Turkish Journal of Agriculture - Food Science and Technology

www.agrifoodscience.com,
Turkish Science and Technology

Elemental Composition of Soils Mixed with the Grape Molasses

Aslı Kurnaz*, Şeref Turhan, Muazzez Gezelge, Aybaba Hançerlioğulları, Mehmet Atıf Çetiner

Department of Physics, Faculty of Arts and Sciences, Kastamonu University,37150 Kastamonu, Turkey

A R T I C L E I N F O

Article history:
Received 07 June 2016
Accepted 29 June 2016
Available online, ISSN: 2148-127X

Keywords:
Molasses Soil
Chemical Composition
Oxides
EDXRF
Zile

* Corresponding Author:
E-mail: akurnaz@kastamonu.edu.tr

A B S T R A C T

Molasses, which is a traditional food substance obtained by boiling the fruit with local procedures and is abundantly eaten by Turkish people, are commonly produced from grapes. Zile, which is county of Tokat city placed in Central Black Sea region, is famous with molasses in Turkey. A special soil called as molasses soil containing CaO is added into to molasses in order to resolve acidification during production process. The purpose of this study is to determine the element concentration levels in grabe molasses soil samples collected from Zile by using energy dispersive X-ray fluorescence spectrometry (EDXRF). For this purpose, thirty-eight elements and eleven oxides were detected in molasses soil samples. The average concentrations of six major oxides (MgO, Al_2O_3, SiO_2, K_2O, CaO and Fe_2O_3) were found as 1.58%, 7.96%, 17.01%, 1.01%, 30.52% and 8.72%, respectively. Also, the average concentrations of three minor (Na_2O, P_2O_5 ,TiO_2) and two trace (SO_3, MnO) oxides were found as 0.96%, 0.12%, 0.95% and 0.04%, 0.1%, respectively.

Türk Tarım – Gıda Bilim ve Teknoloji Dergisi, 4(9): 748-751, 2016

Pekmez Topraklarının Elementel İçeriği

M A K A L E B İ L G İ S İ

Geliş 07 Haziran 2016
Kabul 29 Haziran 2016
Çevrimiçi baskı, ISSN: 2148-127X

Anahtar Kelimeler:
Pekmez Toprağı
Kimyasal Bileşim
Oksitler
EDXRF
Zile

* Sorumlu Yazar:
E-mail: akurnaz@kastamonu.edu.tr

Ö Z E T

Geleneksel bir gıda maddesi olan pekmez, meyvelerin kaynatılması ile elde edilir ve Türk insanı tarafından bolca tüketilen pekmez çoğunlukla üzümden üretilmektedir. Zile/Tokat, Türkiye'de pekmezi ile meşhur bir bölgedir. Asitlenmeyi önlemek amacıyla üretimi sırasında pekmezin içine CaCO içerikli özel bir toprak katılmaktadır. Bu çalışmanın amacı, enerji dağılımlı X-ışını floresans spektrometresi (EDXRF) kullanarak, pekmez topraklarındaki element konsantrasyonlarının dağılımını belirlemektir. Bu amaçla toprak örneklerinde 38 tane element ve 11 oksit analiz edilmiştir. 6 major oksitin (MgO, Al_2O_3, SiO_2, K_2O, CaO ve Fe_2O_3) ortalama konsantrasyonları sırasıyla %1,58, %7,96, %17,01, %1,01, %30,52 ve %8,72 olarak bulunmuştur. Ayrıca 3 minor (Na_2O, P_2O_5, TiO_2) ve 2 trace (SO_3, MnO) oksitin ortalama konsantrasyonları sırasıyla %0,96, %0,12,% 0,95 ve %0,04, %0,1 olarak bulunmuştur.

Introduction

Soil can be defined as a dynamic and complex system and plays both an important role in protecting the groundwater acting and contribute to the maintenance of all forms of life that occur in the terrestrial surface (De Sousa et al., 2008). Soil pollution by heavy metals is a significant and increasingly common environmental problem all over the World (Hu et al., 2013; Alloway, 1995). Heavy metals can occur naturally in the soil, but rarely at toxic levels. The geologic and anthropogenic activities increase the concentration (Chibuike and Obiora, 2014). Mining, manufacturing, burning of fossil fuels, use of fertilizers and pesticides in agriculture, batteries and other metal products in industries and municipal waste disposal can cause in heavy metal contamination of urban and agricultural soils (USDA, 2000).

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metal contamination is colourless and odourless. It is difficult to be noticed and does not clearly damage the environment in a short period. When environmental conditions have changed or the heavy metal concentration exceeds the environmental tolerance, heavy metal accumulation in the soil can degrade soil quality; reduce crop yield and the quality of agricultural products. Also, once the soil suffers from heavy metal contamination, it is difficult to be remediated. This situation cause serious ecological damage and thus negatively impacts the health of human, animals due to their non-biodegradability and tendency to accumulate in plants, animal and human tissues (Su et al., 2014; Nagajyoti et al., 2010; De Souza et al., 2013).

Heavy metals are elements that exhibit metallic properties such as ductility, malleability, conductivity and cation stability. They are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 (Alloway, 1990; Chibuike and Obiora, 2014). The concentrations of some heavy metals are beneficial and essentially required for normal body growth and functions of living organisms such as metal nutritional requirements (Cu, Fe, Mn, Zn, Co, Mo, Ni and V). On the other hand, the heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr) and arsenic (As), etc.

In recent years, with the development of the global economy, both type and content of heavy metals in the soil caused by human activities have gradually increased, resulting in the deterioration of the environment (Su et al., 2014; Sayyed and Sayadi, 2011; Raju et al., 2013; Prajapati and Meravi, 2014; Zojaji et al., 2014). Thus, it is important to identify the quantifying of heavy metal concentrations, to determine the spatial variability in the soils and to monitor possible changes. The aim of this research is to ascertain the heavy metal concentrations of soils mixed with the grape molasses collected from Zile/Tokat region which is famous with grape molasses which is an abundantly consumed foodstuff in Turkey (Zile molasses). Molasses soil is added into to Zile grape molasses during production to resolve acidification of its (Kurnaz et al., 2016). Up to now, no survey has been reported on the heavy metal concentrations of the Zile molasses soil. In addition, this information will contribute to the literature of the heavy metal pollution measurements in soil.

Material and Methods

Sample Collection and Preparation

Zile is a county of Tokat Province in the Black Sea region of Turkey and is 67 km away from Tokat city centre. The study area lies between40° 19' N and 35° 45' E (peak elevation: 2428 m, elevation: 740 m average height above sea level for the entire province) and covers an area of 1542 km^2. The study area has a geology that shows various lithological units beginning from Palaeozoic formations consisted of partly marbled limestones extending to Quaternary Era (Anonymous, 2014; Kurnaz et al., 2016). According to the 2014 census, population of Zile region is 56727.

The five different type molasses soil samples were collected from uncultivated locations of the study area. After cleaning the ground from stones, pebbles and vegetation, about 1 kg of material from the first 15 cm of top soil samples was placed in polythene bags. The samples were first pulverized and air dried at room temperature in open air. The samples were sieved to about 100 meshes. About 50 g of each homogenized sample was packed in polyethylene containers.

Heavy Metal Concentrations in Soil

The elemental analysis survey was conducted using energy dispersive x-ray fluorescence (Spectro Xepos, Ametek). This device is a very versatile EDXRF spectrometer. It optimizes excitation using polarization and secondary targets. It has an auto sampler for up to 12 items and software modules. It uses a 50 watt end-window X-ray tube to excite the samples. The target changer, with up to 8 polarization and secondary targets, offers many different excitation conditions ensuring optimum determination of all elements from ^{11}Na to ^{92}U. The measurements are conducted in Helium gas atmosphere. A spectral resolution of less than 155 eV at Mn K_γ is achieved. The sample chamber is equipped with a sample spinner for 40 mm sample cups (Anonymous, 2015).

Results and Discussion

Five type soil samples mixed into molasses collected from Zile county of Tokat province in Turkey were analysed using EDXRF spectrometer for determining chemical compositions and elemental distribution of the samples.

The concentrations of the oxides and elements in the samples were ascertained and compared with their mean abundance in the earth's crust (Yaroshevsky, 2006) (Table 1, 2). The major, minor and trace element contents, expressed as weight percentage of oxides, for the molasses soils are reported in Table 1. As can be seen from Table 1, among the major oxides, the mean concentrations of CaO and Fe_2O_3 are higher than the mean abundance of earth's crust. TiO_2 is single minor oxide and SO_3 is single trace oxide which have larger the mean concentration than the mean abundance of earth's crust while the mean concentrations of the other oxides are lower than or equal the mean abundance of earth's crust.

Table 1 Distribution of the major, minor and trace oxides concentrations and their earth's crust abundance (%)

Molasses soils	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Fe_2O_3	SO_3	MnO
First kind	0.766	0.571	1.688	4.991	0.111	1.513	48.5	0.142	0.839	0.067	0.085
Second kind	0.861	1.672	13.03	24.54	0.144	2.346	22.97	1.411	13.24	0.034	0.106
Third kind	1.379	2.777	11.18	25.35	0.104	1.123	19.77	1.336	12.09	0.019	0.119
Fourth kind	0.762	1.26	6.755	14.21	0.114	0.862	30.78	0.894	8.676	0.043	0.096
Fifth kind	1.031	1.629	7.141	15.95	0.119	0.709	30.56	0.943	8.755	0.047	0.115
Mean	0.96	1.58	7.96	17.01	0.12	1.31	30.52	0.95	8.72	0.04	0.1
Standard Deviation	0.26	0.80	4.40	8.36	0.02	0.65	11.13	0.50	4.85	0.02	0.01
MAES	2.74	4.91	16.17	54.55	0.2	1.32	8.72	0.86	0.92	0.063	0.159

MAES: Mean abundance in the earth's crust

Table 2 Elemental analysis results of molasses soil samples and their earth's crust abundance ($mgkg^{-1}$)

Elements ($mgkg^{-1}$)	First kind	Second kind	Third kind	Fourth kind	Fifth kind	Mean	Standard Deviation	Mean abundance in the earth's
Na	5680	6380	10230	5660	7650	7120	1715	25000
Mg	3440	10080	16750	7598	9825	9539	4321	18700
Al	8932	68950	59170	35750	37800	42120	20839	80500
Si	23330	114700	118500	66400	74540	79494	34961	295000
P	484.5	629.2	454.6	497.7	521.5	517.5	59.9	930
S	270.5	134.9	76.8	171.7	187.5	168.3	63.7	470
K	12560	19470	9321	7155	5890	10879	4854	25000
Ca	346600	164200	141300	220000	218400	218100	71161	29600
Ti	852	8457	8008	5361	5655	5667	2703	4500
V	59.2	274.6	299.9	202.9	216.5	210.6	83.8	90
Cr	21.9	497	372.1	265.7	362.2	303.8	158.9	83
Mn	660.5	819.2	924.9	746.6	893.5	808.9	96.6	1000
Fe	5864	92610	84540	60680	61230	60985	30310	46500
Co	19.4	13.5	35.7	15.2	24.6	21.7	8.0	18
Ni	14.9	150.9	310.3	145.1	195	163.2	95.0	58
Cu	8	27.3	45.5	26.3	31.6	27.7	12.0	47
Zn	12.8	59.7	101.2	52.7	66.6	58.6	28.3	83
Ga	4.1	17.6	20.4	13.6	15.5	14.2	5.6	19
As	3.6	91.3	86	58	58.4	59.5	31.1	1.7
Br	10.2	2.1	2.5	4	4.2	4.6	2.9	2.1
Rb	3.8	63.3	41	35.7	31.8	35.1	19.1	150
Sr	211.2	74.3	131.7	132.9	140.5	138.1	43.6	340
Y	4.6	17.3	20.8	15.5	15.3	14.7	5.4	29
Zr	23.8	127.1	118.8	101.6	89.3	92.1	36.6	170
Cd	2.5	1.5	0.6	0.9	1.8	1.5	0.7	0.13
Sn	14.4	5.3	12.7	1.2	11.7	9.1	5.0	2.5
Sb	6.8	13.3	10.2	3.5	8.4	8.4	3.3	0.5
Te	19.8	19.3	19.1	16	14.6	17.8	2.1	0.001
I	6.7	1.8	3.2	2.4	5.3	3.9	1.8	0.4
Ba	24.5	142.5	89.4	89.2	64.5	82.0	38.4	650
La	0	0	3.3	0	13.3	3.3	5.2	29
Ce	33.1	15.7	0	0	0	9.8	13.2	70
Pr	25.1	4.6	0	6.3	0	7.2	9.3	9
Nd	35.8	17.4	12.1	9.1	14	17.7	9.5	37
Ta	25.9	28.7	26.2	22.6	24.6	25.6	2.0	2.5
Hg	2.3	3	1.1	2	1.4	2.0	0.7	0.083
Pb	3.7	8.5	10.1	6.5	7.1	7.2	2.1	16
Th	2.3	4.7	2.9	4.2	2.7	3.4	0.9	13

The mean concentrations of Ca (Calcium), Ti (Titanium), V (Vanadium), Cr (Chromium), Fe (Iron), Co (Cobalt), Ni (Nickel), As (Arsenic), Br (Bromine), Cd (Cadmium), Sn (Tin), Sb (Antimony), Te (Tellurium), I (Iodine), Ta (Tantalum), and Hg (Mercury) are higher than their mean abundance of earth crust (Table 2). Among the metals analysed in this research, toxic elements Cd, Hg, Pb (Lead) and as are especially important because these metals are in the World Health Organisation's list of ten chemicals of major public health concern (WHO, 2010). The concentrations of Cd, Hg, Pb and As were determined in the ranges 0.6-2.5, 1.1-3, 3.7-10.1 and 3.6-91.3 $mgkg^{-1}$ for all of the soil samples with corresponding mean values of 1.5, 2, 7.2 and 59.5 $mgkg^{-1}$, respectively. When the Table 2 is examined, it is clearly seen that the mean concentrations of As, Hg and Cd in the molasses soil samples are 35, 24.1 and 11.5 times higher while Pb is 2.2 times lover than the their mean abundance in the earth's crust.

The concentrations of some heavy metals (Na (Sodium), Mg (Magnesium), P (Phosphorus), S (Sulphur), K (Potassium), Ca (Calcium), Mn (Manganese), Fe, Co, Ni, Cu (Copper), Zn (Zinc) and I) are essential for numerous enzymes involved in numerous body functions for human health (Prashanth et al., 2015). The concentrations of these heavy metals were ascertained in the ranges 5660-10230, 3440-16750, 454.6-629.2, 76.8-270.5, 5890-19470, 141300- 346600, 660.5-924.9, 5864-92610, 13.5-35.7, 14.9-310.3, 8-45.5, 12.8-101.2 and 1.8-6.7 $mgkg^{-1}$, respectively for all of the soil samples. The mean concentrations of these metals were found to be 7120, 9539, 517.5, 168.3, 10879, 218100, 808.9, 60985, 21.7, 163.227.758.6 and 3.9 $mgkg^{-1}$, respectively in this research (Table 2). As can be seen from the results, between the essential heavy metals for body functions, the mean concentration of Ca, Fe, Co, Ni and I are notable higher than the their mean abundance in the earth's crust.

The concentration of Th (Thorium) radioactive elements detected in all soil samples varied from 2.3 to 4.7 $mgkg^{-1}$ and the mean value was found as 3.4 $mgkg^{-1}$. Also in this research, Y (Yttrium), La (Lanthanum), Ce (Cerium), Pr (Praseodymium) and Nd (Neodymium) which is known as rare earth elements was observed. Y and Nd were determined in all samples in the ranges 4.6-20.8 $mgkg^{-1}$ and 9.1-35.8 $mgkg^{-1}$ with corresponding mean values of 14.7 $mgkg^{-1}$ and 17.7 $mgkg^{-1}$, respectively. La was determined only 3rd and 5th type soil samples while Ce was determined 1st and 2nd type soil samples. The concentrations of La and Ce were ascertained as 3.3 $mgkg^{-1,}$ 13.3 $mgkg^{-1}$ and 33.1 $mgkg^{-1}$, 15.7 $mgkg^{-1}$, respectively. Pd was determined in three sample type and the mean value was found to be 7.2 $mgkg^{-1}$. The highest concentration of Nd (35.8 $mgkg^{-1}$), Pr (25.1 $mgkg^{-1}$) and Ce (33.1 $mgkg^{-1}$) was determined in first kind of the molasses soil samples (Table 2).

Conclusion

Environmental contamination with chemicals and heavy metals from different sources has become a global concern since 1990's. Anthropogenic activities such as agriculture and industrial processing are the main sources of heavy metal contamination in the environment. These contaminations under certain conditions have important reflection both the environment and human health because heavy metals may accumulate to a toxic concentration level, which can lead to ecological damages. Because of this reason, elemental analysis of the five different types of the molasses soil samples collected from Zile/Tokat region in Turkey using EDXRF technique. Because the molasses soils are directly incorporated into the foodstuff (grape molasses), it is even more important to determine of the element concentrations in the soils. Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Fe_2O_3, SO_3, MnO oxides and the specific element concentrations given Table 2 were detected. The mean concentrations of Ca, Ti, V, Cr, Fe, Co, Ni, As, Br, Sn, Sb, Te, I and Ta are higher than their average abundance in the earth's crust. The accumulations of Cd, Hg, Pb, and especially As were observed through the investigation of the molasses soil samples. These elements are not essential for body growth. It is well known theirs toxic effects. The major threat to human health of Cd is chronic accumulation in the kidneys leading to kidney dysfunction and Pb can cause serious injury to the brain, nervous system, red blood cells, and kidneys (Baldwin and Marshall, 1999; Wuana and Okieiman, 2011). Hg is associated with kidney damage and As is associated with skin damage, increased risk of cancer and the cause problems with circulatory system (Scragg, 2006; Wuana and Okieiman, 2011). Among the all metal analysed, it is said that As has the highest risk because the mean value was 35 times higher than the earth's crust abundance and this accumulation comes from probably both natural and anthropogenic sources. The results of the present study will be valuable database in keep track and assessment of soil pollution.

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