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Research Article/Araştırma Makalesi

Comparision of XRF and ICP-OES methods to determine total element concentrations of soils formed on different parent materials in the Sanliurfa province of Turkey

Türkiye'nin Şanlıurfa ilinde farklı ana materyaller üzerinde oluşan toprakların toplam element konsantrasyonlarının belirlenmesinde XRF ve ICP-OES yöntemlerinin karşılaştırılması

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ABSTRACT

The use of different instrumental methods as an alternative to traditional methods has become an important issue in order to detect soil change accurately, quickly and economically. In this study, soil profiles formed over four common parent materials (Mudflow, Basalt, Limestone and Marl) in Sanliurfa province of Turkey were described. Soil samples were collected from each horizon, in addition, surface soil samples (0-20 cm) of cultivated and uncultivated lands around the soil profiles were collected. Soil samples were analyzed using instrumental (ICP, XRF) techniques to determine total element (Si, Al, Fe, Ca, Mg, K, P, Mn, Cr) concentrations as oxides, and assess the impact of parent materials and tillage (cultivated vs uncultivated) on the elemental composition. The highest percent total oxides in the soils were SiO_2, CaO, AlO_2, and MgO. The total oxide concentrations determined by both techniques were close to each other except SiO_2, they were statistically different. In general, differences in the mean total oxide values of the investigated elements among the soils formed on different parent materials determined by both methods were found to be statistically significant ($p < 0.05$) while the effect of soil tillage was significant ($p < 0.05$) only for the results obtained with the XRF. The impacts of soil tillage status on other elements were statistically negligible ($p>0.05$), but only MgO was shown to be significantly affected. The percent SiO_2 values obtained by the ICP technique were quite low compared to the values obtained by the XRF technique. Overall, in terms of total elemental oxide values obtained, the XRF method was considered more advantageous over the ICP technique as it provides more accurate results and requires less soil samples.

Key Words: Soil, Total oxides, Soil tillage, XRF, ICP

ÖZ

Toprak değişiminin doğru, hızlı ve ekonomik olarak tespit edilebilmesi için geleneksel yöntemlere alternatif olarak farklı enstrümantal yöntemlerin kullanılması önemli bir konu haline gelmiştir. Bu çalışmada Şanlıurfa'da dört yaygın ana materyal (Çamur akıntısı, Bazalt, Kireçtaşı ve Marn) üzerinde oluşan toprakların profilleri tanımlanmış, horizon esasına göre alınmış bu profillerin yüzey horizonları ve çevresindeki işlenmiş ve işlenmemiş arazilerin yüzey örnekleri enstrümantal (ICP, XRF) teknikler kullanılarak araştırılmıştır. Farklı ana materyaller üzerinde oluşan toprakların toplam element (Si, Al, Fe, Ca, Mg, K, P, Mn, Cr) konsantrasyonlarını ölçmek için her iki yöntem de kullanılmış ve çeşitli ana materyallerin ve toprak işleme uygulamalarının sonuçlar üzerindeki etkisi ANOVA ve Tukey's analizleri ile

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değerlendirilmiştir. Farklı ana materyale bağlı olarak, topraklardaki SiO_2, CaO, AlO_2 ve MgO oranları en yüksek bulunmuştur. Her iki teknikle belirlenen toplam oksit değerleri SiO_2 hariç birbirine yakın olmakla birlikte istatistiksel olarak farklı çıkmıştır. Farklı ana materyaller üzerinde oluşan topraklar arasında incelenen elementlerin ortalama toplam oksit değerleri arasındaki farklılıklar istatistiksel olarak önemli bulunmuşken ($p < 0.05$), toprak işlemenin toplam oksitler üzerindeki etkisi sadece XRF tekniği ile elde edilen sonuçlardan elde edilmiştir ($p < 0.05$). Toprak işleme durumunun diğer elementler üzerindeki etkileri MgO hariç istatistiksel olarak önemsiz bulunmuştur ($p > 0.05$). ICP tekniği ile elde edilen yüzde SiO_2 değerleri, XRF tekniği ile elde edilen değerlere göre oldukça düşük bulunmuştur. Genel olarak, elde edilen toplam elementer oksit değerleri açısından XRF yöntemi, daha doğru sonuçlar vermesi ve daha az toprak örneği gerektirmesi nedeniyle ICP tekniğine göre daha avantajlı bulunmuştur.

Anahtar Kelimeler: Toprak, Toplam oksitler, Toprak işleme, XRF, ICP

Introduction

Soil is a complex structure containing inorganic and organic materials, that have been formed as a result of various soil formation processes. The physical, chemical and morphological properties of soils are the function of natural factors such as climate, topography, living things, parent material and vegetation, which are called "soil formation factors" by Dokuçayev (Jenny, 1941). The important processes causing the morphological, physical, chemical and biologic differentiation of soils as a result of soil formation processes are the displacement, transport, gain and loss of energy and material (Simonson, 1959).

Soil ecosystem has a very complex structure such as soil water movement, soil air, solar radiation, cation exchange, clay mineral decomposition, humus formation, pH, oxidation and reduction potential, and other physicochemical and biological interactions.

Soils differ in terms of their complex biological, chemical, physical, mineralogical and hydrological properties and have a dynamic structure that changes over time. The speed of this change mostly depends on climatic, biological and topographic conditions. Some soil properties may change in a very short time, while others may take a very long time.

In recent years, different instrumental analysis methods such as ICP, XRF and XRD have been developed as an alternative to conventional methods to detect changes in soil properties more accurately, quickly and economically. Techniques such as X Ray Fluorescence spectroscopy and ICP can be used to provide comprehensive and numerical data both in situ and in the laboratory. X-ray fluorescence (XRF) spectroscopy is an analytical tool that directly measures the concentration of atomic elements in a wide range of materials and has a great advantage in analyzing small samples (Rawlins and Cave, 2004).

The potential of XRF was tested for distinguishing the soil samples on the same parent material from eastern England (Rawlins and Cave, 2004). The X-ray fluorescence technique was used to determine the exchangeable nutrient content of 58 soil samples taken from 0 to 0.2 m soil depth in an agricultural field in Brazil's southeast region (Tavares et al., 2019).

The soils in a tropical humid area in Nigeria were classified by examining the formation of soils formed on limestone and analyzing the routine and morphological properties of soil samples, which were taken from 5 different profiles formed on sandstone and limestone main material, on the basis of horizon, as well as the total element contents with ICP-OES (Ofem et al., 2020).

The researchers collected 2200 soil samples from 0-20 cm depth from agricultural areas and 2100 soil samples from 0-10 cm from grassland areas and analyzed 94 different elements, including SiO_2, K_2O, Na_2O, Fe_2O_3, Al_2O_3 using ICP-MS and XRF in 2009, within the scope of the project named GEMAS (Geochemical Mapping of European Agricultural Soils) in order to determine whether the nutrients or pollutants in the soil are of agricultural or terrestrial origin (Saaltink et al., 2014). The obtained element concentrations were compared with the Terrestrial Surface values in the World and Europe. Average SiO_2, K_2O, Na_2O,

Fe_2O_3, Al_2O_3 concentration values were 66.37%, 1.94%, 1.10%, 3.69%, 9.83%, respectively for agricultural areas, and 63.78%, 1.84%, 0.95%, 3.62%, 9.83% for grassland areas, respectively. The researchers who compared the results obtained with the Earth's Terrestrial Surface values (SiO_2: 53.03%, K_2O: 2.45%, Na_2O: 1.64%, Fe_2O_3: 2.35%; Al_2O_3: 11.77%) reported that an enrichment (increase) in SiO_2 and Fe_2O_3 values to date, and impoverishment (decrease) in Al_2O_3, Na_2O and K_2O values. The researchers attributed the decreases in Al_2O_3, Na_2O and K_2O to the leaching of these oxides as a result of chemical weathering, while the enrichment in SiO_2 and Fe_2O_3 made them more resistant to decomposition. In addition to the soil elemental analysis results, the researchers used factor analysis on the data set they created together with soil properties including clay content, pH, LOI, KDK, total organic carbon. They interpreted the reactions of minerals as being of geological origin, such as clay minerals and carbonate minerals.

Geochemical indices obtained by proportioning the elements are generally used to obtain information about the level of chemical weathering in rocks and soil profiles. Geochemical indices assume that mobile elements in the soil decrease, while the amount of stable inert elements increases during weathering. Major oxides such as Al_2O_3, Fe_2O_3 are considered as immobile while oxides such as SiO_2, K_2O, Na_2O, MgO and CaO are considered mobile. The concentrations of these oxides in the soil vary according to the pedogenic functions or the parent rock. During soil formation, major elements such as Mg, Ca, K and Na are reduced in environments where leaching occurs. SiO_2 also generally decreases depending on the dissociation intensity, but since Al_2O_3 has low solubility, its relative ratio generally increases. Similar to Al, Fe concentration increases with increasing the weathering ration of materials (Stockmann et al., 2016).

In this study, soil profiles formed over four common parent materials in Sanliurfa were defined, soil samples were taken from the horizons and also surface samples of tilled and untilled lands around the profiles were investigated using instrumental (ICP, XRF) techniques. The total element concentrations of the soils formed on different parent materials were determined by both techniques, and the effects of differences in parent material and soil tillage treatment on the results were compared.

Material and Methods

Study area

The study area covers the province of Sanliurfa, located in the Southeastern Anatolia region of Turkey, is approximately 200 thousand km^2 and is located between 36^0 38´ 00´´-37^0 59´37´´ northern latitudes and 37^0 49´ 03´´ - 40^0 14´ 37´´ east longitudes. Sanliurfa province has arid and semi-arid climate characteristics. The summers are hot and dry, and the winters are mild and rainy. The geology of Şanlıurfa province consists of tertiary aged terrestrial sedimentary carbonate rocks, volcanic rocks and locally quaternary alluvial and colluvial materials. While Eocene limestones are widespread in the southwestern and southern parts of the province, basalts formed as a result of the Karacadağ eruption are dominant in the northeast of the province. Colluvium and alluviums are mostly located in depressions such as the Harran plain and on the valley floors. In addition to these formations, in the east and northeast sections, there are loose lacustrine limestones, which start with white gray marls at the bottom and very clayey at the top, over siliceous limestones (MTA, 1996).

In the study, three profiles were dug on four common parent materials in Sanliurfa: I-Mud flows, II- Eocene-Miocene limestones, III-Neogene marls, IV-Basalt materials (Figure 1). Soil surfaces of profiles (12 in total) and surface (@ 0-20 cm) samples from surroundings of each profile (58 in total) were collected (Inci et al., 2021).

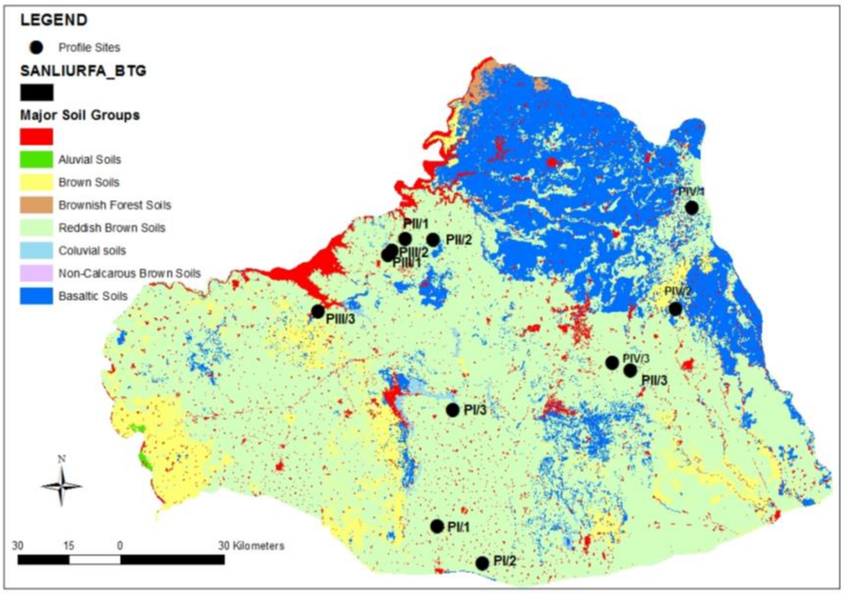

Figure 1. The profiles opened on the common parent materials in the Sanliurfa Province

Geochemical analysis

Sub-samples of 4 g were taken for bulk elemental analysis by ICP and X-ray Fluorescence (XRF), which provides a non-destructive bulk analysis with simple sample preparation.

ICP (Inductively Coupled Plasma - Optic Emission Spectroscopy (ICP-OES)) was used for analyses of major, minor and some trace elements and it is an analytical technique used to determine the concentration of certain elements in a sample. A further sub-sample (0.1 g) was taken for ICP analyses and digested with HF/HNO_3 at 70°C. Three HNO_3/HF fluxes (4 ml and 2 ml, respectively) were followed by two additions of HNO_3 (2 ml), the first of which was evaporated off to near dryness before being made up to 100 ml with deionized water to give a 2% solution. These samples were then analyzed by ICP OES (PerkinElmer Optima 5300 DV). All samples were tested against SSP certified reference material (MBH Analytical Ltd, registration number 034/04) and control blanks were run throughout the analysis in accordance with standard procedures.

For XRF analysis, Organic materials, such as plant matter, were removed from the sub-samples before manually homogenizing them with an agate pestle and mortar. Powdered samples were then analyzed by XRF (Spectro X-Lab 2000) with a helium carrier gas. X-ray emission spectrograph method is fast, reliable, generally non-destructive, and in many cases faster and more accurate than conventional chemical analysis techniques. XRF is an elemental analysis method that evaluates the presence and concentration of various elements in soil and plant materials by measuring the characteristics of secondary radiation emitted from a sample excited by an x-ray source. Elemental analysis with XRF spectroscopy is based on the principle that primary x-rays from a target tube cause elements present in the sample to emit secondary (fluorescent) x-radiation. When each element is excited, it emits x-rays that have a specific wavelength (inversely proportional to the square of the atomic number) and intensity that is roughly proportional to the amount of that element. Elements with high atomic number emit short wavelength and high energy radiation, while elements with low atomic number emit long wavelength and low energy radiation.

Statistical analyses

ANOVA ("analysis of variance") was used to compare the differences between the analysis findings of soil samples obtained from various parent materials under various soil tillage treatments (cultivated and uncultivated soils).

Tukey's multiple comparison test was then used to measure the significance of the differences between them. MINITAB program was used for ANOVA – Tukey analysis. Basic descriptive statistical and correlation analyzes of soil properties were performed in the R program.

Result and Discussions

Total oxide values of soil samples taken from different parent materials, determined by XRF and ICP methods are given in Table 1 and 2; Figure 2 and 3. According to oxide values calculated based on ICP technique, average values of CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, P_2O_5, MnO and Cr_2O_3 were respectively 9.44, 3.94, 3.89, 1.06, 0.21, 0.005, 0.09 and 0.01%. The same values calculated with XRF technique were 14.44, 9.63, 7.47, 2.31, 1.26, 0.13 and 0.036%, respectively (Table 1 and 2). LOI (Lost of Ignition) values, which are known to be correlated with the amount of organic materials in the soil, ranged from 3.84 to 32.22% (Table 2).

SiO_2 values obtained with XRF method ranged from 14.00 to 59.76 % with an average value of 44.91%, while SiO_2 values obtained with ICP method ranged from 0.02 to 0.21 % with an average value of 0.11%. As can be seen, the percent SiO_2 values obtained by the ICP technique were lower compared to the values obtained by the XRF technique. The extremely low percentage SiO_2 values detected with the ICP technique can be attributed to the pretreatment of soil samples in this method. In the ICP analysis, HNO_3 and HCl acids were used to pass the metals in the samples to the solution during the pre-treatment of the soil samples from the microwave oven to the solution. At the end of this process applied in the microwave oven, all compounds except the silicon oxides are dissolved, so since the silicon in the soil samples cannot be dissolved, errors are possible in the silicon values determined by this method. The use of HF is required in order to dissolve the silicon, which will result in incorrect results by passing the silicon into solution in the glass material if glass materials are used during the ICP analysis. Therefore, problems may be encountered in the determination of silicon by the ICP method. According to the sample t-test results, there is a significant difference between ICP and XRF for some selected elements (Co, Cu, Ni and Zn), and it is seen that XRF had the highest mean and ICP had the lowest mean values for all analyzes ($p < 0.05$) (Table 3).

Table 1. Descriptive statistics of oxide levels of soil samples determined by ICP OES

Oxides (%)	Mean	Std Dev[†]	Min	Max	Range	CV[‡]
CaO	9.44	11.46	0.24	43.05	42.81	121.35
SiO_2	0.086	0.048	0.02	0.81	0.78	55.8
Al_2O_3	3.94	1.74	0.80	7.58	6.78	44.19
Fe_2O_3	3.89	1.78	1.16	7.81	6.66	45.62
MgO	1.06	0.40	0.15	2.03	1.88	37.64
K_2O	0.21	0.10	0.04	0.50	0.46	45.42
P_2O_5	0.005	0.003	0.000	0.01	0.01	55.49
MnO	0.09	0.04	0.03	0.23	0.21	52.48
Cr_2O_3	0.01	0.005	0.001	0.02	0.02	54.31

[†]Std Dev: Standard Deviation; [‡] CV: Coefficient of Variation (%)

O'Rourke et al. (2016) compared elemental concentrations determined using XRF with reference ICP technique. They reported that XRF produced accurate results for macro elements such as K and micro elements such as Mn, Zn, and C, which can be found in high concentrations in soils as well as elements such as Cr and Cu, which can be found at low concentrations. They also stated that the ICP method may be more suitable for the measurement of elements that can be found at low concentrations (<5 mg/kg). In the study, a very weak relationship was obtained between XRF and ICP for Se, which is found at low concentrations. The same researchers also compared the XRF and VNIRS technique and stated that the XRF method gave more successful results than the VNIRS method in most of the total elements estimation.

Ofem et al. (2020) investigating five different profiles formed on the sandstone and limestone parent material in a tropical humid area in Nigeria determined the total element contents with ICP-OES and XRF. The researchers obtained positive correlation (r=0.68) between Fe_2O_3 determined with XRF and Fe, Mg, Na and Al contents determined with ICP-OES, statistically significant positive relations ($p<0.05$) between MnO_2 determined with XRF and Mg, Fe contents determined with ICP-OES and between SiO_2 determined with XRF and Al and Mg contents determined with ICP-OES.

The elemental composition data of the surface samples taken from the profiles formed on different parent material and around the profiles were graphed for visual comparison (Figure 2 and 3). By looking at figures, the abundance or lack of CaO, Fe_2O_3, TiO_2 and SiO_2 can be used to distinguish the parent materials at the initial stage. While CaO is quite high in soils formed on parent material Marn and Mud flows, CaO content is quite low in soils formed on parent material Basalts with relatively higher Fe_2O_3 content. Fe_2O_3 density can be helpful in distinguishing soils at the initial level.

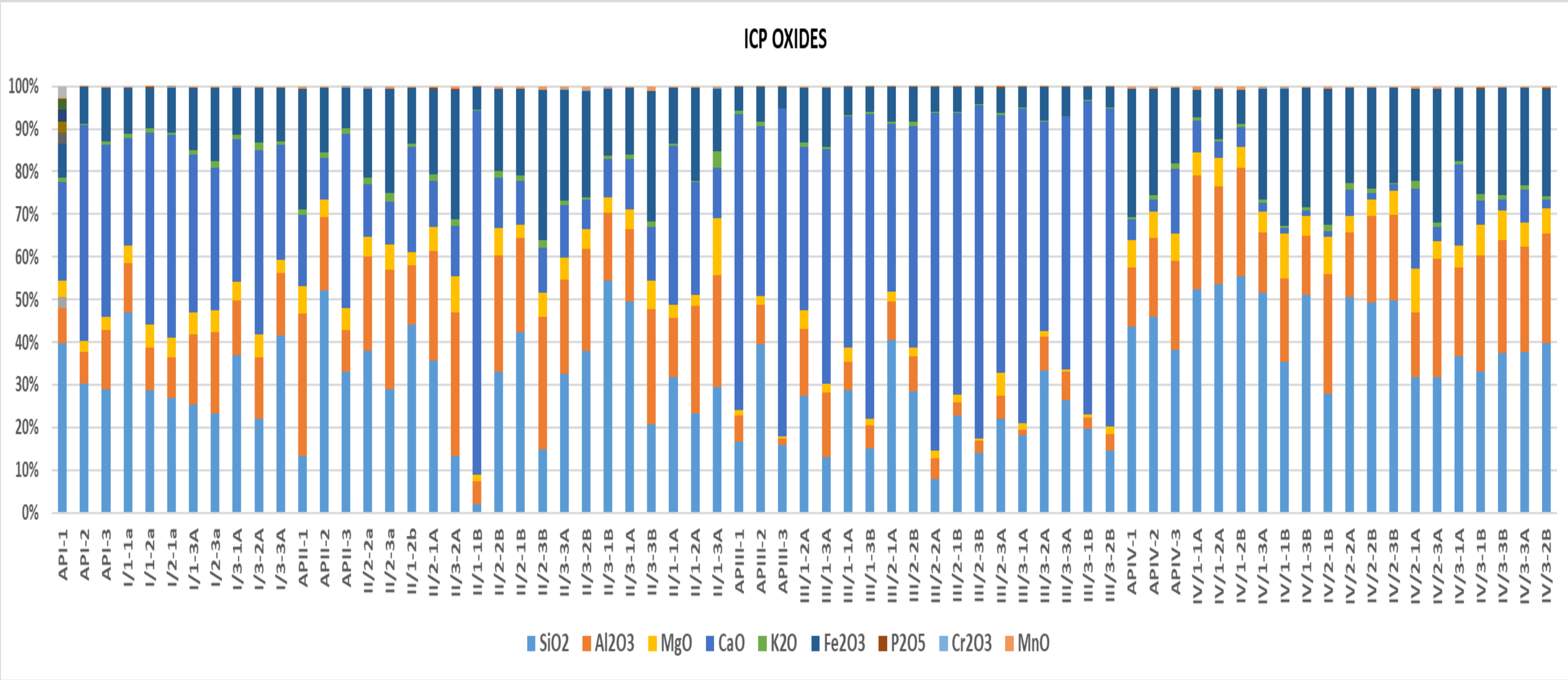

Figure 2. Proportional distribution of oxides determined by ICP on different parent material (I,II,III,IV are profile names shown as Roman numerals (I-Mud flows, II-Limestones, III-Marls and IV-Basalt); A and B represent surface samples taken from cultivated and uncultivated lands, respectively; AP represent plow horizon).

The soils formed over basalt parent material had high Fe_2O_3 content, and were distinguished from other parent materials. The Al_2O_3 content of the soils formed on the parent material Marn is also quite low. Among the soils formed on different parent materials (Alluvial deposits, Colluvial deposits, Marl and Basalt), the soils with the highest Fe_2O_3 content were determined in soils formed on basalt parent materials (Tunçay and Dengiz, 2020). Similarly, the researchers found that the % Al_2O_3 values in the soils formed on the Marl parent material (13.06 %) were relatively lower than the soils formed on the Basalt (13.94 %) and Limestone (13.29 %).

Table 2. Descriptive statistics of oxide levels of soil samples determined by XRF

Oxides (%)	Mean	Std Dev	Min	Max	Range	CV
SiO_2	44.91	14.10	14.00	59.76	45.76	31.39
CaO	14.44	13.25	1.73	48.04	46.31	91.75
Al_2O_3	9.63	2.96	2.31	14.23	11.92	30.69
Fe_2O_3	7.47	3.52	2.06	16.05	13.99	47.10
MgO	2.31	0.61	0.37	3.47	3.10	26.43
K_2O	1.26	0.53	0.59	4.03	3.44	41.64
TiO_2	1.12	0.90	0.19	3.89	3.70	80.26
P_2O_5	0.24	0.21	0.09	1.26	1.17	88.83
SO_3	0.23	0.15	0.12	1.25	1.13	64.45
MnO	0.13	0.06	0.03	0.25	0.23	42.51
Na_2O	0.043	0.002	0.04	0.05	0.01	5.71
Cr_2O_3	0.036	0.014	0.010	0.071	0.06	38.56
V_2O_5	0.027	0.013	0.009	0.063	0.05	47.33
Cl	0.002	0.003	0.000	0.016	0.02	171.37
LOI	18.29	8.27	3.84	32.22	28.38	45.20

†Std Dev: Standard Deviation; ‡ CV: Coefficient of Variation (%)

SiO_2 contents varied between 14.00% and 59.76% with the average highest (56.12%) detected in soils on Basalt parent material and with the average lowest (25.64%) detected in soils on Marl parent material. Al_2O_3 contents varied between 2.31% and 14.23%, with the average highest (12.07%) detected in soils on Limestone parent material and with the average lowest (5.83%) detected in soils on Marl parent material. The CaO contents varied between 1.73% and 48.04% with the average highest (31.54%) detected in the soils on the Marl parent material and with the average lowest (3.32%) detected in soils on Basalt parent material. MgO contents varied between 0.37% and 3.47% with the average highest (3.07%) detected in soils on mud flow parent material and with the average lowest (1.84%) detected in soils on Marl parent material. P_2O_5 contents varied between 0.09% and 1.26%, with the average highest (0.39%) detected in soils on Basalt parent material and with the average lowest (0.15%) detected in soils on the mud flow parent material. The K_2O contents varied between 0.59% and 4.03% with the average highest (1.52%) detected in soils on limestone parent material and with the average lowest (0.90%) detected in soils on Marl parent material. MnO contents varied between 0.03% and 0.25% with the average highest (0.175%) detected in soils on Basalt parent material and with the average lowest (0.07%) detected in soils on Marl parent material. Fe_2O_3 contents varied between 2.06% and 15.92% with the average highest (11.49%) detected in the soils on the basalt parent material and with the average lowest (3.88%) detected in soils on Marl parent material. TiO_2 contents varied between 0.19% and 3.89% with the average highest (2.13%) detected in soils on Basalt parent material and with the average lowest (0.45%) detected in soils on Marl parent material.

The oxide values found in this study are consistent with those found in earlier studies. Heidari et al. (2022) analyzed a total of 184 soil and rock samples in the profiles they defined at 56 points in Iran, which has a semi-arid climate. According to the results of the XRF analysis of the samples taken from the rocks and soils at the opened points, the highest element in the soil and rocks was SiO_2 (40% to > 65%) with an average of 48%. Other oxides varied as Al_2O_3 (0.08 – 23 %), Fe_2O_3 (0.07 – 16.26 %), CaO (0.30- 52.98%), Na_2O

(0.23- 1.18%), K_2O (0.01-4.76%), TiO_2 (0.02-2.49%), MnO (0.01- 0.21%) and ZrO_2 (0.00-0.08%). The researchers also found that the total extracted element concentrations as a percentage varied between 73% and 97%, and the LOI values varied between 3% and 27% depending on the organic matter in the soil. Badia et al. (2015) measured elemental distribution at different depths of the soil profiles that have occurred on the calcareous fluvial deposits along the Alcanadre river in the Ebro basin, which has a semi-arid climate in the North East of Spain in order to examine the temporal changes of soils of different ages and depths. They found the element with the highest amount in the profiles was SiO_2 (6.8-82.9%), followed by CaO (5.8-56.5%), Al_2O_3 (2.9-14.4%), K_2O (0.7-8.0%), TiO_2 (< 0.6%) and MnO (<0.1%) according to XRF analysis results. The researchers attributed the decreases in Al_2O_3, Na_2O and K_2O to the leaching of these oxides as a result of chemical decomposition, while they attributed the enrichment in SiO_2 and Fe_2O_3 to their being more resistant to weathering.

Table 3. Comparison of ICP and XRF techniques for some selected elements

Element (%)	Group	n	Min	Max	Average	Std. D	Std. E	t-value	sd	p
Co	ICP	58	2.5	81.1	21.3	19.0	2.5	7.5	113	0.000***
	XRF	57	21.2	144.0	54.1	26.6	3.5			
Cu	ICP	58	5.6	41.6	18.3	9.4	1.2	8.2	113	0.000***
	XRF	57	14.9	83.1	38.3	15.7	2.0			
Ni	ICP	58	28.7	200.2	89.8	44.2	5.8	5.6	113	0.000***
	XRF	57	49.6	287.5	143.8	57.9	7.6			
Zn	ICP	58	25.1	162.3	71.6	26.5	3.4	4.5	113	0.000***
	XRF	57	42.0	182.5	95.3	29.6	3.9			

*** p significant at $p<0.001$ level

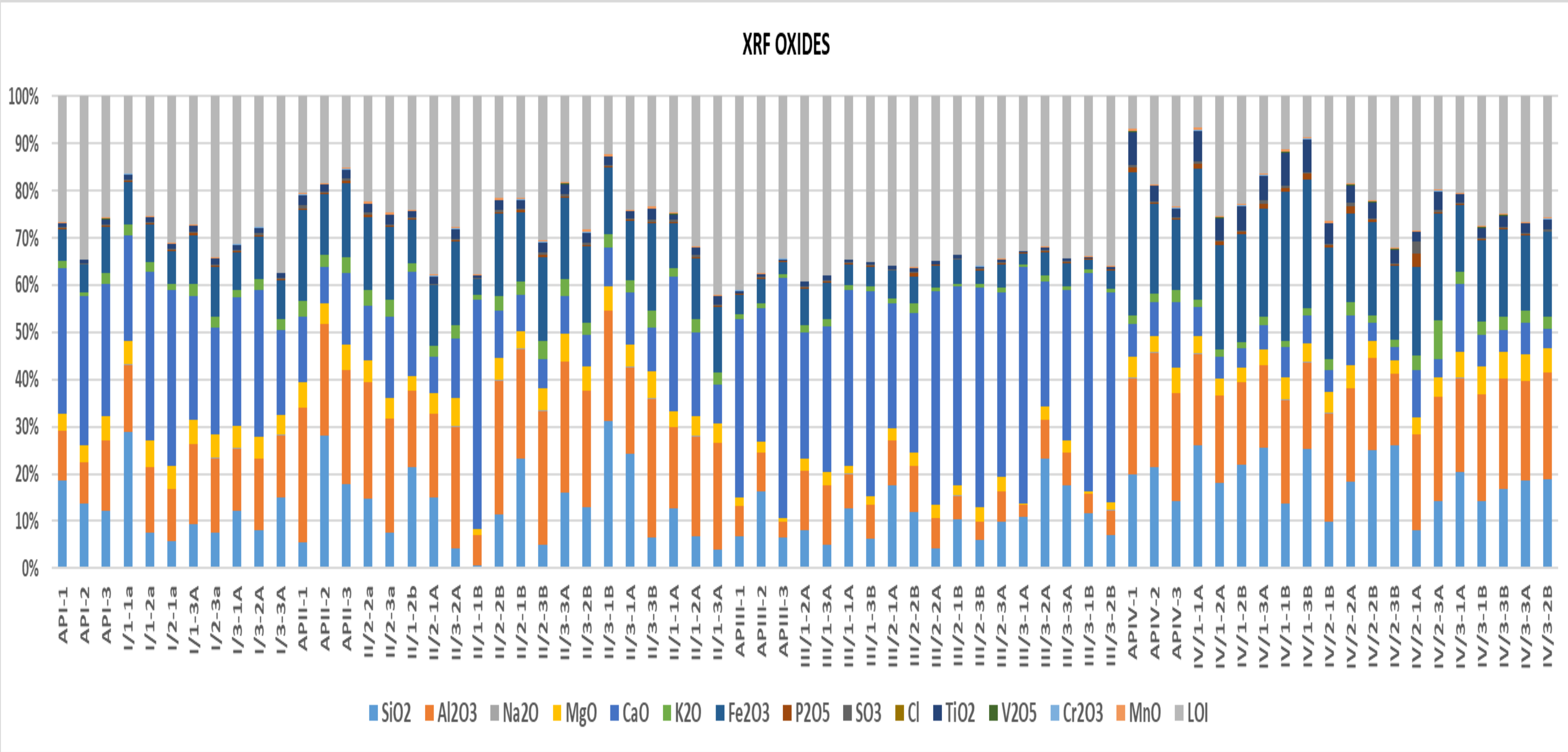

Figure 3. Proportional distribution of oxides determined by XRF on different parent material (I,II,III,IV are profile names shown as Roman numerals (I-Mud flows, II-Limestones, III-Marls and IV-Basalt); A and B represent surface samples taken from cultivated and uncultivated lands, respectively; AP represent plow horizon).

SiO_2/Al_2O_3, SiO_2/Fe_2O_3, CaO/MgO and Al_2O_3/K_2O ratios were obtained by using oxides determined in soil samples by XRF technique. Si/Al ratios give information about the weathering levels of rocks (Ruxton, 1968). Silicon loss is related to total-element losses, the Si/Al ratio can provide information about the level of decomposition if Al remains constant during decomposition. In order to achieve this ratio, total iron oxides (SiO_2/Fe_2O_3) can be used instead of aluminum (Ruxton, 1968).

SiO_2/Al_2O_3 ratios varied between 3.27 and 6.47. The highest average value (5.2) was obtained from soils formed on basalt parent material (Figure 3). The CaO/MgO ratios varied between 0.79 and 129.49 and the highest average value (28.73) was obtained from the soils formed on the marl parent material. SiO_2/Fe_2O_3 ratios varied between 3.23 and 9.29 and the highest average value (7.8) was obtained from the soils formed on the mudflow parent material. Al_2O_3/K_2O ratios varied between 3.83 and 16.49 and the highest average value (10.16) was obtained from soils formed on basalt parent material.

The Ruxton weathering index (SiO_2/Al_2O_3) was developed to determine the level of chemical weathering in rocks and relates silicon to the total elemental loss during weathering. Here it is assumed that silicon is mobile oxide, while sesquioxide aluminum is immobile.

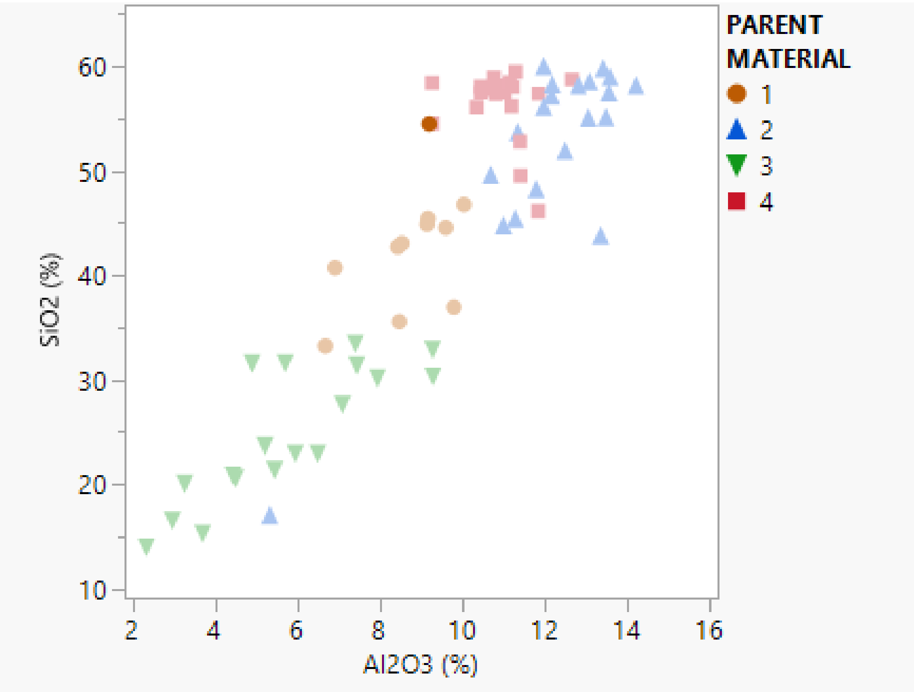

Figure 3. Comparison of oxides ratios (SiO_2 and Al_2O_3) belonging to the surface samples of soils formed on different parent materials (1-Mudflow, 2-Limestone, 3-Marl, 4-Basalt).

The decrease in the Ruxton index (SiO_2/Al_2O_3) indicates an increase in the separation intensity. This ratio is generally between 0 and 10; the lowest value, 0, indicates optimum separation, and 10 indicates fresh material (Stockmann et al., 2016). Low SiO_2/Al_2O_3 ratios may indicate possible advanced chemical weathering (Andreeva et al., 2011). Low Si/Al ratios can be seen especially in semi-humid areas with high precipitation, where the movement of elements from the profile is high. In addition, in the early stages of weathering, the basalts lose their mobile elements (Mg, Ca, Na and K) and retain elements such as Al, Fe and Ti (Heidari and Raheb, 2020). In basaltic rocks, at the beginning of the weathering, there is a loss of Ca and a decrease in silicon, and relatively increases in Al and Fe. During the ongoing decomposition, there is an increase in Fe by washing Al.

Statistical analysis

The results of ANOVA analysis showing the effects of factors such as soil cultivation and parent material on the element concentrations obtained by ICP and XRF techniques are given in the Tables 4- 9. While the effect of the parent material on the elemental analysis results obtained with both techniques was generally found to be statistically significant ($p<0.05$), the effect of soil tillage was only found to be significant ($p<0.05$) only on the analysis results obtained with the XRF technique. Soil tillage status was found to be significant only in terms of MgO, but its effects on other elements were statistically insignificant ($p>0.05$).

Considering the oxide values calculated by the ICP technique, the averages of the other total elements except for P_2O_5, K_2O and Cr_2O_3, the differences between the parent materials were found to be statistically significant (Table 4). Considering the oxide values calculated by the XRF technique, the differences in the averages of all the total elements between the parent materials were found to be statistically significant (Table 7).

Soils formed on basalt parent material had the highest values among soils formed on different parent materials in terms of average SiO_2, P_2O_5, TiO_2, Fe_2O_5 and MnO, so they were in a different group from other parent materials (Table 8). Soils formed on mudflows had the highest average MgO values and therefore were in a different group from other parent materials (Table 8). While the soils formed on the marl parent material had the highest average CaO values, the soils formed on the lime parent material were classified in a different group as having the highest K_2O values (Table 8). In a different study evaluating soils formed on different parent materials in terms of elemental concentrations, it was determined that soils formed on basalt parent material contained relatively higher rates of SiO_2, P_2O_5, TiO_2, Fe_2O_3 compared to soils formed on Marl and Limestone (Tunçay and Dengiz, 2020). The researchers determined the highest per cent CaO ratios in soils formed on limestone. In a different study, it was determined that areas dominated by Marl parent material had relatively high CaO ratios (Tunçay et al., 2019). In general, the results obtained in this study and from different studies show that the parent material can have significant effects on the soil elemental contents.

When XRF analysis results are subjected to ANOVA analysis; except for the MgO variable, other variables were not significant for tillage (Table 7). According to Tukey's multiple comparison test, T1 (cultivated lands) had the highest mean and T2 (uncultivated lands) had the lowest mean in terms of MgO ($p<0.05$). No difference was found in terms of tillage levels for other variables ($p>0.05$) (Table 9).

Table 4. ANOVA results of ICP analyses results

	Al_2O_3	CaO	MgO	P_2O_5	K_2O	Cr_2O_3	MnO	Fe_2O_3
Soil tillage	0.323	0.519	0.238	0.382	0.399	0.653	0.577	0.866
Parent material	**0.000*****	**0.000*****	**0.001****	0.097	0.050	0.058	**0.000*****	**0.000*****
Soil profile	0.385	0.079	0.921	0.574	0.504	0.616	0.621	0.249
Soil tillage * Parent material	0.234	0.421	0.142	0.644	0.733	0.282	**0.049***	0.226
Soil tillage * Profile	0.146	0.406	0.649	0.700	0.855	0.621	0.091	0.358
Parent material * Profile	0.196	**0.000*****	0.358	0.684	0.387	0.456	**0.002****	0.519
Soil tillage * Material * Profile	0.913	0.836	0.574	0.922	0.88	0.897	0.851	0.957

*** significant @ $p < 0.001$ level; ** significant @ $p < 0.05$ level; * significant @ $p < 0.05$ level;

Table 5. Turkey statistical results of the averages of total oxides obtained by the ICP Method of different parent materials

Parent material	n	Al_2O_3	CaO	MgO	P_2O_5	K_2O	Cr_2O_3	MnO	Fe_2O_3
Basalt	17	10.49 a	1.21 c	1.40 a	0.010	0.211	0.012	0.112 a	5.35 a
Mud flow	9	6.32 b	7.56 b	1.06 ab	0.006	0.274	0.006	0.061 b	2.93 b
Carbonates	17	9.66 a	5.25 ab	1.24 ab	0.048	0.462	0.015	0.117 a	4.96 a
Marn	14	5.00 b	25.90 a	0.78 b	0.005	0.15	0.006	0.054 b	2.81 b
P		**0.000*****	**0.000*****	**0.001****	0.097^{ns}	0.050^{ns}	0.058^{ns}	**0.000*****	**0.000*****

*** significant @ $p < 0.001$ level; ns: statistically not significant ($p<0.05$)

Table 6. Tukey statistical results of averages of total oxides obtained by ICP Method according to soil tillage status

Soil tillage	n	Al_2O_3	CaO	MgO	P_2O_5	K_2O	Cr_2O_3	MnO	Fe_2O_3	LOI
T	35	8.009	9.884	1.155	0.022	0.3	0.01	0.085	3.912	18.72
NT	22	8.677	8.958	1.146	0.008	0.252	0.011	0.101	4.784	17.153
P		0.323^{ns}	0.519^{ns}	0.238^{ns}	0.382^{ns}	0.399^{ns}	0.653^{ns}	0.577^{ns}	0.866^{ns}	0.438^{ns}

*** significant @ $p < 0.001$ level; ns: statistically not significant ($p<0.05$); T: Tilled soils; NT: Non- tilled soils

Table 7. ANOVA results of XRF

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	LOI
Soil tillage	0.533	0.047*	0.150	0.090	0.386	0.092	0.059	0.725	0.791	0.877	0.360	0.430
Parent material	**0.014***	**0.000*****	**0.000*****	**0.000*****	**0.001****	**0.004****	**0.000*****	**0.000*****	**0.000*****	**0.000*****	**0.000*****	**0.000*****
Soil Profile	**0.003****	0.149	0.717	**0.008****	**0.017***	0.255	0.062	**0.000*****	**0.001****	0.582	**0.001****	0.871
Tillage x Material	0.772	0.612	0.309	0.160	**0.020***	0.237	0.091	0.198	0.264	**0.042***	0.083	0.763
Tillage x Profile	0.730	0.715	0.086	0.117	0.330	0.527	0.064	0.850	0.126	0.080	0.288	0.827
Material x Profile	0.143	**0.002****	0.055	**0.007****	0.051	0.151	**0.038***	**0.000*****	**0.000*****	**0.000*****	**0.000*****	**0.002****
Till x Mater x Profile	0.505	0.413	0.196	0.195	**0.034***	0.058	0.273	0.494	0.264	**0.004****	0.170	0.243

Table 8. Turkey statistical results of the averages of total oxides obtained by the XRF Method of different parent materials

Parent Material	n	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	LOI
Basalt	17	0.045a	2.30b	10.85a	56.12a	0.39a	1.28ab	3.32c	2.13a	0.042 a	0.175a	11.49a	11.57c
Mudflow	8	0.042b	3.07a	8.95b	44.26b	0.15b	1.33ab	17.41b	0.67bc	0.032b	0.107b	5.54c	18.39b
Carbonates	17	0.043b	2.38b	12.07a	51.14a	0.17b	1.52a	8.82c	0.91b	0.042a	0.16a	7.55b	15.27bc
Marn	14	0.043ab	1.84c	5.83c	25.64c	0.18b	0.90b	31.54a	0.45c	0.023c	0.07c	3.88d	29.30a
P		0.014*	0.000***	0.000***	0.000***	0.001**	0.004**	0.000***	0.000***	0.000**	0.000**	0.000**	0.000*

Table 9. Turkey statistical results of averages of total oxides obtained by XRF Method according to soil tillage status

Soil tillage	n	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	LOI
T	35	0.043	2.448 a	9.632	44.835	0.243	1.347	14.429	1.029	0.034	0.127	7.177	18.546
NT	21	0.044	2.119b	9.803	46.075	0.239	1.143	13.456	1.313	0.039	0.148	8.163	17.368
P		0.533 ^{ns}	**0.047***	0.150 ^{ns}	0.090 ^{ns}	0.386 ^{ns}	0.092 ^{ns}	0.059 ^{ns}	0.725 ^{ns}	0.791 ^{ns}	0.877 ^{ns}	0.360 ^{ns}	0.430 ^{ns}

*significant @ p < 0.05 level; ns: statistically not significant (p<0.05)

Conclusions

Total element concentrations of soils formed on different parent materials were determined by ICP and XRF techniques. SiO_2, CaO, AlO_2 and MgO had the highest ratios among the total oxides in the soils, depending on the difference in the parent material. The ANOVA analysis successfully grouped different parent materials in terms of their average total element contents determined by both ICP and XRF techniques. Except for MgO detected by XRF, no statistically significant difference in average total element contents was found between different tillage applications. In terms of total element contents determined, statistical differences were found between the two compared instrumental techniques (ICP vs. XRF). Especially SiO_2 values were found to be low in the analyses results of the total elements using the ICP technique due to the acid solutions used in the pretreatment of soils. Therefore, XRF technique provided more accurate results for SiO_2 values. On the other hand, in the analysis of soil samples in XRF technique, relatively less soil samples are required compared to the ICP technique, which is an important advantage especially in fields such as forensic soil science, which requires very little soil.

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