-MS). The accuracy and precision of the method was evaluated by CRM 1573a Tomato Leaves. Additionally, metal content analyzes of samples were evaluated chemometrically. Principal Component Analyses (PCA) was applied to analyze of 11 common metals. According to the PCA, three principal components eigen value were higher than 1. The first 3 main components explained 78.9% of the total variance. According to the results of ICP-MS, it has been determined that the soil difference does not affect metal content much.

KEYWORDS: Soil; medicinal plants; trace elements; PCA; ICP-MS.

1. INTRODUCTION

It is known that the homeland of purslane (*Portulaca oleracea*), which is a family of Portulacaceae, is the region of India. Also, this plant has been consumed for thousands of years in Turkey. Purslane is an alternative to fish in this respect due to the high content of omega 3 it contains [1]. Ethnobotanical use of the *Convolvulus arvensis* species, a member of the Convolvulaceae family, is limited. However, there are some uses among the public. Tea made from leaves is used against spider bites. At the same time, its flowers and leaves have a laxative function. Tea made from flowers is antipyretic and used to heal wounds [2]. Dog tooth (*Bermuda grass*, *Cynodon dactylon*), which is widely used in the world, belongs to Poaceae family. Dog tooth grass originated in India and South Africa and has been adapted to all hot regions [3]. Generally, it is used in urinary tract inflammation and prostate inflammation. With this aspect, it also has a diuretic effect [4]. *Sorghum halepense*, which homeland in Anatolia and Mesopotamia, is one of the leading problematic plant species of the agricultural world as a weed. The plant is also a problem in animal nutrition, especially since it carries durrin glycoside. When the content of durrin glycoside in this plant breaks down in the stomach, hydrogen cyanide is released, and when consumed too much, it can cause death [5]. *Physalis angulata*, a member of the Solanaceae family, has been used for centuries against malaria and oriental boils, especially in Brazil. Tea is also used in liver dysfunction. Again in this area, it is used in traditional folk medicine against postpartum infections and itching [6].

It is known that different soil structures are effective in the development of plants and the minerals they contain. For example, a good crumb structure in the soil will allow both air and water to move easily within the soil. Thus, it is effective on the easy development and spreading of plant roots in the soil, as well as providing a necessary environment for getting enough water and air. The plant roots dissolve the ferrous and

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aluminum compounds of the soil around them with the secretions they have extracted and enable them to move away from the root. Soil organic matter is a source that provides the circulation of mineral substances as it contains the necessary nutrients for plants. Some substances consisting of organic residues prevent toxic development by making toxic effects on plants (such as benzoic acid and vanillin). Humus can absorb them and make them harmless. In contrast, even small amounts of certain organic substances have a significant positive effect on the development of the plant (such as significantly dispersed humus acids, some aromatic compounds, some decomposition products of amino acids). In the same way, it is known that plants add different properties to the soil on which they grow. For example, plants reduce the water content of the soil to a certain depth by evapotranspiration. In addition, the plant roots and the soil act as a composite material and take a role in the strengthening of the soil. Roots that act as reinforcement increase soil strength [7,8].

The heavy metal accumulation in plants occurs during the plant drawing water from the soil since the heavy metals are available in soil and water resources. In addition, heavy metal accumulation may also occur in plants when dust particles of heavy metals in the atmosphere pass into the plant. Heavy metals that penetrate into the plant prevent and/or change the physiological activities of the plant, and can cause the death of the plant in further stages. Therefore, the accumulation of heavy metals in plants is an important factor that reduces vegetative yield and quality [9].

Trace elements play an important role in the formation of active chemicals in medicinal plants and are responsible for the toxicity of medicinal plants [10]. Physiological activities of twenty-three elements in humans and other mammals are known. Some metals (Co, Cr, Cu, Fe and Zn) are required to be taken for certain levels, and only toxic in high concentrations, while Mercury, Lead and cadmium are toxic at all levels, they do not have beneficial properties known. Metal ions in the chemical components of plants determine the medicinal, nutritional and toxic properties of that plant [11,12]. Trace elements play an important role in plant metabolism and biosynthesis as cofactors for enzymes [13]. Medical plants are widely used in treating human diseases and reducing pain due to their low side effects Although widely used medicinal plants are described as natural and harmless, they have negative effects, which plays an important role in the general health condition of the population. Unknown effects of the use of medicinal plants, such as allergic reactions, toxic reactions, have been identified. Some medicinal plants and their mixtures may pose a health risk due to their toxic element content. Especially, toxic effects are caused by heavy metal poisoning [14]. Contaminated irrigation water, atmospheric dusts, automobile and industrial exhausts, pesticides and fertilizers and soils contaminated in terms of heavy metal content play an important role in the contamination of medicinal plants. The geochemical property of the soil and the ability of the medicinal plant to accumulate heavy metals is another effect in the contamination of medical plants. Plants are an important way in the transition of trace elements from soil to human [15]. Therefore, the trace element content and the evaluation of their amounts with statistical techniques such as chemometric are important for the quality control of medicinal plants [16-20].

From this point, the aim of this study is to determine the trace element concentration of some medicinal plant species (aerial parts) collected from Diyarbakır and widely used among the people by using ICP-MS technique, to classify heavy metal components using PCA analysis methods and to determine the content of samples taken in different soil types. In this context, the effect of metal contents of soil samples on metal content of plant species was investigated.

2. RESULTS

2.1. Sieve analysis method

According to the sieve analysis result of the samples (0.075 mm), the amount passing through the sieve is more than 50% fine-grained soil, and if the amount passing through the sieve is less than 50%, it is classified as coarse-grained soil. The results of this study are given in Table 1.

2.2. General characteristics of soil sample A

Soil has a clay structure (Table 2). Soil salinity value is 0.04% and there is no salinity problem. Soils with low (1.13%) organic matter have a slightly alkaline pH level. Soils with a lime level of 9.12% are in the class of lime. Soils not rich in nutrients are very low in terms of phosphorus (2.40 kg/da); in potassium (95.70 kg/da) class (Table 2).

Table 1. Soil class according to the result of sieve analysis.

Sample	Remaining (Gravel)	Screened (Clayl+Silt)	Atterberg Limits			soil Class
			LL	PL	PI	TS 1500
A	0.00	81.37	50.05	21.10	29.03	CH
B	0.00	80.44	54.10	24.30	32.80	CH
C	8.98	45.35	31.70	20.40	11.30	SC

Table 2. A, B, and C soils Characteristics.

Parameters	A	B	C
Dewpoint (%)	71.30	71.5	69.30
EC (Salt) %	0.04	0.05	0.06
Organic Substance (%)	1.13	2.26	1.56
Phosphorus (kg/da)	2.40	9.45	8.36
pH	7.76	7.68	7.73
Lime (%)	9.12	6.08	7.60
Potassium (kg/da)	95.70	109.70	97.40

2.3. General characteristics of soil sample B

In terms of soil texture, it has similar characteristics with group A soils and has a clay structure (Table 2). Soils are in the salt-free class in terms of salinity and salinity value is at the level of 0.05%. Soils with moderate organic matter (2.26%) have a slightly alkaline pH level (7.68). According to the results of analysis, there is 6.08% lime in medium-calcareous soils. Soils that are not rich in nutrients are low in phosphorus (9.45 kg/ha); It is in the middle (109.70 kg/da) class in terms of potassium (Table 2).

2.4. General characteristics of soil sample C

Soils, which differ from the other two groups in terms of soil texture, have a sandy clay structure (Table 2). Soils are in the salt-free class in terms of salinity and salinity value is at the level of 0.06%. Soils with low levels of organic matter (1.56%) have a slightly alkaline pH level (7.73). According to the results of analysis, there is 7.60% lime in medium-calcareous soils. Soils not rich in nutrients are in the low classes in terms of phosphorus (8.36 kg/da); and in terms of potassium (97.40 kg/da) (Table 2).

2.5. Concentrations of elements in studied species

Total aluminum is a parameter measured in soils because it provides useful information about the characterization of soils according to the origin of the parent materials and weather conditions. No correlation was found between the total aluminum in the soil causing toxicity to the plants and soil invertebrates tested. Aluminum toxicity is associated with soluble aluminum, not total aluminum. Soluble aluminum is associated with the uptake and bioaccumulation of aluminum taken from the soil into plants [21]. When the aluminum (Al) amounts of the plants grown in A, B and C soils are examined, following values were determined respectively; 896±8, 79±1, 1476±13 mg/kg for plant 1; 835±7, 217±3, 526±6 mg/kg for plant 2; 900±9, 2251±9, 319±7 mg/kg for plant 3, 193±8, 5104±10, 268±5 mg/kg for plant 4; values between 5967±15, 4911±12, 3296±12 mg/kg for the plant 5 (Table 3). That is, among the concentrations of the same plants grown in different soils, it was determined that there is a relationship, C1> A1> B1 for plant 1; A2> C2> B2 for the plant 2; B3> A3> C3 for the plant 3; B4> C4> A4 for the plant 4 and A5> B5> C5 for the plant 5 and the highest Al amount is at the plant 5. In general, when the results are examined, it is determined that the amount of Al in plants grown in different soils is the lowest B1 (79±1 mg/kg) and the highest is 5967±15 mg/kg (A5). When the results of the soil analysis are examined, it was observed that the amount of Al in soil C (6258±10 mg/kg) is very high compared to the soil of A (67±2 mg/kg) and B (7.61±0.76 mg/kg) and there is a relationship in the form of C> A> B. Comparing the amount of Al in the plants with the amount of Al in the soil, it was observed that there was no such relationship in the plants although Al was the highest in soil C. Basgel and Erdemoglu [14] indicated that the content of aluminum in the herbs, which is known as one of the toxic elements, varied between 87 mg/kg (linden) and 596 mg/kg (nettle). Muller et al [22] indicated that most investigated foodstuff (vegetables, meat and dairy products) contained less than 5 µg/g of Al (fresh weight) and high concentrations were determined in cocoa–cocoa products (33 µg/g) spices (145 µg/g) and black tea leaves (899 µg/g).

Barium (Ba) is found around 390 mg/kg in the earth's crust. It is found in the world soil as an average of 460 mg/kg. In Russia, Ba is considered a moderately dangerous element. Ba affects calcium metabolism and causes a disease in the skeletal system known as osteoarthrits [21]. When the barium (Ba) amounts of the plants grown in A, B and C soils are examined, it was determined respectively as 9.67±0.23, 6.03.00±0.01, 8.80±0.12 mg/kg for the plant 1; 64±4, 30.90±1.02, 35.80±1.45 mg/kg for the plant 2; 16.63±0.56, 21.00±0.98, 14.60±0.18 mg/kg for the plant 3; in the plant 4 growing in soil C Barium cannot be detected, whereas in A and B soils it was determined as 1.39±0.01, 8.50±0.03 mg/kg, respectively (Table 3). In the plant 5, 88±4, 77±2, 74±2 mg/kg values were found, respectively. In other words, among the concentrations of the same plants growing in different soils, it is observed that there is a relationship as A1> C1> B1 for plant 1; A2> C2> B2 for the plant 2; for the plant 3, B3> A3> C3; B4> A4 for the plant 4 and A5> B5> C5 for the plant 5. In addition, it is observed that the highest amount of barium is in the plant 5. In general, when the results were analyzed, it was determined that the amount of Barium in plants grown in different soils was 1.39±0.01 mg/kg (A4) and the highest was 88±4 mg/kg (A5). As a result of soil analysis, the amount of Ba in the A, B and C soils is not very large and there is a relationship between them A (134±6 mg/kg)> B (102±4 mg/kg)> C (85±3 mg/kg). In the light of these results, it was observed that the results of plants 1, 2 and 5 grown in soil A were higher than those grown in other soil. It can be said that these results may be related to the amount of Ba in the soil. Basgel and Erdemoglu [14] indicated that the content of Ba in the herbs was varied between 5.40 mg/kg (fennel) and 74 mg/kg (senna tea).

Calcium (Ca) is an element in the cell wall in plants. In calcium plants, cell division affects root elongation and root secretion [23]. Most of the calcium is located on the outer surface of the plasma membrane in plant tissues, which can be changed in cell walls. Calcium regulates ion uptake by strengthening the cell membrane and affecting its permeability, replacing it with other cations (K^+, Na^+ or H^+) in the exchange regions of the membrane. It has an important role in root and leaf development. It protects plants against freezing and thawing stress by reducing substance release from the cell under adverse conditions [24]. There are no signs of deficiency in plants in soils with high calcium content. When the calcium amounts of plants grown in A, B, and C soils are examined, the following values were found respectively; 5345±15, 5552±9, and 5121±13 mg/kg for the plant 1; 10010±26, 9038±18, and 9902±9 mg/kg for the plant 2; 8982±18, 8152±16, and 9726±10 mg/kg for the plant 5; 2745±11, 4729±7, and 1570±11 mg/kg for the plant 4; 9998±12, 10010±14, and 7709±8 mg/kg for the plant 5. That is, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as B1> A1> C1 for the plant 1; A2> C2> B2 for the plant 2; C3> A3> B3 for plant 3; B4> A4> C4 for the plant 4 and B5> A5> C5 for the plant 5. While Calcium content was found to be close to each other or higher in 2,3, and 5 plants, calcium content was found to be the lowest in plant 4 species. In general, when the results were analyzed, it was determined that the amount of calcium was 2745±11 mg/kg (A4) and the highest was 10010±26 mg/kg (A4 and B5) in plants grown in different soils. It was observed that the amount of calcium was not very different in all three soils and there was a relationship between C (30.12±0.56 mg/kg)> A (28.58±1.23 mg/kg)> B (26.15±1.26 mg/kg). Koca et al. [25], in a study with Arnebia densiflora plant, investigated the calcium concentration in different parts of the plant, and in another study, observed that the calcium content varied between 9203 and 37637 mg/kg. Basgel and Erdemoglu [14] indicated that the content of Ca in the herbs varied between 30.480 mg/kg (nettle) and 10.780 mg/kg (fennel).

Chromium (Cr (III)) is recognized as a trace element that is essential to both humans and animals. Chromium(VI) compounds are toxic and carcinogenic, but the various compounds have a wide range of potencies. Chromium levels in soil vary according to area and the degree of contamination from anthropogenic chromium sources. Tests on soils have shown chromium concentrations ranging from 1 to 1000 mg/kg, with an average concentration ranging from 14 to 70 mg/kg. Chromium(VI) in soil can be rapidly reduced to chromium(III) by organic matter [18]. When the chrome amounts of plants grown in A, B and, C soils are examined, following results were found, respectively, 6.90±0.01, 10.01±0.32, 12.16±0.34 mg/kg for the plant 1; 6.40±0.02, 14.40±0.05, and 12.90±0.45 mg/kg were found for the plant 5 (Table 3). Cr was not detected in any of the plant 2 grown in A, B and C soils. While Cr was not detected in the plant 3 and plant 4 grown in soil A and C, the amount of Cr in the plant 3 and plant 4 grown in soil B was 7.10±0.20, and 13.62±0.22 mg/kg, respectively. In general, when the results were analyzed, it was determined that the chrome amount was the lowest B1 (10.01±0.32 mg/kg) and the highest was B5 (14.40±0.05 mg/kg). It was observed that the amount of chromium was not very different in all three soils and there was a relationship between them A (90±3 mg/kg)> C (75±3 mg/kg)> B (71±2 mg/kg). Tokalioglu [11] indicated that the Cr contents in the medicinal herbs were found to be in the range of 0.44 μg/g (*opium poppy*)– 8.71 μg/g (*nettle*). The mean Cr concentration was found to be 2.59 μg/g. The limit values for chromium in raw herbal materials and finished herbal products in Canada are given as 2 μg/g and 0.02 mg/day, respectively [26].

It is known that copper (Cu) has negative effects besides positive effects on plants. The effects of copper on plants and living things vary depending on the chemical form of copper, as well as on the size of living things [27]. Copper, which has a poison effect for small and simple organisms, is the basic structural component for large organisms. For this reason, copper and its compounds are used effectively against various agricultural pests as fungicides, biocides, antibacterial agents and insect venom. Plants show different susceptibilities to copper deficiency. Stunted growth in plants, twisting and twisting of young leaves and fading of young leaves are typical signs of copper deficiency [27]. Organic and chemical fertilizers are used as a source of copper. However, special attention should be paid to the application of copper resources at levels that will not cause toxic effects, regardless of their origin. Due to its high water solubility, relatively cheap and easily available, $CuSO_4$ is the most widely used copper source [24,28]. When the copper amounts of the plants grown in A, B and C soils are analyzed, it is seen that there are values as 6.40±0.03, 7.00±0.06, 7.25±0.06 mg/kg for the plant 1; 15.13±0.23, 10.23±1.01, 11.04±0.13 mg/kg for the plant 2; 9.03±0.07, 6.56±0.01, 13.54±0.23 mg/kg for the plant 3; 9.80±0.08, 21.50±1.09, 12.50±0.16 mg/kg for plant 4; 14.50±0.16, 16.90±0.12, 15.60±0.14 mg/kg values for the plant 5. In other words, among the concentrations of the same plants grown in different soils, It is observed that there is a relationship as A1> B1> C1 for plant 1; A2> C2> B2 for the plant 2; A3> B3> C3 for the plant 3; B4> C4> A4 for the plant 4 and B5> C5> A5 for the plant 5. WHO [26] has set 3 mg/kg as the allowable value for edible plants. In general, when the results were examined, the amount of copper grown in different soils was found to be the lowest C1 (7.25±0.06 mg/kg) and the highest B4 (21.50±1.09 mg/kg). It was observed that copper amounts were similar in all three soils and there was a relationship between them B (37.36±2.12 mg/kg)> A (34.39±1.12 mg/kg)> C (75±2 mg/kg). The Cu levels in thirty medicinal herb samples widely consumed in Kayseri, Turkey by Tokalioglu [11] were found to be 3.32–30.2 µg/g. The Cu levels in seven types of medicinal plant samples by Maiga et al. [13] were found to be in the range of 2.4 to 17.1 µg/g. More than normal levels for copper are stated as 20-100 mg/kg in plants [29]. It is reported that copper will have a toxic effect if it is more than 100 ppm in soil and 15-30 ppm in plant dry matter. In this respect, it can be said that this study is compatible with the literature information and the plants we work with are not toxic in terms of copper.

The amount of iron (Fe) locks in the soils with high organic matter content is between 10-4–10^{-3} µg/g. Iron absorption by plant roots is carried out by active root tips. In low soil temperature, root growth and root activity decreases [24]. Additionally, it causes a decrease in iron uptake due to the increase in HCO_3 concentration and CO_2 solubility in the soil [30]. In high soil temperature, iron intake decreases, respiratory rate increases in plants and photosynthesis products, which are the energy source for metabolic functions, cannot be carried to the root sufficiently. Iron absorption by plant roots is carried out by active root tips. It was determined that the plant could not get enough iron in hot and dry conditions even if there was enough iron in the soil due to the restriction of root tip development in dry surface soils [30,31]. When the iron amounts of the plants grown in A, B and C soils are examined, following values are observed: 795±11, 101±2, 819±8 mg/kg for the first plant; 583±8, 141±3, 252±5 mg/kg for the plant 2; 546±7, 1120±9, 157±4 mg/kg for the plant 3; 157±2, 2515±9, 153±5 mg/kg for the plant 4; 2395±13, 3337±13, 1232±10 mg/kg for the plant 5. That is, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as C1> A1> B1 for plant 1; A2> C2> B2 for the plant 2; B3> A3> C3 for the plant 3; B4> A4> C4 for the plant 4 and B5> A5> C5 for the plant 5. In general, when the results were examined, the amount of iron grown in different soils was found to be the lowest B1 (101±2 mg/kg) and the highest B5 (3337±13 mg/kg). It was observed that the amount of iron was similar in all three soils and there was a relationship between them as A (4503±13 mg/kg)> C (4193±18 mg/kg)> B (4129±15 mg/kg). Abu-Darwish et al. [32] reported that the heavy metal contents (Cd, Co, Cr, Cu, Fe, Ni, and Pb) of thyme plants grown wild in different ecological regions in Jordan are very variable. It was determined that the variation in iron content was much higher and the iron content of the samples varied between 15.31 and 205.80 mg/kg. The Fe levels in thirty medicinal herb samples widely consumed in Kayseri, Turkey by Tokalioglu [11] was determined the highest level in the nettle samples, 3456 µg/g whereas the lowest was in the jujube samples, 41.9 µg/g.

Potassium (K) that is available in soil varies under the influence of various factors such as the type and amount of other cations found, plant species, development status, age. Potassium is relatively higher in the regions of plants such as metabolically effective growth tip, young leaf and root tip [24]. Plants take most of the potassium they need during the vegetative development period [33]. It has been reported that the amount of potassium needed for optimum plant growth varies between 1-5%, this value in the soil is between 0.5-2.5% and the average amount is 1.2%. Intake of potassium below 200 mg/kg, defined as exchangeable potassium, is accepted as a deficiency limit in plants [33]. Potassium is an essential element in all living organisms and mostly for enzyme activities. For this reason, important chemical changes occur in the plants that are found insufficient. Potassium increases the resistance of plants to diseases and pests, and reduces the development and harm of parasites. It has very important functions such as balancing salt-water ratio in the plant, increasing enzyme activity, regulating stomatal movements, and increasing the rate of photosynthesis. It has extraordinary importance on water balance in plants. The potassium that is present in the development environment allows the plant to absorb and retain more water. In its insufficiency, parallel to the decrease in the amount of water in the tissues, the growth rate of the cell and plant also decreases [24]. When the potassium amounts of the plants grown in A, B and C soils are examined, the K values were 1216±18, 2911±13, 2556±14 mg/kg for the plant 1; 2215±17, 1935±17, 1644±13 mg/kg for plant 2; 343±7, 371±6, 277±5 mg/kg for the plant 3; 2031±9, 1722±17, 1900±9 mg/kg for the plant 4, whereas no K values were determined in the plant 5 grown in A, B and C soils. In other words, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as B1> C1> A1 for plant 1; A2> B2> C2 for the plant 2; B3> A3> C3 for the plant 3; A4> C4> B4 for the plant 4. Potassium values in the plant 1, plant 2, and plant 4 grown in different soils were close to each other, while the values in the plant 3 was lower than other plants. In general, when the results were examined, the amount of potassium grown in different soils was found to be the lowest C3 (277±5 mg/kg) and the highest was C4 (1900±9 mg/kg). It was observed that potassium amounts were similar in all three soils and there was a relationship between them A (45.20±1.56 mg/kg)> B (41.80±2.12mg/kg)> C (33.45±1.23 mg/kg) [34]. In the study of 4 species of wild plants (*Nettle*, *Chicory* (*Trachystemon orientalis*), Smilax (*Smilax excelsa*) and Sakarca (*Ornithogalum umbellatum*)) that grow in the natural vegetation of Ordu and its surroundings, consumed by the local people, in the samples of potassium, wild plants. He stated that it had a wide range of oscillation between 213.34 and 7741.89 mg/kg. It can be say that this study is compatible with the literature and plants have normal values in terms of potassium density.

Lithium (Li) is a naturally occurring element; However, it is one of the metals that is not essential for life. Due to limited information on its transicion from soil to plants, the negative effects of Li toxicity on plants are still uncertain [35]. When the lithium (Li) amounts of the plants grown in A, B and C soils are examined, the following values are observed, respectively: 12.12±0.05, 11.53±0.13, 12.80±0.23 mg/kg for plant 1; 12.60±0.02, 12.10±0.15, 12.22±0.16 mg/kg for the plant 2; 51±2, 20.23±0.45, 12.30±0.43 mg/kg for the plant 3; 11.60±0.04, 10.54±0.13, 11.61±0.32 mg/kg for plant 4; 83±2, 10.10±0.02, 15.50±0.34 mg/kg for the plant 5. That is, among the concentrations of the same plants grown in different soils, It is observed that there is a relationship as C1> A1> B1 for plant 1; A2> C2> B2 for the plant 2; A3> B3> C3 for the plant 3; B4> A4 = C4 for the plant 4 and A5> B5> C5 for the plant 5. Li value in the plant 3 and plant 5 grown in the soil A was found to be quite higher than the others. In general, when the results were analyzed, it was determined that the amount of lithium was the lowest B1 (10.10±0.02 mg/kg) and the highest was A5 (83±2 mg/kg). Stepniowska et al., 2010 determined that various pumpkin varieties are not rich in Li. Among the analyzed pumpkins, the highest amount of Li was 17.4 µg/kg [35].

The most important task of the magnesium (Mg) element is that it takes place as the central atom in chlorophyll molecules that give the plant a green color. In plant cells, Mg (II) is usually found in the form of inorganic salts in cell sap, in the structure of the chlorophyll molecule and in the cytoplasm [36]. There are also differences among plants in terms of magnesium content. For example, legume plants (chickpeas, lentils, etc.) contain more magnesium than non-legume plants, while different parts of the plants also differ. In addition, the amount of magnesium in the leaves and seeds of plants is higher than other organs [37]. Leaves with magnesium deficiency mostly fall prematurely [24]. When magnesium amounts of plants grown in A, B and C soils are examined, following values are observed, respectively: 1848±18, 2097±12, 1894±10 mg/kg for plant 1; 2760±17, 2050±13, 1877±12 mg/kg for the plant 2; 3967±13, 3487±18, 2962±10 mg/kg for the plant 3; 2396±12, 3214±9, 1868±16 mg/kg for the plant 4; 6241±15, 5769±11, 5548±11 mg/kg for the plant 5. In other words, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as B1> C1> A1 for plant 1; A2> B2> C2 for the plant 2; A3> B3> C3 for the plant 3; B4> A4> C4 for the plant 4 and A5> B5> C5 for the plant 5. In general, when the results were examined, it was determined that the magnesium amount was the lowest A1 (1848±18 mg/kg) and the highest was A5 (6241±15 mg/kg). In a study conducted by Gupta et al. [38], they found that 100 grams of 13 wild plants varied between 35 and 253 mg Mg. Basgel and Erdemoglu [14] indicated that the content of Mg in the herbs, varied between 3778 mg/kg (*nettle*) and 1643 mg/kg (*chamomile*).

Excessive amounts of lime and pH changes in acid-reacted soils negatively affect manganese intake. Excess water in the soil, low temperature, low oxygen density negatively affect the manganese intake of plants [39]. It is generally found in nature linked to iron elements and many other elements. In plants with manganese deficiency, there is a significant decrease in the amount of soluble carbohydrates in plant roots due to the decrease in photosynthesis. In mangan deficiency, root growth is negatively affected due to the lack of sufficient carbohydrate transfer to the root [23]. It is known that mangan also regulates the water content of plants. Plants with sufficient manganese need less water. It is known that while manganese insufficiency is observed against diseases, flowering is delayed [24]. When the manganese (Mn) amounts of the plants grown in A, B and C soils are examined, it is seen that the value are, respectively, 48.58±1.21, 36.13±1.45, 39.70±1.15 mg/kg for plant 1; 50.76±2.12, 25.68±1.09, 27.60±1.09 mg/kg for the plant 2; 25.57±1.09, 37.09±2.06, 13.84±0.45 mg/kg for the plant 3; 46.08±1.34, 72±2, 27.06±1.23 mg/kg for the plant 4; 83±4, 87±3, 45.52±2.11 mg/kg for the plant 5. In other words, among the concentrations of the same plants growing in different soils, it is observed that there is a relationship as A1> C1> B1 for plant 1; A2> C2> B2 for the plant 2; B3> A3> C3 for the plant 3; B4> A4> C4 for the plant 4 and B5> A5> C5 for the plant 5 (Table 3). In general, when the results were analyzed, it was determined that the amount of manganese was the lowest C3 (13.84±0.45 mg/kg) and the highest was B5 (87±3 mg/kg). The manganese toxic values in the plant are 300-500 mg/kg [29]. According to a study conducted on plants that grow naturally and are consumed as vegetables in Ordu province and its region, they stated that the plants have a manganese concentration of 21.40–77.40 mg/kg [40]. From this point of view, it could be said that the plants we work with do not have toxic values in terms of manganese content. The Mn levels in thirty medicinal herb samples widely consumed in Kayseri, Turkey by Tokalioglu [11] was determined the highest level in the reddish orange (454 µg/g), whereas the lowest was in the jujube samples, 3.44 µg/g.

Sodium (Na) is dissolved in the soil as sodium compounds. These compounds are NaCl, $NaNO_3$, borax, albite and diorite [23]. By lowering the freezing point in plant sap, it greatly reduces the damage of the plants from frost in winter and early spring, helping the phosphorus, which is insoluble in the soil, to pass into soluble form and remain in this way. This is especially important in calcareous soils. Sodium is an absolute essential nutrient for many plants [23]. Critical sodium levels in plants and soil vary depending on environmental factors, plant species and varieties, age of leaves or plant tissues [24]. In general, symptoms of sodium deficiency are not seen in plants. The main reason for this is that the agricultural land contains enough sodium and it is applied to the soil in various ways. Sodium requirements of plants can be met with chemical fertilizers and barn manure, as well as waste of vegetable and animal origin [41].

When the sodium levels of the plants grown in A, B and C soils are examined, It is observed that there are values as 232±3, 187±5, 270±3 mg/kg for the plant 1; 479±5, 779±8, 802±5 mg/kg for the plant 2; 539±8, 412±4, 197±5 mg/kg for the plant 3; 946±9, 496±4, 569±6 mg/kg for plant 4; 547±7, 1253±11, 910±7 mg/kg for the plant 5. That is, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as C1> A1> B1 for plant 1; C2> B2> A2 for the plant 2; A3> B3> C3 for the plant 3; A4> C4> B4 for the plant 4 and B5> C5> A5 for the plant 5. In general, when the results were examined, the sodium amount was found to be the lowest B1 (187±5 mg/kg) and the highest was B5 (1253±11 mg/kg). International studies on wild plants have also increased in recent years. In a study, they stated that being on 100 g of fresh leaves of *C. maritimum* was highest in sodium (290 mg) [42]. In a study by Colak [24], some mineral elements and heavy metal quantities were determined in the flowers and root parts of plants purchased in three different regional herbalists in Istanbul, Kadiköy, Bakirköy and Güngören. In the study, sodium amount was determined as the highest in *Calendula* (1648.676 mg/kg) and lowest in *Linden* (25.743 mg/kg) [24]. In a study by Koca et al. [25], they found that the sodium concentration in different parts of medicinal plants was in the range of 31.90 to 860.20 mg/kg.

Nickel (Ni) can be easily absorbed from the soil and nutrient solution by the plant [27]. The amount of nickel in the leaves of plants grown in soils where the nickel amount is normal is generally less than 10 ppm. Nickel content of soils varies according to the main material from which they are formed and the level of pollution created by humans. In order for the plants not to affect the growth negatively, the amount of nickel in the soil should be 3-5 µg/g on average. However, the amount of organic matter and clay contained in the soils and the amount of nickel taken by plants according to the type of clay may also vary [24]. The action of Ni (II) ion taken up by the plant more quickly and easily in the soil reaction with low pH is also high. WHO [26] reported the allowable limit for Ni in edible plants as 1.63 mg/kg. However, there is no limit value determined by WHO [26] for Ni in medicinal plants. Ni toxicity is not common in humans since the absorption of Ni is very low in the human body. When the nickel amount of plants grown in A, B and C soils is examined, the values of C5 (15.08±0.12 mg/kg)> A5 (10.98±0.24 mg/kg)> B5 (7.31±0.12 mg/kg) were determined in the plant 5, respectively. While the amount of Ni was not determined in the plant 1, plant 2, and plant 3, the 12.31±0.21 mg/kg value was determined in the plant 4 grown in soil B. In general, when the results were analyzed, it was determined that the nickel amount was the lowest B5 (10.98±0.24 mg/kg) and the highest was C5 (7.31±0.12 mg/kg). More than normal nickel level in plants is stated as 10-100 mg/kg according to Kabata et al. [29].

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Table 3. Quantification of studied trace elements in soil and plants species by ICP-MS.

	Quantitative results of analyzed metals (mg/kg)												
Samples	Al	Ba	Ca	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Sr
A	67±2	134±6	28.58±1.23	15.00±0.12	90±3	34.39±1.12	4503±13	45.20±1.56	-	-	-	-	-	-
A1	896±8	9.67±0.23	5345±15	-	6.90±0.01	6.40±0.03	795±11	1216±18	12.12±0.05	1848±18	48.58±1.21	232±3	-	21.14±0.13
A2	835±7	64±4	10010±26	-	-	15.13±0.23	583±8	2215±17	12.60±0.02	2760±17	50.76±2.12	479±5	-	58±2
A3	900±9	16.63±0.56	8982±18	-	-	9.03±0.07	546±7	343±7	51±2	3967±13	25.57±1.09	539±8	-	64±3
A4	193±8	1.39±0.01	2745±11	-	-	9.80±0.08	157±2	2031±9	11.60±0.04	2396±12	46.08±1.34	946±9	-	45.13±1.03
A5	5967±15	88±4	9998±12	-	6.40±0.02	14.50±0.16	2395±13	tr	83±2	6241±15	83±4	547±7	15.08±0.12	77±2
B	7.61±0.76	102±4	26.15±1.26	13.10±0.23	71±2	37.36±2.12	4129±15	41.80±2.12	-	-	-	-	-	-
B1	79±1	6.03±0.01	5552±9	-	10.01±0.32	7.00±0.06	101±2	2911±13	11.53±0.13	2097±12	36.13±1.45	187±5	-	29.54±1.04
B2	217±3	30.90±1.02	9038±18	-	-	10.23±1.01	141±3	1935±17	12.10±0.15	2050±13	25.68±1.09	779±8	-	72±6
B3	2251±9	21.00±0.98	8152±16	-	7.10±0.20	6.56±0.01	1120±9	371±6	20.23±0.45	3487±18	37.09±2.06	412±4	-	69±4
B4	5104±10	8.50±0.03	4729±7	-	13.62±0.22	21.50±1.09	2515±9	1722±17	10.54±0.13	3214±9	72±2	496±4	12.31±0.21	18.03±0.89
B5	4911±12	77±2	10010±14	-	14.40±0.05	16.90±0.12	3337±13	tr	10.10±0.02	5769±11	87±3	1253±11	10.98±0.24	55±1
C	6258±10	85±3	30.12±0.56	11.43±0.13	75±3	75±2	4193±18	33.45±1.23	33.30±1.18	-	-	-	-	-
C1	1476±13	8.80±0.12	5121±13	-	12.16±0.34	7.25±0.06	819±8	2556±14	12.8±0.23	1894±10	39.70±1.15	270±3	-	33.04±1.24
C2	526±6	35.80±1.45	9902±9	-	-	11.04±0.13	252±5	1644±13	12.22±0.16	1877±12	27.60±1.09	802±5	-	52±1
C3	319±7	14.60±0.18	9726±10	-	-	13.54±0.23	157±4	277±5	12.3±0.43	2962±10	13.84±0.45	197±5	-	54±2
C4	268±5	tr	1570±11	-	-	12.50±0.16	153±5	1900±9	11.61±0.32	1868±16	27.06±1.23	569±6	-	49.85±1.45
C5	3296±12	74±2	7709±8	-	12.90±0.45	15.60±0.14	1232±10	tr	15.50±0.34	5548±11	45.52±2.11	910±7	7.31±0.12	56±3

In a study conducted by Colak [24], some mineral elements and heavy metal quantities were determined in the flowers and root parts of plants purchased in three different regional herbalists in Istanbul, Kadıköy, Bakırköy and Güngören. In the study, the amount of nickel was determined to be the highest in perennial (2.409 mg/kg) and the lowest in blackberry (0.255 mg/kg) [24]. It has been determined that plants have normal values in terms of nickel amounts and do not show toxic effects.

When the strontium (Sr) amounts of plants grown in A, B and C soils are examined, it is seen that there are values, respectively, as 21.14±0.13, 29.54±1.04, 33.04±1.24 mg/kg for plant 1; 58±2, 72±6, 52±1 mg/kg for the plant 2; 64±3, 69±4, 54±2 mg/kg for the plant 3; 45.13±1.03, 18.03±0.89, 49.85±1.45 mg/kg for the plant 4; 77±2, 55±1, 56±3 mg/kg for the plant 5. In other words, among the concentrations of the same plants grown in different soils, it is observed that there is a relationship as C1> B1> A1 for plant 1; B2> A2> C2 for the plant 2; B3> A3> C3 for the plant 3; C4> A4> B4 for the plant 4 and CA> C5> B5 for the plant 5. In general, when the results were examined, it was determined that the strontium amount was the lowest B4 (18.03±0.89 mg/kg) and the highest was A5 (77±2 mg/kg). The mean Sr level in seven types of medicinal herbs of Turkey by Basgel and Erdemoglu [14] were found to be 69.2 µg/g. The mean Sr levels in thirty medicinal herb samples widely consumed in Kayseri, Turkey by Tokalioglu [11] was found to be 112 µg/g, The highest Sr levels was found in *Horsetail* sample (669 µg/g).

2.6. Principal component analysis (PCA)

Principal Component Analyses (PCA) was applied to analyze of 11 common metals, since Co, Cr, and Ni were not detected in all samples. In the PCA analysis, the average of the metal content results was evaluated. According to the PCA, three principal components eigenvalues were higher than 1. The first 3 main components explained 78.9% of the total variance. Briefly, the first component (PC1) explained 48.6%, while PC2 21.1%, and PC3 9.2% of variance (Table 4). The main components explaining the dominant values were given and highlighted in Table 4. The highest variance belonged to PC1 in the dataset. Al, Ba, Fe, Li, Mg, and Mn were dominant in PC1, while Ca, and Sr were for PC2, and Cu, and Na for PC3.

Table 4. The loadings, eigenvalues, variance and cumulative variance values for principal components of studied species.

Variable	PC1	PC2	PC3	PC4
Al	**0.323**	-0.305	-0.215	0.024
Ba	**0.351**	0.048	0.145	-0.256
Ca	0.248	**0.317**	-0.021	-0.365
Cu	0.244	-0.286	**0.395**	0.258
Fe	**0.307**	-0.339	-0.133	-0.003
K	-0.3	-0.14	0.189	0.138
Li	**0.259**	0.153	-0.438	0.373
Mg	**0.372**	-0.037	-0.119	-0.065
Mn	**0.272**	-0.382	-0.061	0.129
Na	0.204	-0.096	**0.675**	-0.087
Sr	0.22	**0.399**	0.134	-0.108
Eigen value	6.3147	2.7399	1.1996	0.9168
Proportion (%)	48.6	21.1	9.2	7.1
Cumulative (%)	48.6	69.7	78.9	85.9

Table 4 shows the score values of the first four principal components. Herein, it was observed that A5, B5, and C5 could be characterized with Al, Ba, Fe, Li, Mg, and Mn for the PC1, while A3, B2, C3, B3, C2, and A2 with Ca, and Sr for PC2.

B1, C1, C4, A4, A1, and C3 were negatively characterized with metals; namely, Al, Ba, Fe, Li, Mg, and Mn for PC1. As for PC2, B4, B5 and C1 were negatively characterized with Ca, and Sr. Figure 1 shows PC1 vs PC2 score plot of species which the details were given in Table 5. The score plot graph indicated that four groups occurred according to metal analyses quantitative results. It is clearly seen that the groups of A, B and C species is irresponsible for the discrimination (Figure 1).

Table 5. The scores of the first four rotated principal components.

Samples	PC1	PC2	PC3	PC4
A1	-1.75414	-0.397	-0.90246	0.60879
A2	0.75407	**1.25234**	1.13715	0.43598
A3	1.08053	**2.85929**	-0.37724	1.97957
A4	-1.91484	-0.79304	1.24502	0.62415
A5	**5.23202**	0.00104	-1.82842	0.24104
B1	-3.1679	-0.54736	-0.82981	-0.25309
B2	-0.70966	**1.54214**	1.35361	-0.41066
B3	0.54656	**1.34891**	-0.78036	0.19376
B4	0.2913	-3.85472	-0.25907	0.98281
B5	**4.39088**	-1.93362	0.95819	-1.03911
C1	-2.65891	-1.06334	-1.11092	-0.56537
C2	-0.72832	**0.84166**	1.16464	-0.70243
C3	-1.35022	**1.52638**	-1.31213	-2.00644
C4	-2.5479	-0.75013	0.63804	0.56779
C5	**2.53653**	-0.03257	0.90374	-0.65679

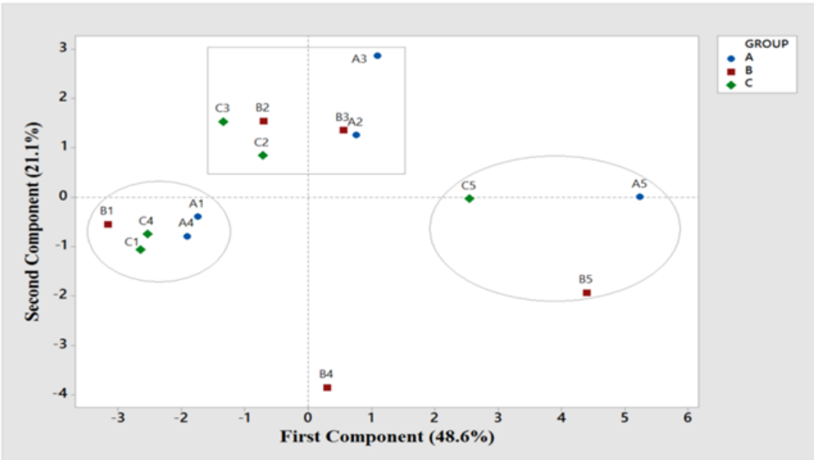

Figure 1. Score plot graphic for PC1 and PC2 in A1-C5, ● A species in group A, ■B species in group B, ♦ C species in group C.

The loading graphs were given in Figure 2. Figure 1 and Figure 2 considering together gave information about the sample having the highest concentration of metals in species. A1, B1, C1, A4, C4 had more potassium than the others. Similarly, A5, B5, and C5 had more Al, Cu, Fe, Mg, Mn, and Na.

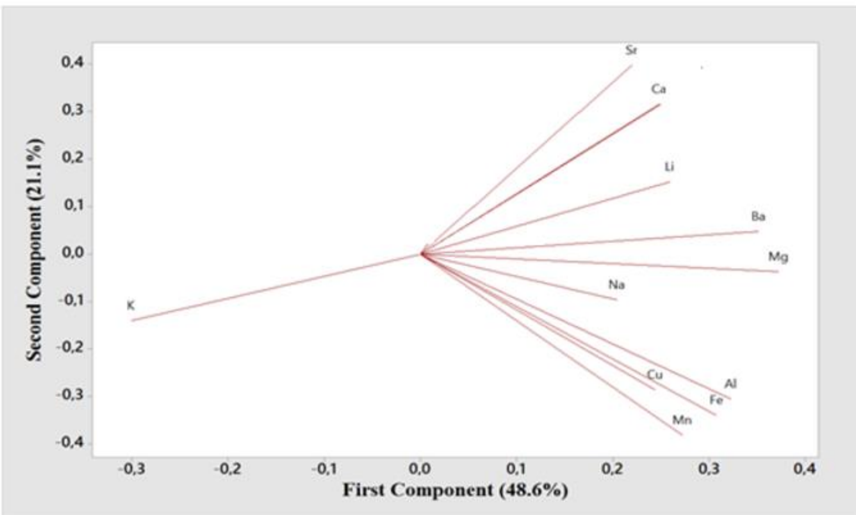

Figure 2. Loading plot for PC1 and PC2 in A, B and C.

Samples coded A1, B1, C1, A4, and C4 grouped together, which K was the major metal characterizing this group. A5, B5, and C5 were grouped together where Al, Cu, Fe, Mg, Mn, and Na were the abundant metals in these group members. Third group consisted of A2, B2, C2, A3, B3, and C3 species which were abundant with Sr. The last group consists of only B4 which was abundant with Mn.

3. CONCLUSIONS

It is known that different soil structures are effective in the development of plants and the minerals they contain. The heavy metal accumulation in plants is caused by the metal content in the air, water resources, especially the soil [9]. Plants prevent heavy metal contamination of soil by accumulating heavy metals in their different organs. However, it is possible for these metals accumulated by plants to enter the food chain easily and quickly. Soil structure and metal content are known to have an effect on the metal content of some plants [12,29,41].

In this study conducted with a limited number of soils (3 types) and plants (5 species), when the metal content of the soil samples was compared with the metal content of the plants, it was observed that there was no linear relationship between the values in the soils and the values in the plants In addition, it can be said that the particle size and physical properties of the soil don't have a direct effect on the metal content of the species studied. When all the results are evaluated, It was determined that Al, Ba, Li, Mg and Sr are at most at A5; Ca, Cr, Fe, Mn, and Na are at B5; Ni's at C5, Ca at A2; Cu was at B4 and K was at C4. In other words, plant 5 was found to contain the highest element content, even in different soils. It is known in the literature that the metal content of the plants changes according to the soil structure in which they grow. In this study, a limited number of soils (3) and a limited number of plants (5) did not reveal a relationship between the metal content of the soil samples and the metal content of the plants. According to the few examples in this study, it can be said that the metal content variability of the plants is affected by factors such as genetic variability, climatic conditions, and harvesting times rather than the soil content factor. It has been determined that this type of analyzed edible medicinal plants is a good mineral source and varies according to the species.

4. MATERIALS AND METHODS

4.1. Soil analysis

Soil samples are classified as high, very high, and much higher plasticity soil according to IAEG (1976) liquidity-bound plasticity classification. According to Burmister (1951), high and very high plasticity clay-silty clay. Plastic and very plastic floor according to the plasticity classification of Leonards (1962); and high-very high plasticity soil according to the plasticity classification based on the plasticity index of IAEG (1976).

4.2. The plant material

Studied species were collected from southeast of Turkey in 2019 by Dr. Cumali Ozaslan (Department of Plant Protection, Faculty of Agriculture, Dicle University) and Mehmet Firat (Department of Biology, Faculty of Education, Yüzüncü Yıl University) and they were identified by Mehmet Firat (Table 6).

Table 6. Plant strains growing on different soil.

No	Plant name	A soil	B soil	C soil	Collection time
Plant 1	*Sorghum halepense*	A1	B1	C1	July 2019
Plant 2	*Convolvulus arvensis*	A2	B2	C2	June 2019
Plant 3	*Physalis angulata*	A3	B3	C3	June 2019
Plant 4	*Cynodon dactylon*	A4	B4	C4	July 2019
Plant 5	*Portulaca oleracea*	A5	B5	C5	July 2019

4.3. Instrument, reagents and solutions

An Agilent 7700X model ICP-MS system was used for simultaneous multi-element detection of Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, and Sr. The ICP-MS operating conditions are shown in Table 7. Syringefilters (Germany) were used to separate the undissolved parts of plant samples. A microwave oven equipped with PTFE vessels, MilestoneEthos One (Italy), was used for sample digestion. The methanol (Merck), nitric acid (Merck) and hydrogen peroxide (Merck) used were of analytical reagent grade. Ultrapure water (New Human UP 900, Human Corp., Seoul, Korea) was used in all experiments.

Table 7. Optimal ICP-MS operating conditions for analysis of samples.

Instrument Parameter	Value
Plasma mode	Normal
RF forward power (W)	1550
Carrier gas flow rate (L/min)	0.96
Spray chamber temperature (°C)	2
Make up gas flow rate (L/min)	0.9
Plasma gas flow rate-Argon gas (L/min)	15
Plasma gas	Ar X50S 5.0
Nebulizer gas flow rate (L/min)	1.1
Sample uptake rate (L/min)	0.8
Interface cone	Ni
Short-term stability (RSD)	<3%
Long-term stability (RSD)	<4%
Isotopes measured	^{107}Ag, ^{27}Al, ^{75}As, ^{137}Ba, ^{43}Ca, ^{111}Cd, ^{59}Co, ^{52}Cr, ^{63}Cu, ^{57}Fe, ^{39}K, ^{7}Li, ^{24}Mg, ^{55}Mn, Na, ^{60}Ni,^{88}Sr

4.4. Sample preparation

For ICP-MS method, 0.300 g (±0.001 g) dried samples of plants were transferred to a Teflon vessel, digested with 6 mL of concentrated ultrapure nitric acid (65%) and 2 mL of ultrapure hydrogen peroxide(36%) [18,43]. Dry soil samples (0.250 g (± 0.001 g) were weighed precisely and transferred to teflon vessel which was placed in microwave tubes. And then 6 mL HNO_3 (65%) and 4 mL HF (40%) were added to the vessel, to use the microwave digestion technique [21]. Decomposition of the samples was carried out in a microwave digestion system (Milestone Srl, Ethos One, Italy). A one-step microwave program, ramping for 15 min up to 200°C at 1000 W, holding for 10 min at 200°C at 1000 W, was applied to the samples [18,43]. The undissolved parts were separated with 25 mm polyethylene syringe filters (Millex, Merck KGaA, Germany).

4.5. Method validation

The analytical characteristics of the proposed method were obtained for the ten elements studied under the optimized conditions. Table 8 presents the linear ranges used for calibration and the coefficients of determination (r^2) used to assess the linearity (r^2:0.99). The limits of detection (LOD) and limits of quantification (LOQ) for each metal were determined as follows: 10 independent analyses of a blank solution spiked with the metal at a lower level of concentration of the analytical curve were performed. The LOD and LOQ were calculated from the standard deviation (σ) of these determinations (LOD = 3.σ and LOQ = 10.σ).

4.6. The chemometric analysis

The chemometric analyses for these species collected in Diyarbakır were carried out using Principal Component Analysis (PCA) examples of the multivariate data analysis methods. All methods for clustering and classification are mainly based upon the principal component analysis, which is a multivariate data analysis method. PCA is a method which reduces multiple variables into a set of fewer components created by their linear combinations by hindering correlations between those examined variables. PCA-based methods can classify the samples by clustering into various groups, based on various values for variables. The first three principal components having eigenvalue higher than one were chosen. PC1, PC2 and PC3 explain 78.9% of total variance in the data set. In this context, all classification and clustering analyses for species were carried out using MINITAB Statistical Software.

4.7. Statistical method

All statistical calculations were made using MINITAB 16.2.1 Statistical Software (MINITAB Inc. 2010). Multivariate Analysis regarding 18 heavy metal components in species was carried out using Principal Component Analysis (PCA). The accuracy and precision of the method was evaluated by CRM 1573a Tomato Leaves (Table 9)

Table 8. Linear Range, regression correlation coefficient (r^2), LOD, LOQ.

Element	Lineer Range	Regression	r^2	LOD (µg/kg)	LOQ (µg/kg)
Ag	5-100	y= 0.1201x + 0.0012	0.9997	0.0165	0.0544
Al	5-100	y= 0.0229x+ 0.0014	0.9995	0.1569	0.5177
As	5-100	y= 0.0429x + 0.0012	0.9999	0.0188	0.0620
Ba	5-100	y= 0.0189x+ 0.0025	0.9986	0.2556	0.8434
Ca	5-100	y= 0.6431x+ 0.0074	0.9975	0.5715	1.8859
Cd	5-100	y= 0.0270x+ 0.0019	0.9957	0.3817	1.2596
Co	5-100	y= 1.654+ 0.0674	0.9987	0.0247	0.0815
Cr	5-100	y= 0.6283x+ 0.0472	0.9969	0.5069	1.6727
Cu	5-100	y= 1.4789x+ 0.1564	0.9965	0.5451	1.7988
Fe	5-100	y= 1.1674x+ 0.0164	0.9992	0.5892	1.9443
K	5-100	y= 0.9951x+ 0.0175	09985	0.6373	2.1030
Li	5-100	y= 0.0974x+ 0.0067	0.9957	0.3456	1.1404
Mg	5-100	y= 0.0862x+ 0.0040	0.9967	0.3962	1.3074
Mn	5-100	y= 0.7920x+ 0.0134	0.9967	0.4295	1.4173
Na	5-100	y= 0.0663x+ 0.0023	0.9988	0.3410	1.1253
Ni	5-100	y= 0.6829x+ 0.0817	0.9963	0.2118	0.6989
Sr	5-100	y= 0.0164x+ 0.0021	0.9957	0.1962	0.6474

Table 9. Accuracy assessment of analysis of CRM NIST 1573a tomato leaves.

Elements	Certificate value (mg/kg)	Found value (mg/kg)	Recovery (%)
Ba	(63)[a]	64±2	101.50
Cr	1.99±0.06	1.96±0.03	98.49
Co	0.57±0.02	0.60±0.06	105.26
Cu	4.70±0.14	4.71±0.22	100.21
Ni	1.59±0.07	1.60±0.06	100.62
Cd	1.52±0.04	1.55±0.08	101.97
Fe	368±7	371±11	100.81

[a]Values in parentheses are not certified values.

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