

## Determination of Minerals and Trace Elements in Soils and The Relation with its Concentrations in Sugar Beets

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Twelve sugar beets and corresponding soil samples from the plantation near Malatya, Turkey were analyzed for mineral and trace element contents. Thirteen metals (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se and Zn) were selected and analyzed quantitatively by FAAS/FAES and ETAAS. Principal component analysis and hierarchical cluster analysis were used to explore samples based on the element contents. The principal component analysis of sugar beet samples yielded five principal components which were able to explain about 84 % of the total variance in the data set. The number of principal components that are higher than one was four for the soil samples and were able to explain 83 % of total variance. Hierarchical cluster analysis of sugar beet samples and corresponding soil samples resulted in two main clusters based on the geographic regions of the samples. In terms of the elements being analyzed, the hierarchical cluster analysis method resulted in 3-4 clusters of the elements in both sugar beet and soil samples.

**Key Words:** Sugar beet, Trace elements, Minerals, Atomic absorption spectrometry, Microwave digestion, Principal component analysis, Hierarchical cluster analysis.

### INTRODUCTION

Some metals and their compounds are essential to human health (*i.e.*, Fe, Zn, Cr), although they are potentially harmful if consumed in large quantities. Other metals may be harmful to health, *e.g.*, As, Pb, Cd and Hg are non beneficial for biological function and long-term exposure may be toxic even at low doses<sup>1</sup>.

Although some individuals are exposed to toxic elements chiefly in the workplace, for most people the main route of exposure to the toxic elements is through the diet. Consequently, information concerning dietary intake is of the utmost importance in being able to assess risks to human health<sup>2</sup>. This type of information is usually compiled by means of previously validated food surveys.

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Heavy metal contamination in agricultural environments may result from atmospheric fall-out, pesticide formulations, contamination from chemical fertilizers and irrigation with low quality water. The capacity of certain plant species to concentrate heavy metals within their tissues enhances the risk for contamination of the food chain<sup>3</sup>. The presence of trace elements and minerals in sugar beet plants is an indication that these elements are mainly taken through the roots from soil when plants absorb other essential and necessary trace elements required for growth<sup>4</sup>. In recent years, there has been increasing interest in determining the concentration levels of trace and heavy metals in various food sources<sup>5-7</sup>. The elements which are present at varying concentration in different part of the plants, especially in roots, seeds and leaves, all consumed as dietary items or ingredient in the Ayurvedic medicinal preparation<sup>8</sup>.

Accurate and adequate heavy metal contents in food are very important for estimating the adequacy of intakes and assessing exposure risks from intake of toxic non-essential elements. In many less-developed countries such data are not readily available<sup>9</sup>. Plants like sugar beet may be easily contaminated during growing and processing. Plants are the main links of trace element transfers from soil to man and other animals. The level of conditional, the content being affected by the geochemical characteristics of the soil and by the ability of plants to selectively accumulate some of these elements<sup>10</sup>. Trace heavy metals are significant in nutrition, either for their essential or their toxicity. On the other hand, heavy metal contamination of soil due to industrialization and other human activities has become an environmental problem with consequent problems for the human population. High concentration of heavy metals in soil have a selective effect on plant populations. This results in a low diversity of species in different trophic levels. When information is collected from several different variables it becomes quite complicated for modelling complex and high dimensional quantitative relationships between plants and soils using unvaried approaches. In order to analyze these multivariate dependencies, additional approaches are needed and chemometrics could provide detailed solutions in this regard.

Principal component analysis (PCA) is a powerful chemometrics technique<sup>11,12</sup> used to reduce high dimensional data sets to lower dimensions by means of so called principal components (PCs). Principal component analysis is used for several different types of applications including pattern recognition<sup>13</sup> classification<sup>14</sup> and modelling<sup>15</sup>. The PCA model for a given multidimensional data set with  $m$  number of variables and  $n$  number of samples to be classified or clustered is given as:

$$A = T \times B + E_A \quad (1)$$

where  $A$  is  $n \times m$  matrix of original data,  $T$  is  $n \times h$  matrix of so called score vectors or principal component scores,  $B$  is  $h \times m$  matrix of loading vectors that relates the principal component scores to the original data,  $E_A$  is  $n \times m$  matrix of residuals that are not fit by the model and  $h$  is the number of principal components which must be less or equal to the smallest of  $n$  or  $m$ . It can be seen from the eqn. 1 that PCA is

actually a decomposition method of original data matrix into two smaller matrices namely scores and loadings. Here, each columns of T are the principal components and the first principal component accounts for the maximum variance and the second one for the maximum of the residual variance and so on until the total variance was explained. For some particular data sets, only few of the principal components would be sufficient to explain about 90 % of the total variance in the data whereas in some cases a significant number of principal components may be needed to explain the data. As a result, PCA is a method to determine the variables and samples which are close to each other and contain similar information.

Hierarchical cluster analysis (HCA) is a method of classifying samples and variables into groups by means of measuring their similarities<sup>16</sup>. Hierarchical cluster analysis can be applied directly to the original raw data or it can be applied to the principal components obtained from PCA analysis where the number of original variables is quite large. There are a number of distance measures such as Euclidean and Mahalanobis distance methods each with its own advantages and disadvantages. For example, the use Mahalanobis distance method requires that the number of variables in the data must be smaller than the number of objects or samples. The choice of distance method depends on the nature of the data and the information sought from the data. Once the distance measurements are performed, the next step in HCA is the selection of most appropriate clustering algorithm and Ward's method one of the most used algorithms. Hierarchical cluster analysis is used to create a cluster tree with a multilevel hierarchy in which the clusters in one level are combined to the clusters at the next higher level.

Little information is available concerning minerals and trace element content of sugar beet cultivated in Turkey<sup>17</sup>. Thus, the objective of this study are (a) to provide information about the levels of some minerals and trace elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se and Zn) in sugar beets plants and soils (b) to examine relationships between minerals and trace elements content of sugar beet plants and certain soil properties using multivariate classification methods such as PCA and HCA. Furthermore, it is well known that not only the determination of element concentrations in food and food sources is important, but also a reliable analytical procedure is a serious step in the studies on trace element analysis for preventing heavy metal poisoning. For this purpose, prior to determination of the elements FAAS and GFAAS in the sugar beet plants and in the soil, optimization of microwave digestion procedure for dissolution of the all samples is also examined, where the analytical characteristics of the proposed method, the accuracy and precision were tested and verified by a certified reference material (NIST-SRM 1515 Apple Leaves).

## EXPERIMENTAL

This study was conducted in 2006 on 12 sugar beet samples and soil on the surface of tubers from a harvest brought to a sugar plant in Malatya, Turkey.

A Perkin-Elmer AAnalyst 800 atomic absorption spectrometer (FAAS), equipped with THGA graphite furnace and with Zeeman-effect background corrector, was

used in the experiments. For flame measurements, a 10 cm single slot-burner head, a lamp an air-acetylene flame was used. For graphite furnace measurements, argon was used as inert gas. The operating parameters for the working elements were set as recommended by the manufacturer. Pyrolytic-coated graphite tubes (Perkin-Elmer part No. B3 000641) with a platform were used. Samples were injected into the graphite furnace using a Perkin-Elmer AS-91 auto sampler.

A milestone start D closed vessel microwave digestion system (maximum pressure 1450  $\psi$ , maximum temperature 300 °C) of Teflon reaction vessels was used in all the digestion procedures. The reaction vessels were cleaned using 5 mL of concentrated nitric acid before each digestion.

Unless stated otherwise, all chemicals used were of analytical-reagent grade. Throughout all analytical work, doubly distilled water (Milli-Q, Millipore 18, 2 M $\Omega$  cm resistivity) was used. In the digestion, concentrated nitric acid (65 %, E. Merck, Darmstadt) and hydrogen peroxide (30 %, E. Merck, Darmstadt) were used. All the plastic and glassware were cleaned by soaking in diluted HNO<sub>3</sub> (1 + 9) and rinsed with distilled water prior to use. The elements standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/L of each element supplied by Inorganic Ventures/IV Labs.

### Digestion procedures

**General:** Three different types of digestion procedures were applied to the digestion of all samples: dry, wet and microwave digestions.

**Dry ashing:** Approximately 0.5 g of each sample was placed in a high form porcelain crucible. The furnace temperature was slowly increased from room temperature to 480 °C and ashed at 480 °C in ashing furnace for 4 h. This process was repeated if necessary until a white or grey ash was obtained. The residue was dissolved in 5 mL of HNO<sub>3</sub> (25 % v/v) and dried with occasionally stirring on a hot plate with low heat. The residue was then dissolved with 3.0 mL of 1.5 mol/l HNO<sub>3</sub>. The solution was transferred to a 25 mL volumetric flask and make up to the volume. The clear digests were analyzed for each element by FAAS or GFAAS. The same digestion procedure was also used for blank.

**Wet ashing:** A 0.5 g portion of each sample was placed into a flask and a mixture of 2:1, HNO<sub>3</sub>: H<sub>2</sub>O<sub>2</sub> (6 mL for 0.5 g sample) was added. This mixture was digested, with stirring, until a clear digest was obtained (approximately 4 h). The clear digest was made up to a volume of 25 mL with deionized water and analyzed for each elements by FAAS or GFAAS. A blank digest was carried out in the same way.

**Microwave digestion:** Each sample was transferred to Teflon bomb and digested with 7 mL of HNO<sub>3</sub> (65 %) and 1 mL of H<sub>2</sub>O<sub>2</sub> (30 %) in a microwave digestion system. After cooling, the mixture was transferred to the volume with deionized water. The blank digest was carried out in the same way. Digestion conditions for the microwave system applied were: 10 min for 500 W, 10 min for 1000 W, went: 10 min.

**Analytical procedure:** The samples were digested by the wet ashing, dry ashing and microwave digestion and analyzed using a Perkin-Elmer AAnalyst 800 model atomic absorption spectrometer (FAAS), equipped with THGA graphite furnace and with Zeeman-effect background corrector. The elements were quantified against standard solution of known element concentrations that were analyzed concurrently. The amounts of Se, Pb, Ni, Cd, Cu and Zn metal ions were determined at the  $\mu\text{g g}^{-1}$  level and the other elements; Al, Mn, Fe, Na, K, Ca and Mg were determined at the  $\text{mg g}^{-1}$  level.

Matrix modifier were added:  $30 \mu\text{g Mg(NO}_3)_2$  for Se;  $20 \mu\text{g Mg(NO}_3)_2$  for Al, Ni and Cr;  $50 \mu\text{g Mg(NO}_3)_2$  for Pb.

**Data analysis:** All spectroscopic measurements were made in triplicate and averages of the quantitative data were calculated for both sugar beet samples and soil samples. Principal component analysis and HCA analysis of the data were performed with these averages. All the PCA and HCA algorithms were written in Matlab programming language using Matlab 5.3 (Mathworks Inc., Natick, MA).

## RESULTS AND DISCUSSION

In the present work, mineral and trace elements (Al, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Se and Zn) were determined in sugar beet plants and soil samples by means of common spectroscopic techniques (FAAS/FAES and ETAAS) after the complete dissolution of their matrices with microwave assisted digestion. Fig. 1 shows the geographic regions from where the sugar beets were collected. In order for convenience in the PCA and HCA analysis the name of the regions were abbreviated as shown in Table-1. Reduced time required for sample preparation and reduced amounts of acids and oxidants used, minimal contamination within the laboratory, reduced the loss of more volatile analytes and consequently better detection limits and accuracy of the method are advantageous over the numerous preparation procedures, which include classical dry or wet digestion.

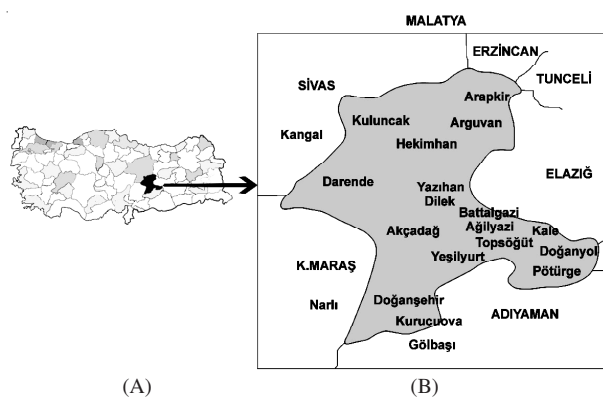


Fig. 1. Maps showing the location of the area considered for sampling: (A) the province of Malatya in Eastern Turkey and (B) the sampling sites

TABLE-1  
 NAMES OF THE REGIONS AND THEIR ABBREVIATIONS AROUND THE MALATYA  
 (TURKEY) WHERE THE SUGAR BEET AND SOIL WERE TAKEN

|                       |    |
|-----------------------|----|
| Akcağaç               | Ad |
| Darende               | DA |
| Dilek                 | DL |
| Döğüşehir             | DS |
| Döğüşehir-Kurucaova   | DK |
| Eski Malatya-Ağilyazi | EA |
| Eski Malatya-Cöğlü    | EC |
| Gölbasi               | GB |
| Maras-Narlı           | MN |
| Sivas-Kangal          | SK |
| Töpsöğüt              | TS |
| Yazihan               | YH |

The accuracy of all the digestion methods was checked by standard reference material (NIST-SRM 1515 apple leaves) for the reliability of the method used in this work. The results are given in Table-2. A good harmony was observed between the certified values and present values for the analyte ions. Table-2 also shows the results of the recovery of the standard reference material (NIST-SRM 1515 apple leaves) for the three different digestion methods. The recovery rates of the trace elements were the highest with microwave-digestion method. Therefore, the microwave-digestion method was used for the digestion of all samples. Similar results were also reported for honey samples<sup>18</sup>.

TABLE-2  
 OBSERVED AND CERTIFIED VALUES OF ELEMENTAL CONCENTRATIONS IN  
 NIST-SRM 1515 APPLE LEAVES AS AVERAGE  $\pm$  SD, n = 3

| Element | Certified<br>( $\mu\text{g g}^{-1}$ ) value | Observed values        |                 |                   |                 |                   |                 |
|---------|---|------------------------|-----------------|-------------------|-----------------|-------------------|-----------------|
|         |   | Microwave<br>digestion | Recovery<br>(%) | Dry ashing        | Recovery<br>(%) | Wet digestion     | Recovery<br>(%) |
| Se      | 0.050                                       | 0.05 $\pm$ 0.001       | 100             | 0.02 $\pm$ 0.001  | 40              | 0.04 $\pm$ 0.002  | 80              |
| Pb      | 0.470                                       | 0.45 $\pm$ 0.01        | 96              | 0.43 $\pm$ 0.02   | 91              | 0.44 $\pm$ 0.02   | 94              |
| Ni      | 0.910                                       | 0.87 $\pm$ 0.01        | 96              | 0.78 $\pm$ 0.01   | 86              | 0.84 $\pm$ 0.01   | 92              |
| Cu      | 5.640                                       | 5.45 $\pm$ 0.07        | 97              | 5.18 $\pm$ 0.08   | 92              | 6.30 $\pm$ 0.04   | 94              |
| Zn      | 12.500                                      | 12.3 $\pm$ 0.2         | 98              | 11.5 $\pm$ 0.2    | 92              | 11.63 $\pm$ 0.3   | 93              |
| Al      | 286.000                                     | 283 $\pm$ 4            | 99              | 263 $\pm$ 5.0     | 92              | 266 $\pm$ 4.0     | 93              |
| Mn      | 54.000                                      | 52.2 $\pm$ 0.4         | 97              | 49.1 $\pm$ 0.4    | 91              | 50.2 $\pm$ 0.5    | 93              |
| Fe      | 83.000                                      | 77.4 $\pm$ 1.3         | 93              | 74.7 $\pm$ 1.8    | 90              | 75.5 $\pm$ 2.1    | 91              |
| Na      | 24.400                                      | 25.8 $\pm$ 2.0         | 106             | 22.9 $\pm$ 2.5    | 94              | 22.7 $\pm$ 1.8    | 93              |
| K (%)   | 1.610                                       | 1.66 $\pm$ 0.01        | 103             | 1.49 $\pm$ 0.02   | 93              | 1.50 $\pm$ 0.02   | 93              |
| Ca (%)  | 1.526                                       | 1.600 $\pm$ 0.011      | 105             | 1.434 $\pm$ 0.020 | 93              | 1.420 $\pm$ 0.010 | 93              |
| Mg (%)  | 0.271                                       | 0.264 $\pm$ 0.04       | 97              | 0.249 $\pm$ 0.04  | 92              | 0.257 $\pm$ 0.04  | 95              |

In the analysis of individual trace element contents, 13 elements were identified and then quantified in both sugar beet and soil samples and the results are shown in Tables 3 and 4. These elements were selenium, lead, nickel, cadmium, copper, zinc, manganese, iron, aluminium, sodium, potassium, calcium and magnesium. Concentration of nickel and cadmium were the lowest among the analyzed elements in both sugar beet plants and the soil samples.

In order to carry out PCA and HCA analysis, the data given in Tables 3 and 4 were converted to a text file without the standard deviation values associated with the concentrations of the each metal in all samples. As can be seen from Table-3, some of the metal concentrations are missing as they are labelled as "nd" (not detected). For these samples we have replaced the "nd" with one third of the limit of quantification (LOQ) values for these elements. For Pb the LOQ was  $0.01 \text{ mg g}^{-1}$  and that for the Ni  $0.001 \text{ mg g}^{-1}$ . The two other metals that had nd label in Table-2 were Cd and Mn and their LOQ was  $0.005 \text{ mg g}^{-1}$ . On the other hand, results of soil samples do not contain "nd" labels as shown Table-4. In addition to these changes, the raw data sets were mean centred and standardized so that the preprocessed data would have a mean of zero and a variance of one. This is needed since the concentrations of the elements studied here varied significantly from element to element. For example, the concentration of Mn was ranging between 290 and  $1900 \text{ mg g}^{-1}$  whereas for Cd the concentration values were between 0.32 and  $0.70 \text{ mg g}^{-1}$ . If the raw data were to be used for PCA and HCA analysis then the results of these methods will be weighed towards to the elements that have higher concentrations.

Once the text files of the sugar beet samples and soil sample were prepared each data set were separately analyzed with both PCA and HCA algorithms. Fig. 2 shows the scores and loading plots of the first two principal components obtained from PCA analysis for the sugar beets data along with the biplot of scores and loadings. The biplot of scores and loading for the first two principal components are formed after normalizing the scores and loading matrices so that they would have the same scale. The PCA analysis of sugar beet samples gave five principal components having eigen values that are higher than one.

These five principal components were able to explain about 84 % of the total variance in the data set. Only 26 % of the cumulative variance in the data set were explained with the first principal component (PC1) and the second principal component (PC2) explained about 19 % of the total variance. Thus, 45 % of the cumulative variance were explained with PC1 and PC2. The percentage of the variance covered by the PC3 was 17 % and that for the PC4 was 13 %. Keeping in mind that explained total variance with the first two principal components was only 45 %, the score plot given in Fig. 2a was not able to indicate well separated grouping of the samples based on the regions of the samples except a few regions. On the other hand, it may be possible that elemental profiles of the regions studied have similar compositions. This issue is addressed in detail in the analysis of HCA results. Loadings plot given in Fig. 2a shows rather like a circular distribution of the elements. Here the PC1



TABLE-3  
SOME TRACE METALS AND MINEARALS CONTENTS IN MICROWAVE DIGESTED  
SUGAR BEET SAMPLES (Se, Pb, Ni, Cd, Cu AND Zn  $\mu\text{g g}^{-1}$ ), OTHERS ( $\text{mg g}^{-1}$ ), n = 3

| Sugar beet | Se              | Pb             | Ni             | Cd               | Cu              | Zn              | Mn              | Fe               | Al               | Na             | K              | Ca             | Mg              |
|------------|-----------------|----------------|----------------|------------------|-----------------|-----------------|-----------------|------------------|------------------|----------------|----------------|----------------|-----------------|
| Akçadag    | 0.55 ±<br>0.04  | 0.10 ±<br>0.01 | 0.06 ±<br>0.01 | nd               | 1.63 ±<br>0.10  | 0.07 ±<br>0.20  | 2.55 ±<br>0.22  | 0.010 ±<br>0.001 | 0.008 ±<br>0.001 | 2.24 ±<br>0.01 | 1.55 ±<br>0.01 | 0.16 ±<br>0.01 | 0.45 ±<br>0.01  |
| Darende    | 0.40 ±<br>0.07  | 0.07 ±<br>0.01 | 0.05 ±<br>0.01 | nd               | 0.55 ±<br>0.20  | 4.93 ±<br>0.06  | 2.37 ±<br>0.28  | 0.692 ±<br>0.008 | 0.002 ±<br>0.001 | 1.94 ±<br>0.03 | 2.19 ±<br>0.01 | 0.19 ±<br>0.01 | 0.49 ±<br>0.01  |
| Dilek      | 0.22 ±<br>0.09  | 0.12 ±<br>0.01 | 0.02 ±<br>0.01 | nd               | 3.33 ±<br>0.10  | 22.93 ±<br>0.20 | 14.20 ±<br>0.30 | 0.022 ±<br>0.001 | 0.012 ±<br>0.001 | 2.18 ±<br>0.02 | 2.13 ±<br>0.04 | 0.72 ±<br>0.09 | 0.53 ±<br>0.01  |
| Dogansehir | 0.17 ±<br>0.07  | 0.65 ±<br>0.02 | 0.03 ±<br>0.01 | 0.010 ±<br>0.001 | 2.70 ±<br>0.10  | 8.32 ±<br>0.20  | 3.50 ±<br>0.20  | 0.055 ±<br>0.001 | 0.043 ±<br>0.001 | 0.38 ±<br>0.01 | 1.60 ±<br>0.01 | 0.20 ±<br>0.01 | 0.55 ±<br>0.01  |
| Kurucaova  | 0.042 ±<br>0.01 | 0.08 ±<br>0.01 | nd             | nd               | 8.62 ±<br>1.10  | 13.02 ±<br>0.06 | 6.05 ±<br>0.30  | 0.019 ±<br>0.001 | 0.008 ±<br>0.001 | 2.73 ±<br>0.01 | 2.53 ±<br>0.01 | 0.23 ±<br>0.01 | 0.55 ±<br>0.01  |
| Agilyazi   | 0.28 ±<br>0.03  | nd             | 0.02 ±<br>0.01 | 0.024 ±<br>0.001 | 0.90 ±<br>0.20  | 5.00 ±<br>0.09  | 7.25 ±<br>0.30  | 0.023 ±<br>0.001 | 0.042 ±<br>0.001 | 3.65 ±<br>0.01 | 1.22 ±<br>0.01 | 0.34 ±<br>0.01 | 0.53 ±<br>0.01  |
| Çöloglu    | 0.25 ±<br>0.01  | 0.05 ±<br>0.01 | nd             | nd               | 1.08 ±<br>0.50  | 5.12 ±<br>0.03  | 1.30 ±<br>0.20  | 0.019 ±<br>0.001 | 0.037 ±<br>0.001 | 2.32 ±<br>0.02 | 1.50 ±<br>0.02 | 0.46 ±<br>0.01 | 0.54 ±<br>0.001 |
| Gölbasi    | 0.42 ±<br>0.03  | 0.09 ±<br>0.01 | nd             | 0.032 ±<br>0.001 | 1.03 ±<br>0.03  | 5.37 ±<br>1.42  | nd              | 0.18 ±<br>0.001  | 0.021 ±<br>0.001 | 0.46 ±<br>0.01 | 1.50 ±<br>0.01 | 0.19 ±<br>0.01 | 0.51 ±<br>0.01  |
| Narli      | 0.60 ±<br>0.01  | 0.02 ±<br>0.01 | nd             | nd               | 1.30 ±<br>0.09  | 4.53 ±<br>0.62  | nd              | 0.015 ±<br>0.001 | 0.003 ±<br>0.001 | 2.78 ±<br>0.02 | 0.77 ±<br>0.03 | 0.17 ±<br>0.01 | 0.55 ±<br>0.01  |
| Kangal     | 0.19 ±<br>0.02  | 0.07 ±<br>0.01 | nd             | nd               | 2.12 ±<br>0.24  | 6.62 ±<br>0.82  | 0.46 ±<br>0.02  | 0.018 ±<br>0.001 | 0.031 ±<br>0.001 | 1.35 ±<br>0.02 | 1.96 ±<br>0.02 | 0.26 ±<br>0.01 | 0.50 ±<br>0.01  |
| Topsögüt   | 0.18 ±<br>0.01  | 0.08 ±<br>0.01 | nd             | 0.006 ±<br>0.001 | 5.58 ±<br>0.38  | 9.68 ±<br>0.60  | 2.77 ±<br>0.80  | 0.034 ±<br>0.001 | 0.016 ±<br>0.001 | 1.40 ±<br>0.02 | 1.68 ±<br>0.01 | 0.33 ±<br>0.01 | 0.37 ±<br>0.01  |
| Yazihan    | 0.14 ±<br>0.03  | nd             | nd             | 0.019 ±<br>0.001 | 1.68 ±<br>0.012 | 6.98 ±<br>0.13  | 0.21 ±<br>0.01  | 0.024 ±<br>0.001 | 1.016 ±<br>0.001 | 1.32 ±<br>0.01 | 1.68 ±<br>0.01 | 0.27 ±<br>0.01 | 0.46 ±<br>0.01  |

nd = Not detected.



TABLE-4  
SOME TRACE METALS AND MINERALS CONTENTS IN SOIL WHERE SUGAR BEETS  
PLANTS GROWN (Se, Pb, Ni, Cd, Cu AND Zn  $\mu\text{g g}^{-1}$ ), OTHERS ( $\text{mg g}^{-1}$ ), n = 3

| Sugar beet | Se              | Pb              | Ni             | Cd               | Cu               | Zn               | Mn           | Fe                 | Al                 | Na               | K                | Ca              | Mg              |
|------------|-----------------|-----------------|----------------|------------------|------------------|------------------|--------------|--------------------|--------------------|------------------|------------------|-----------------|-----------------|
| Akçadag    | 8.22 ±<br>0.30  | 10.60 ±<br>0.01 | 1.28 ±<br>0.06 | 0.552 ±<br>0.001 | 51.93 ±<br>9.40  | 99.60 ±<br>1.05  | 418 ± 37     | 76.80 ±<br>2.000   | 0.083 ±<br>0.001   | 21.14 ±<br>0.01  | 4.08 ±<br>0.01   | 14.24 ±<br>0.07 | 24.28 ±<br>0.18 |
| Darende    | 10.67 ±<br>0.40 | 15.44 ±<br>0.07 | 1.11 ±<br>0.06 | 0.385 ±<br>0.001 | 34.18 ±<br>1.20  | 77.63 ±<br>0.96  | 607 ± 40     | 36.004 ±<br>0.094  | 31.867 ±<br>0.060  | 71.23 ±<br>0.06  | 19.90 ±<br>0.10  | 33.93 ±<br>0.20 | 13.93 ±<br>0.01 |
| Dilek      | 4.19 ±<br>0.07  | 15.84 ±<br>0.53 | 1.43 ±<br>0.02 | 0.559 ±<br>0.001 | 36.08 ±<br>1.10  | 114.87 ±<br>3.31 | 1335 ±<br>30 | 49.940 ±<br>0.100  | 60.773 ±<br>0.060  | 68.37 ±<br>0.06  | 22.30 ±<br>0.05  | 14.15 ±<br>0.07 | 13.17 ±<br>0.02 |
| Dogansehir | 4.25 ±<br>0.20  | 8.86 ±<br>0.025 | 1.56 ±<br>0.08 | 0.439 ±<br>0.001 | 112.72 ±<br>1.70 | 121.12 ±<br>2.20 | 1909 ±<br>45 | 99.430 ±<br>0.180  | 73.850 ±<br>0.400  | 196.40 ±<br>0.05 | 37.95 ±<br>0.05  | 10.42 ±<br>0.08 | 25.93 ±<br>0.06 |
| Kurucaova  | 1.61 ±<br>0.20  | 1.24 ±<br>0.01  | 1.24 ±<br>0.05 | 0.455 ±<br>0.001 | 112.70 ±<br>1.10 | 127.80 ±<br>2.05 | 1872 ±<br>45 | 97.350 ±<br>0.100  | 21.300 ±<br>0.350  | 310.30 ±<br>0.05 | 137.60 ±<br>0.05 | 8.69 ±<br>0.03  | 23.25 ±<br>0.02 |
| Agilyazi   | 1.16 ±<br>0.10  | 1.07 ±<br>0.01  | 0.55 ±<br>0.10 | 0.332 ±<br>0.001 | 44.13 ±<br>0.30  | 108.42 ±<br>1.10 | 1040 ±<br>25 | 58.180 ±<br>0.170  | 110.533<br>± 0.900 | 226.15 ±<br>0.06 | 100.45 ±<br>0.30 | 7.88 ±<br>0.03  | 13.23 ±<br>0.01 |
| Çöloglu    | 0.54 ±<br>0.04  | 1.78 ±<br>0.02  | 1.29 ±<br>0.07 | 0.320 ±<br>0.001 | 40.68 ±<br>0.50  | 114.90 ±<br>0.90 | 1139 ±<br>25 | 68.900 ±<br>0.200  | 84.117 ±<br>0.200  | 174.32 ±<br>0.20 | 38.15 ±<br>0.05  | 15.82 ±<br>0.01 | 25.32 ±<br>0.04 |
| Gölbasi    | 2.51 ±<br>0.09  | 2.00 ±<br>0.02  | 1.77 ±<br>0.10 | 0.559 ±<br>0.001 | 43.30 ±<br>0.93  | 117.98 ±<br>0.95 | 2415 ±<br>55 | 138.100<br>± 0.100 | 51.400 ±<br>0.10   | 149.46 ±<br>0.05 | 24.70 ±<br>0.40  | 7.81 ±<br>0.02  | 19.02 ±<br>0.04 |
| Narli      | 16.85 ±<br>0.30 | 1.10 ±<br>0.01  | 1.11 ±<br>0.04 | 0.582 ±<br>0.001 | 22.05 ±<br>0.60  | 46.20 ±<br>0.62  | 290 ± 50     | 24.700 ±<br>0.130  | 36.658 ±<br>0.070  | 100.90 ±<br>0.20 | 19.55 ±<br>0.05  | 28.23 ±<br>0.04 | 18.88 ±<br>0.01 |
| Kangal     | 4.02 ±<br>0.10  | 2.23 ±<br>0.10  | 1.47 ±<br>0.08 | 0.652 ±<br>0.001 | 32.98 ±<br>0.12  | 130.38 ±<br>1.30 | 818 ± 2      | 39.270 ±<br>0.150  | 27.072 ±<br>0.030  | 55.49 ±<br>0.30  | 20.05 ±<br>0.20  | 25.58 ±<br>0.04 | 12.84 ±<br>0.01 |
| Topsögüt   | 12.43 ±<br>0.08 | 4.79 ±<br>0.01  | 1.67 ±<br>0.30 | 0.695 ±<br>0.001 | 32.20 ±<br>0.20  | 54.27 ±<br>0.70  | 925 ± 28     | 37.300 ±<br>0.050  | 26.817 ±<br>0.500  | 58.90 ±<br>0.05  | 18.30 ±<br>0.10  | 32.51 ±<br>0.05 | 13.63 ±<br>0.01 |
| Yazihan    | 4.40 ±<br>0.09  | 8.16 ±<br>0.70  | 1.24 ±<br>0.06 | 0.359 ±<br>0.001 | 18.14 ±<br>0.30  | 111.07 ±<br>1.13 | 1115 ±<br>32 | 73.500 ±<br>0.200  | 50.590 ±<br>0.070  | 145.20 ±<br>0.70 | 24.35 ±<br>0.20  | 7.15 ±<br>0.12  | 18.69 ±<br>0.01 |

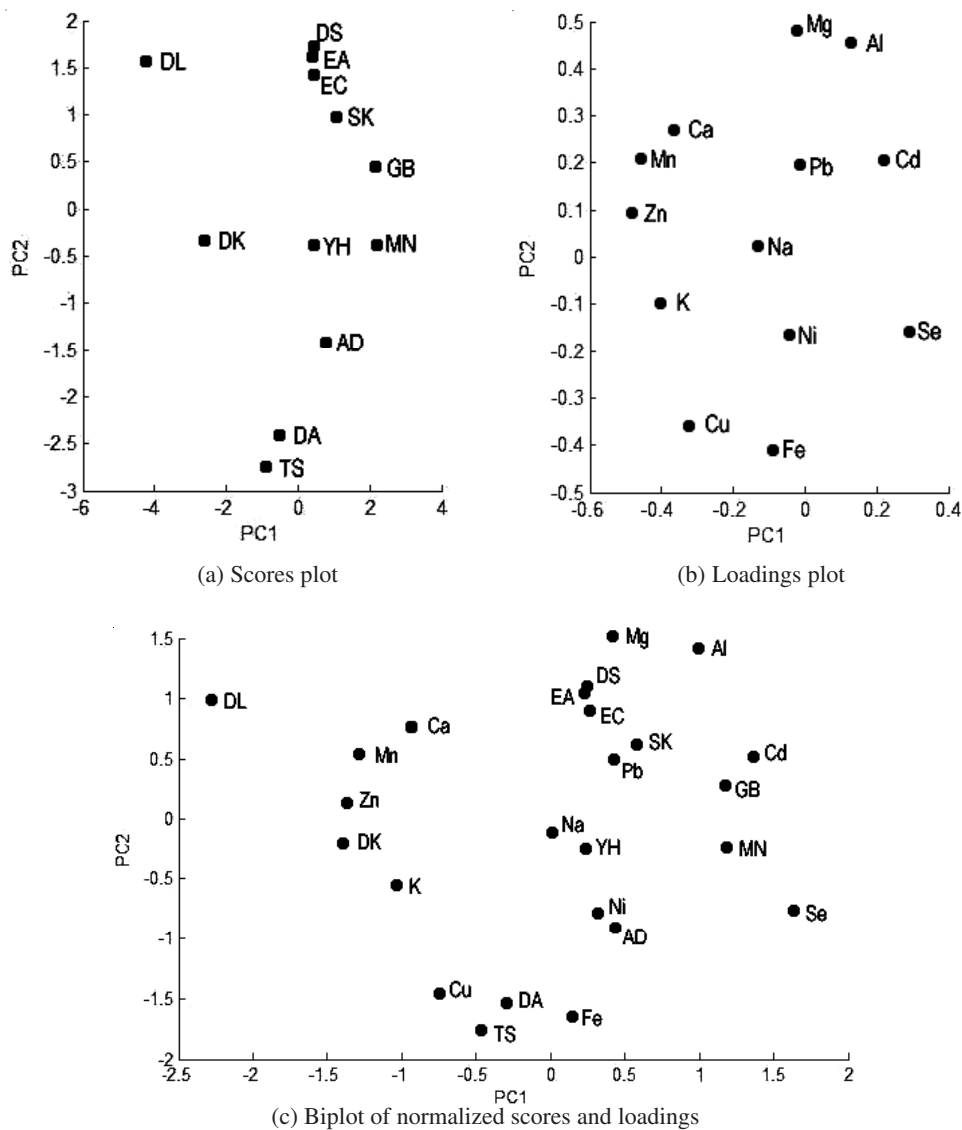


Fig. 2. Plots of PC1 *versus* PC2 for the sugar beet samples

indicates maximum correlation with Zn and Se in the sugar beet samples where Se correlates negatively and Zn correlates positively. For the PC2, the high correlations are seen with Mg, Al, Cu and Fe. Based on the biplot of scores and loadings it is suggested that the sampling region labelled as DK is characterized mainly by Zn and Mn. If one examines the Table-3, it is clear that Zn, Ca and Mn contents in the sugar beet sample taken from DL is the highest among the other samples. The regions DA and TS are best classified by the elements Cu and Fe which is also confirmed from Table-3.

Results of hierarchical cluster analysis are illustrated as dendrograms in Fig. 3 using Ward's method. The distance method used for HCA analysis was Euclidean distance (ED) where four principal components were used to form clusters.

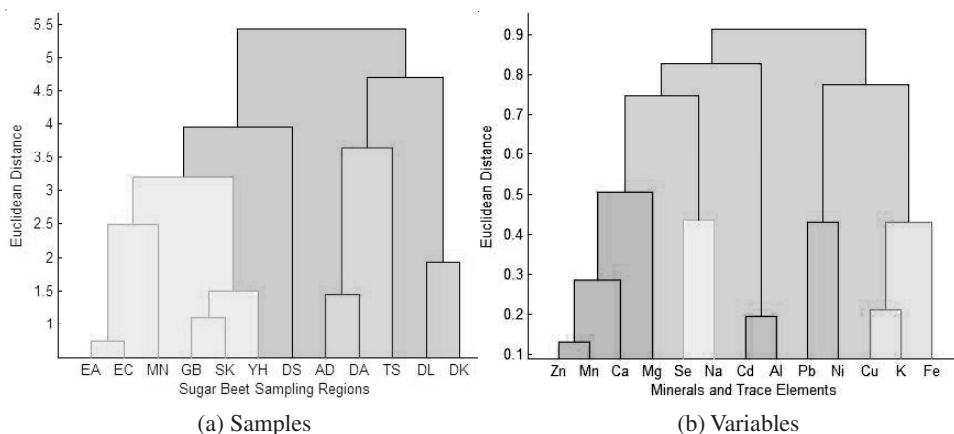


Fig. 3. Dendrograms of sugar beet sampling locations, minerals and trace elements analyzed in the samples

This decision is made after examining results of four principal components and five principal components where no difference were seen in terms of clustering. As can be seen from Fig. 3a, the sugar beet sampling regions were clustered in two main groups. Here, the sampling regions EA, EC, MN, GB, SK, YH and DS were clustered as the regions that have similar patterns. In the same manner the regions AD, DA, TS, DL and DK were clustered as another group. In terms of subclustering, DL and DK show some difference from the group of AD, DA and TS. On the other hand, the region DS seems somewhat different than the group it had hierarchical relationship. The cluster analysis of minerals and trace elements are shown in Fig. 4b. Here, the elements Zn, Mn, Ca and Mg forms one cluster and the nearest cluster to them is the group formed from Se and Na. These two clusters are then joined together at an upper hierarchy whereas the elements Cd and Al are clustered together. The elements Pb, Ni, Cu, K and Fe were clustered in which Pb and Ni as one group and Cu, K and Fe form another group of two subclusters.

Principal component analysis of soil samples where sugar beet samples are grown are illustrated in Fig. 4. Score plot of PC1 versus PC2 is shown in Fig. 4a which is somewhat different than Fig. 2a. There were four eigen values that has values greater than one. The PC1 explained about 42 % of the cumulative variance which is significantly higher compared to sugar beet samples. The PC2, PC3 and PC4 cover about 19, 12 and 10 % of the total variance in the soil data set, respectively. Together with PC1 the sum of the four principal components gave a value of 83 % of total variance. As can be seen from Fig. 4a, the regions DK, GB, DS, YH, EC and EA are different than the regions DL, SK, AF, TS, DA and MN in the sign of the

PC1 scores. In the same manner, Fig. 4b shows that the elements Na, K, Al, Zn, Mn, Mg and Fe all have negative PC1 values whereas all others positive. These two principal component plot were combined into one biplot of scores and loadings after normalizing the scores and loadings matrices as shown in Fig. 4c. As seen from the figure, those regions that have negative PC1 scores are mostly clustered by the elements that have negative PC1 loadings. This could be confirmed when the Table-4 is examined. Fig. 5 shows the dendrograms of the soil sampling regions and minerals and trace elements. In Fig. 5a two main clusters of regions were resulted in which EC, YH, DS, DK, GB and EA formed one cluster on the left and AD, DA, DL, SK, MN and TS formed another cluster on the right. When compared with the dendrogram obtained from sugar beet samples it was seen that the regions DK, SK and MN were differently clustered.

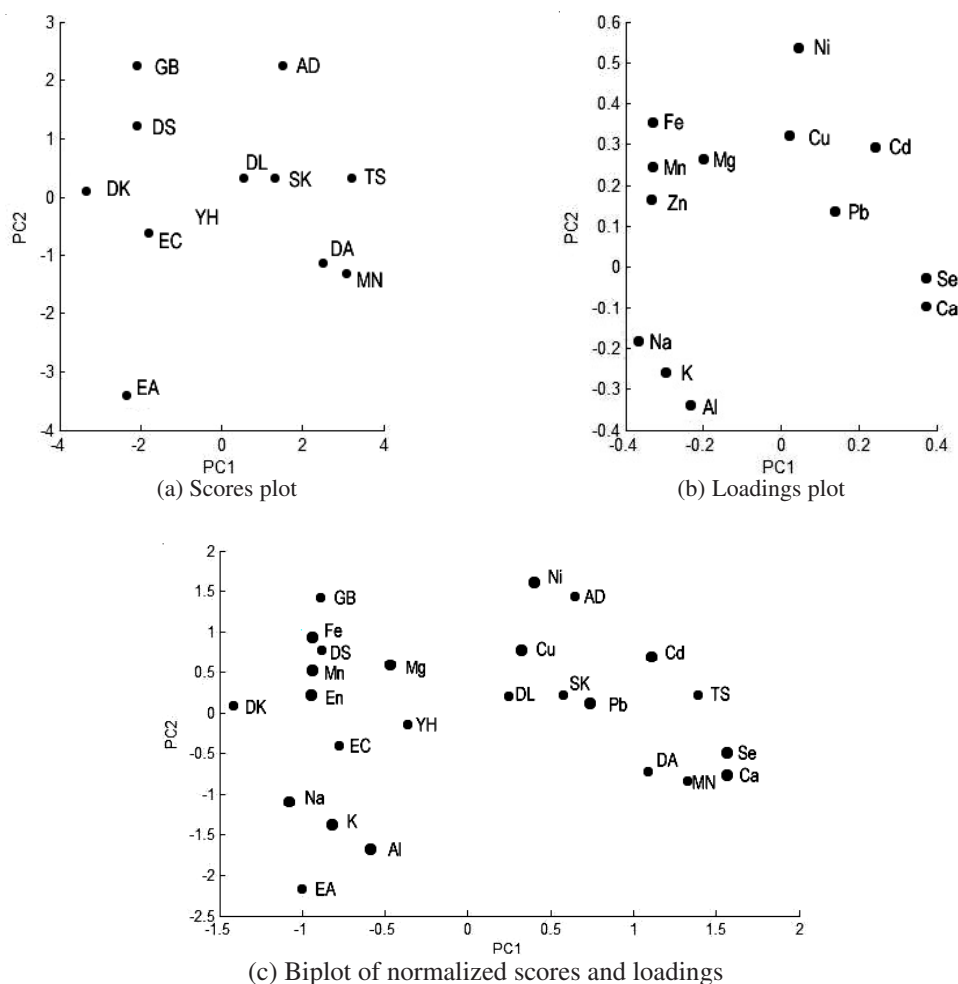


Fig. 4. Plots of PC1 versus PC2 for the soil samples

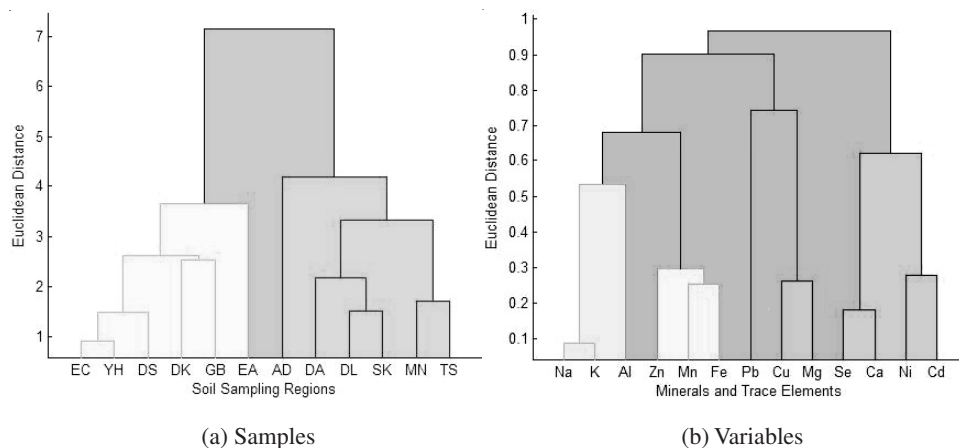


Fig. 5. Dendrograms of soil sampling locations, minerals and trace elements analyzed in the samples

Except these three regions and some differences in the ordering, it is possible to state that elemental composition obtained from soil samples were represented in sugar beet samples which is quite reasonable since the sugar beets were grown in these regions. When one compares PCA with HCA in terms of the clustering, it is evident that HCA performs better since more principal components used. In principal component plots, only the first two principal components were used although the three of them are also tried in this study but no significant differences were observed.

### Conclusion

Thirteen trace and major elements were used to characterize sugar beets and soil samples that are collected at 12 different growing areas around Malatya in eastern Turkey. Multivariate cluster analysis approaches, such as PCA and HCA were used to determine possible correlations between sugar beet and soil samples based on the geographic regions. Results of HCA analysis were demonstrated that the minerals and trace elements analyzed were able to cluster both sugar beet and corresponding soil samples into two main groups. In addition, the elements that show similar compositions in both sugar beet and soil samples were classified to highlight some patterns.

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