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Effect of Biogas Solid Waste on Mineral Content of Barley (*Hordeum vulgare* conv. *distichon*)

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Abstract: In this study, it was aimed to determine the mineral contents and changes in barley (*Hordeum vulgare* conv. *distichon*) grain treated with different doses of biogas solid waste. The study was conducted for two years with 4 replications in a randomized complete block design. In the study, biogas solid waste was applied at doses of 0, 10, 20, 30 and 40 tons ha^{-1} and the macro (nitrogen, phosphorus, potassium, calcium and magnesium) and microelement (iron, manganese, zinc and copper) contents of the barley grains obtained were determined. Macro and microelement contents of barley grain increased with the increase in biogas solid waste application in both experimental years. It was determined that 40 tons ha^{-1} dose of biogas solid waste application was the most effective application on macro and micro nutrient contents of barley grain. Compared to the control treatment, 40 tons ha^{-1} biogas waste application increased the macroelement contents by 3.02% (maximum increase N, 7.87%) and microelement contents by 9.97% (maximum increase Cu, 22.84%). As a result, 40 tons ha^{-1} biogas waste application enriched the macro and micronutrient content of barley grain and biogas waste application can be used to increase the nutrient composition of barley grain, which has important areas of use in human and animal nutrition.

Keywords: Barley, biogas solid waste, macro nutrients, micro nutrients, principal component analysis

1. Introduction

Barley (*Hordeum vulgare* conv. *distichon*) is one of the main cool climate cereals grown in the world. Türkiye, one of the important gene centers of barley, is among the top 10 countries in barley production in the world. However, it ranks fourth among cereals in the world and second in Türkiye (Anonymous, 2023). Barley is a staple food in many parts of the world, especially due to its adaptation to high altitudes, drought and soil salinity (Kumar et al., 2020). Barley and barley-based food products have a wide range of uses in various sectors, including food, beverages, bread, animal feed and cosmetic ingredients (Lukinac and Jukić, 2022). The barley grain is rich in proteins and carbohydrates, including beta-glucan, lipids, vitamins and minerals (Oso and Ashafa, 2021). Especially in recent years, its use for food purposes has been increasing in human nutrition due to its health benefits (Czembor, 2023). In this context, enriching the elemental content of barley, which is an important food in human and animal nutrition, is of great importance.

Fertilization in agricultural production plays a major role in the quality of crops as well as in modeling the quantitative and qualitative characteristics of the composition of cereals (Lin et al., 2015). Nowadays, due to environmental protection issues and efforts to increase agricultural productivity, various organic and mineral wastes are used to fertilize crops and improve soil properties. Such organic wastes can be an alternative to conventional fertilization and can significantly reduce production costs (Różyło et al., 2016; Özyazıcı and Özyazıcı, 2019).

Especially as a result of the support of the renewable energy sector, the number of biogas plants has increased in the world and in Türkiye (Anonymous, 2024a). Biogas waste obtained after anaerobic digestion of various organic wastes in biogas plants can be used in agricultural production activities (Demirel and Erekul, 2020; Karaman and Türkay, 2022) and attracts great interest worldwide (Kara et al., 2019). Research on biogas reveals that this waste improves soil physical and chemical properties, increases organic carbon content and grain yield, and reduces nitrate content in plants compared to chemical fertilization (Chen et al., 2012; Lopedota et al., 2013; Demirel and Erekul, 2020; Alaboz et al., 2021). Depending on the raw materials used for biogas production, biogas waste can vary significantly in terms of macro and micronutrient content and ratios (Korkmaz et al., 2012). Compared to other types of organic fertilizers, biogas waste contains more ammonium nitrogen. Odlare et al. (2011) reported that biogas waste application increases the available nutrients in the plant and therefore has good fertilization properties. In addition, in many plant species, biogas waste application has been found to improve the grain yield of plants and many characteristics that affect yield compared to conventional fertilization (Kara et al. 2019; Ferdous et al., 2020; Karaman and Türkay, 2022).

Despite the increasing interest in the use of biogas waste in crop production, there is a lack of comprehensive research on the effectiveness of such treatments and their effects on the nutritional value of cereals. In this study, it was aimed to determine the mineral matter contents and changes in barley (*H. vulgare* conv. *distichon*) grain treated with different doses of biogas waste.

2. Materials and Methods

2.1. Material

The study was established as field trials between 2019-20 and 2020-21 in the experimental field of Isparta University of Applied Sciences, Faculty of Agriculture, Research, Education and Application Farm. Tarm-92, one of the two-row barley (*H. vulgare* conv. *distichon*) varieties, was used as seed material in the study. The biogas waste used in the study was obtained from farmyard manure in Burdur and the content of this waste was determined by Alaboz et al. (2021) as 15.0% moisture, 46.7% organic matter, pH value of 7.70 and carbon/nitrogen (C:N) ratio of 12:1 (Table 1).

The experimental areas were selected as fallow fields in both growing seasons and soil sampling was carried out from 0-30 cm depth before sowing. The chemical and physical properties of the soils in the study area was clay-loam, organic matter was determined as 1.69% in the first year and 1.65% in the second year, lime content was the same in both years (25.4% and 25.5%), there was no salinity problem and slightly alkaline (Table 2). In both years of the study, the average temperatures (11.4 ^{o}C and 12.5 ^{o}C) were above the long-term average temperature (10.2 ^{o}C). The total rainfall during the growing seasons of the study was less than the long-term average rainfall (497.5 mm) in both years (421.5 mm and 374.9 mm) (Figure 1).

Table 1. Content of biogas waste

Properties	Unit	Value
Moisture	%	15.0
Organic matter	%	46.7
pH		7.70
C:N		12:1
Electrical conductivity	dS m^{-1}	1.44
Nitrogen (N)	%	1.5
Phosphorus (P)	%	0.84
Potassium (K)	%	0.75
Zinc (Zn)	mg kg^{-1}	35
Manganese (Mn)	mg kg^{-1}	109
Iron (Fe)	mg kg^{-1}	859
Copper (Cu)	mg kg^{-1}	15.8

Table 2. Some physical and chemical properties of the experimental soil (0-30 cm)

Soil properties	Unit	2019-2020 year	2020-2021 year
pH		7.89	7.92
$CaCO_3$	%	25.4	25.5
Organic matter	%	1.69	1.65
P	mg kg^{-1}	4.5	4.7
K	mg kg^{-1}	350	425
Magnesium (Mg)	mg kg^{-1}	185	192
Calcium (Ca)	mg kg^{-1}	3900	3975
Fe	mg kg^{-1}	5.21	5.59
Cu	mg kg^{-1}	7.52	6.21
Mn	mg kg^{-1}	16.45	17.10
Zn	mg kg^{-1}	1.24	1.19

2.2. Method

In the study, different doses (0, 10, 20, 30 and 40 tons ha^{-1}) of biogas waste obtained from farmyard manure were considered as the subject of research. In order to break down the biogas waste in the soil, biogas waste was applied 45 days before sowing. After the application, this waste was mixed to a depth of 0-20 cm with a hoeing machine.

In both years, the trials were planned as 4 replicates according to the randomized complete blocks experimental design. In the study, sowing was done in plots of 5 m in length and 1.2 m in width and each plot consisted of 6 rows. Barley seeds were sown with the help of a seeder with 500 seeds per square meter. In the experiment, 100 kg N ha^{-1} and 60 kg P_2O_5 ha^{-1} were applied as basic fertilization to all plots according to the analysis results in Table 2. Sowing was done in the first weeks of November. Appropriate selective herbicide was applied when weed emergence occurred. The plants in the first and last rows and

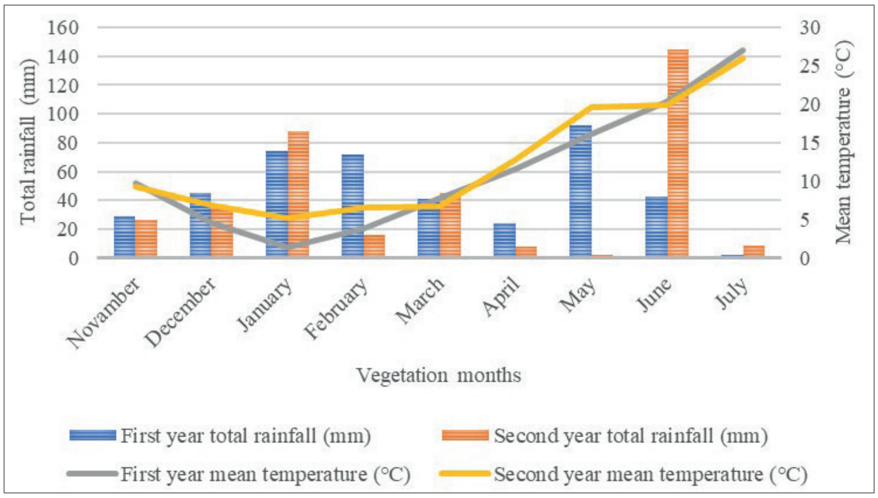

Figure 1. Climatic data of trial years

50 cm from the heads were excluded from the experiment as a side effect, and the remaining plants were harvested. Harvests were made on July 10, 2020 and July 13, 2021, respectively.

The grains obtained from the harvested plants were dehumidified at 65 °C and ground. When the ground materials turned into flour, they were weighed 0.5 g with the help of a precision balance and then burned in a closed system microwave oven with a mixture of 5 ml nitric acid (HNO_3) and 2.5 ml hydrogen peroxide (H_2O_2). The final volume was then made up to 25 ml with ultrapure water. After the digestion process, the samples were filtered with filter paper, placed in capped laboratory bottles and kept in the refrigerator at +4 °C until analysis. Macroelements K, Ca and Mg, and microelements Fe, Mn, Zn and Cu were analyzed by ICP-OES (Inductively Coupled Plasma Optic Emission Spectrometry) and the raw results were multiplied by the coefficient "Last volume/starting weight" and the mineral contents of the samples were calculated in mg kg^{-1}. Total N and P contents of grain samples were determined by modified Kjeldahl method and vanadamolibdat yellow color method, respectively (Kacar and İnal, 2008).

The analysis of variance of the data obtained from the study was performed in MINITAB statistical package program and the differences between the averages of the treatments and years were determined using Tukeys multiple comparison test. Principal component analyses (PCA) of the data obtained in the study were determined using Factoextra, pca3d and, FactoMineR packages in R (Anonymous, 2024b) statistical program. In principal component analysis, cos2 (cosine squared, square coordinates) was displayed to determine the representation quality and total contribution of variables in the factor map.

3. Results and Discussion

It was determined that year, biogas waste treatment and year x biogas waste treatment interactions had statistically significant ($p<0.01$) differences in terms of all macro and microelements determined in the study (Table 3).

Table 3. Analysis of variance results of the traits examined according to different biogas waste applications in barley[1]

Source of variation	DF	N	P	K	Ca	Mg
Block	3	0.01	0.3	1.0	1.56	0.7
Year (Y)	1	0.03**	82656.0**	6572973.0**	8329.0**	23815.1**
Application (A)	4	0.03**	377.0**	8204.0**	207.4**	1505.2**
YxA	4	0.01*	40.2**	1540.0**	50.74**	136.9**
Error	27	0.01	0.4	0.1	0.97	0.8
		Fe	Mn	Zn	Cu	
Block	3	0.01	0.01	0.01	0.01	
Year (Y)	1	44.30**	8.91**	3.12**	11.28**	
Application (A)	4	14.51**	0.90**	3.83**	1.43**	
YxA	4	1.70**	0.05**	0.32**	0.41**	
Error	27	0.01	0.01	0.01	0.01	

[1]: Mean squares values of traits, DF: Degrees of freedom, *: $p<0.05$, **: $p<0.01$

3.1. Macroelements content

The average grain N content varied between 1.65-1.78% according to different doses of biogas waste applied to barley. While the highest N content was determined in 40 tons ha^{-1} biogas waste application, it was in the same statistical group with 30 tons ha^{-1} biogas waste application. The lowest N content (1.65%) was determined in the control (0 tons ha^{-1}) treatment, also 1.67% with 10 tons ha^{-1} treatment was in the same statistical group with the control. The average N content was lower in the first year (1.69%) than in the second year (1.75%) (Table 4). In both years, the highest N content was determined in the 40 tons ha^{-1} (1.78%) and 30 tons ha^{-1} (1.77%) biogas waste treatment and the lowest in the control treatment (Figure 2a). This difference between the years is thought to be caused by climatic and environmental conditions (Figure 1). The amount of organic matter in Türkiye soils is very low and it is also very poor in terms of nitrogen (Eyüpoğlu, 1999; Özyazıcı et al., 2013). In this context, the addition of biogas waste applied to the soil in the study increased the organic matter and nitrogen content of the soil, and it is thought to be beneficial to increase the nitrogen content of barley grain. Staugaitis et al. (2016) found that biogas waste application increased the N concentration of barley and wheat grains. The nitrogen concentration of barley grains can vary depending on the climate and soil conditions of growing region as well as cultural practices. In this context, Demir and Sönmez (2019) reported that the N content of local barley varieties varied between 1.65-2.54%.

The average P content of barley grain varied between 3533.34-3547.63 mg kg^{-1} according to biogas waste treatments. The highest P content was detected in 40 tons ha^{-1} biogas waste treatment, while the lowest was detected in control (3533.34 mg kg^{-1}) and 10 ton ha^{-1} (3533.58 mg kg^{-1}) biogas waste doses. The highest average P content was 3584.96 mg kg^{-1} in the second year (Table 4). In both years, the highest average P content was determined in the 40 kg ha^{-1} biogas waste treatment and the lowest in the control treatment. In addition, the P content of barley grain increased with increasing doses of biogas waste (Figure 2b). Phosphorus is necessary for the formation of ATP compounds, sugars, nucleic acids and DNA, which transfer energy in plants (Bolat and Kara, 2017). Demir and Sönmez (2019) found that the P content of barley grain varied between 3476-5993 mg kg^{-1}; Erbaş Köse and Mut (2019) found that it varied between 2395.9- 4494.2 mg kg^{-1} and the P content of Tarm-92 barley variety was 3743.3 mg kg^{-1}. On the other hand, similar to the results in this study, biogas waste application increased the P content of barley grain compared to the control treatment (Staugaitis et al., 2016).

The highest K content was 4436.32 mg kg^{-1} in 40 tons ha^{-1} biogas waste treatment and the lowest was 4358.23 mg kg^{-1} in the control treatment. The average K content in the first year (4277.70 mg kg^{-1}) was lower than the second year (4534.08 mg kg^{-1}) (Table 4). The K content of barley grains increased with increasing amounts of biogas waste treatment (Table 4, Figure 2c). Potassium, P, Ca, and Mg elements were reported, with K content accounting for 45% of the total amount of these elements (Stewart et al., 1988). Studies have reported that the potassium content of barley grain varies widely between 1156 and 6319 mg kg^{-1} (Villacres and Rivadeneira, 2005; Altuntaş, 2012; Demir and Sönmez, 2019; Erbaş Köse and Mut, 2019).

The average Ca content of grain varied between 491.51-504.12 mg kg^{-1} according to different doses of biogas waste applied to barley plants. While the highest Ca content was determined in 40 tons ha^{-1} biogas waste application, it was in the same statistical group with 30 tons ha^{-1} (503.40 mg kg^{-1}) biogas waste application. The lowest Ca content (491.51 mg kg^{-1}) was determined in the control treatment. The average Ca content was higher in the first year (514.71 mg kg^{-1}) than in the second year (485.85 mg kg^{-1}) (Table 4). Calcium content increased with the increase in the amount of biogas waste application. In both years, the highest Ca content was determined in the 30 and 40 tons da^{-1} biogas waste treatment and the lowest in the control treatment (Figure 2d). Calcium is the third most

Table 4. Averages of macronutrient contents of different biogas waste treatments in barley*

Applications	N (%)	P (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
0 t ha^{-1} (Control)	1.65 c	3533.34 d	4358.23 e	491.51 d	1294.02 d
10 t ha^{-1}	1.67 c	3533.58 d	4388.68 d	500.57 c	1309.36 c
20 t ha^{-1}	1.72 b	3536.93 c	4420.36 c	501.80 bc	1321.37 b
30 t ha^{-1}	1.77 a	3546.04 b	4425.85 b	503.40 ab	1325.82 a
40 t ha^{-1}	1.78 a	3547.63 a	4436.32 a	504.12 a	1326.12 a
Years					
2019-2020	1.69 B	3494.05 B	4277.70 B	514.71 A	1339.74 A
2020-2021	1.75 A	3584.96 A	4534.08 A	485.85 B	1290.94 B

*: There is no difference between the means indicated with the same letter in the same column at 0.01 level of significance.

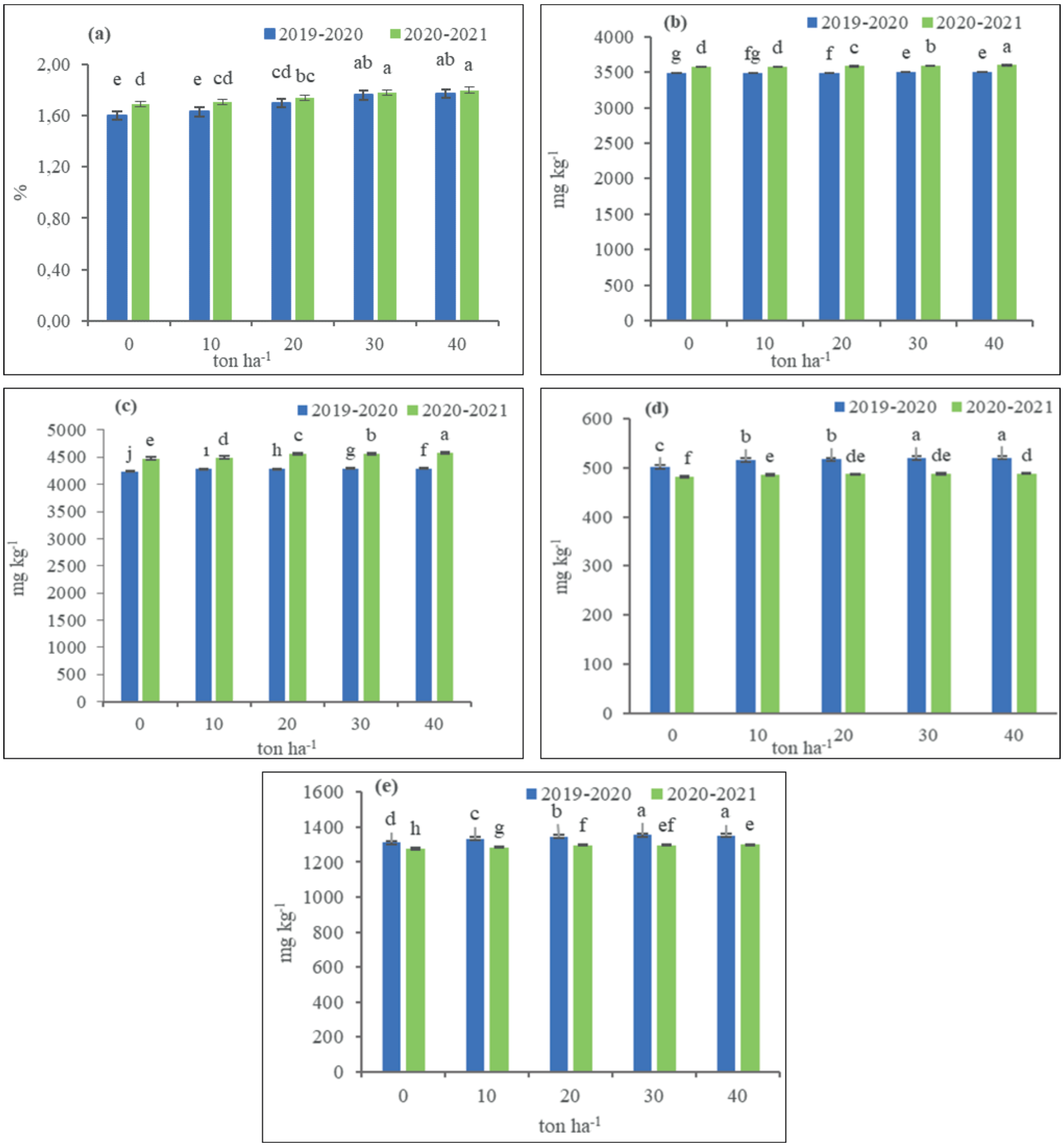

Figure 2. Year x biogas waste application interaction according to different biogas waste applications in barley [**(a)** N, **(b)** P, **(c)** K, **(d)** Ca, **(e)** Mg]*

*: The difference between the means indicated with the same letter is not statistically significant

utilized nutrient element in plants and regulates the structure of the cell wall of plants (McCauley et al., 2009). In addition, as with all cereals, barley has a low calcium content (Anderson et al., 1985). Carr et al. (2004) found that the Ca content of barley grain varied between 295-365 mg kg^{-1}, Demir and Sönmez (2019) found between 725-1616 mg kg^{-1}, Erbaş Köse and Mut (2019) found between 334.6 802.7 mg kg^{-1} and Tarm-92 barley variety was found between 484.4 mg kg^{-1}. On the other hand, Ciolek et al. (2012) reported that the Ca content of barley grain was higher in organic farming (0.393 g kg^{-1}) than in convectional farming (0.365 g kg^{-1}). The results of this study are in agreement with the findings of other researchers.

Magnesium content of barley grains varied between 1294.02-1326.12 mg kg^{-1} according to biogas waste treatments. The highest Mg content was determined in 40 tons ha^{-1} and 30 tons ha^{-1} biogas waste dose, respectively, and there was no statistical difference between these two treatments. The lowest Mg content (1294.02 mg kg^{-1}) was determined in the control treatment. Over the years, Mg content in barley grains increased with the increase in the amount of biogas waste application, and the highest was determined in the first year

(1339.74 mg kg^{-1}). When the interaction was evaluated, the highest Mg values with 1353.73 mg kg^{-1} and 1353.29 mg kg^{-1} were determined in 30 ton ha^{-1} and 40 ton ha^{-1} application in the first year, respectively, and the lowest Mg values were determined in 1276.56 mg kg^{-1} with 0 (control) ton ha^{-1}application in the second year (Table 4, Figure 2e). Magnesium, which is the central atom of chlorophyll, is one of the macro elements that ensure the continuity of life with its important role in photosynthesis (Bolat and Kara, 2017). Erbaş Köse and Mut (2019) determined the Mg content of Tarm-92 barley variety as 1270.6 mg kg^{-1}. Researchers determined that the Mg content of barley grain varied between 853.8-4707 mg kg^{-1} (Alkan and Kandemir, 2015; Erbaş Köse and Mut, 2019). The results of the researchers on the Mg content of barley grain are in agreement with the findings of this study.

3.2. Microelements content

Iron element, which plays a very important role in respiration and photosynthesis reactions in plants, increased with the increase in the amount of biogas waste application. The highest Fe content was determined in 40 tons ha^{-1} (50.98 mg kg^{-1}) biogas waste application and the lowest in the control (48.01 mg kg^{-1}) application. The average Fe content was higher in the first year (50.71 mg kg^{-1}) than in the second year (48.60 mg kg^{-1}). When the interaction was evaluated, the highest Fe values with 52.30 mg kg^{-1} and 52.25 mg kg^{-1} were determined in 30 ton ha^{-1} and 40 ton ha^{-1} application in the first year, respectively, and the lowest Fe values were determined in 47.45 mg kg^{-1} 0 ton ha^{-1} application in the second year (Table 5, Figure 3a). Moreover, Fe content increased with the increase in biogas waste doses in both years. As a matter of fact, this increase is thought to be due to the increase in the mineralization of biogas waste with the organic matter content of the soil. In the literature studies, it was reported that the iron content of barley grain varied between 22.93 and 128.4 mg kg^{-1} (Ghafoor et al., 2015; Jākobsone et al., 2015; Erbaş Köse and Mut, 2019). In addition, Fe deficiency is the most common nutrient element in plants cultivated in arid and semi-arid regions. The high lime and pH values of soils in arid regions are among the reasons for Fe deficiency (Bolat and Kara, 2017). In this study, it is thought that the low amount of rainfall in the second year compared to the first year caused the Fe content of barley grain to differ between years.

Manganese, which is present in the structure of various primary and secondary minerals, is involved in the activation of vital enzymes (Bolat and Kara, 2017). In the study, Mn content varied between 18.07-18.89 mg kg^{-1} in biogas waste treatments, the highest Mn content was obtained in 40 tons ha^{-1} biogas waste treatment and the lowest Mn content was obtained in plants in control plots without biogas waste treatment. Manganese content was higher in the first year (19.01 mg kg^{-1}) than in the second year (18.07 mg kg^{-1}) (Table 5). This difference in Mn content in barley grains is due to the high amount of rainfall between the years (Figure 1). In general, Mn content increased with the increase in biogas waste doses in both years. When the interaction was evaluated, the highest Mn values with 19.37 mg kg^{-1} were determined in 40 ton ha^{-1} application in the first year, and the lowest Mn values were determined in 17.72 mg kg^{-1} and 17.77 mg kg^{-1} with respectively 0 ton ha^{-1} and 1 ton ha^{-1} applications in the second year (Figure 3b). The solubility of manganese in soil may vary according to microorganism activities, soil reaction and soil water properties (Kantarcı, 2000). Manganese content of barley grain was reported to vary between 8.0 and 21.2 mg kg^{-1} by different researchers (Kandemir et al. 2005; Ragaee et al., 2006; Alkan and Kandemir, 2015). Erbaş Köse and Mut (2019) determined the Mn content of Tarm-92 barley variety as 18.08 mg kg^{-1} and reported that the differences in climate and environmental conditions between years caused the manganese content of barley grain to vary. The results obtained from these studies and the results obtained in this study were in parallel.

According to the different doses of biogas waste applied to barley, the highest average grain Zn content was found in 40 tons ha^{-1} (25.46 mg kg^{-1})

Table 5. Means of micronutrient contents of different biogas waste treatments in barley (mg kg^{-1})*

Applications	Fe	Mn	Zn	Cu
0 t ha^{-1} (Control)	48.01 e	18.07 e	23.94 e	3.37 c
10 t ha^{-1}	48.45 d	18.34 d	24.16 d	3.97 c
20 t ha^{-1}	50.11 c	18.61 c	24.83 c	4.00 b
30 t ha^{-1}	50.72 b	18.78 b	25.38 b	4.11 ab
40 t ha^{-1}	50.98 a	18.89 a	25.46 a	4.14 a
Years				
2019-2020	50.71 A	19.01 A	25.03 A	4.31 A
2020-2021	48.60 B	18.07 B	24.48 B	3.25 B

*: There is no difference between the means indicated with the same letter in the same column at 0.01 level of significance.

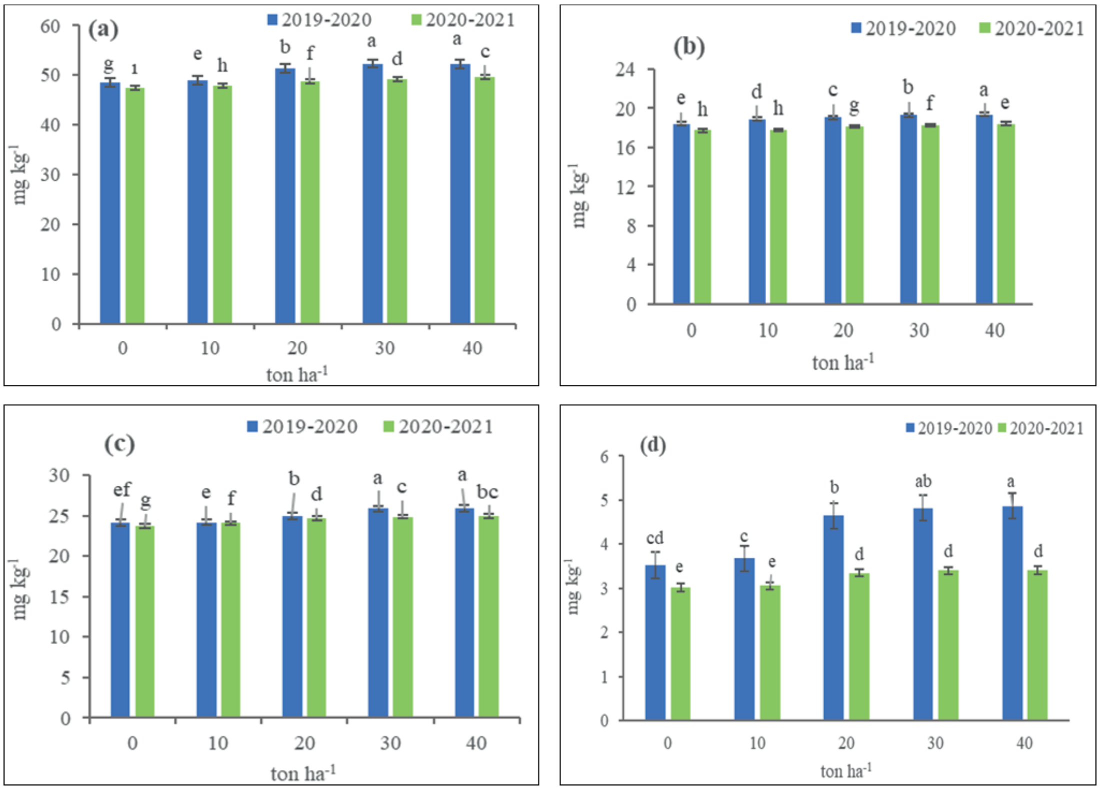

Figure 3. Year x biogas waste application interaction according to different biogas waste applications in barley [**(a)** Fe, **(b)** Mn, **(c)** Zn, **(d)** Cu]*

*: The difference between the means indicated with the same letter is not statistically significant

biogas waste treatment and the lowest in the control (23.94 mg kg^{-1}) treatment. Zinc content was higher in the first year (25.03 mg kg^{-1}) than in the second year (24.48 mg kg^{-1}) (Table 5). In both years, the highest Zn content was determined in the 30 and 40 tons ha^{-1} biogas waste treatment and the lowest in the control treatment. This difference between years is thought to be caused by climatic and environmental conditions (Figure 3c). Zinc is a necessary element for starch formation, nitrogen metabolism, seed maturation and growth hormone production in plants (Bolat and Kara, 2017). Zn is the second most abundant microelement in the human body after iron and is required for the function of more than 300 enzymes (Akdeniz et al., 2016). Erbaş Köse and Mut (2019) reported that increasing the Zn content of cereal grains will help to reduce health problems related to zinc deficiency in humans. Villacres and Rivadeneira (2005) reported that the Zn content of barley grain varied between 30-50 mg kg^{-1}, Demir and Sönmez (2019) reported between 16.9-43.3 mg kg^{-1}, Altuntaş (2012) reported between 28.4-39.6 mg kg^{-1}, Erbaş Köse and Mut (2019) reported between 17.92-30.97 mg kg^{-1}. In addition, Ciolek et al. (2012) found that the Zn content of barley grain was lower in organic farming (30.56 mg kg^{-1}) than in convectional farming (32.18 mg kg^{-1}). The results obtained by other researchers and the findings obtained in this study are similar.

The average Cu content of barley grain varied between 3.37-4.14 mg kg^{-1} according to the biogas waste treatments. The highest Cu content was found in 40 tons ha^{-1} biogas waste treatment; the lowest was found in control and 10 ton ha^{-1} (3.37 and 3.97 mg kg^{-1}, respectively) biogas waste doses. The highest average Cu content was found in the first year (4.31 mg kg^{-1}) (Table 5). In both years, the highest average Cu content was determined in the 30 and 40 kg ha^{-1} biogas waste treatment and the lowest in the control treatment (Figure 3d). The Cu content of barley grain increased with increasing doses of biogas waste. Copper is a plant nutrient required by plants for chlorophyll production, respiration and protein synthesis, protein and carbohydrate metabolism and symbiotic nitrogen fixation (Gardiner and Miller, 2008; McCauley et al., 2009). In addition, due to the binding of copper by organic matter, copper deficiency can be observed in soils with high organic matter (Bolat and Kara, 2017). Erbaş Köse and Mut (2019) found that the Cu content of barley varieties varied between 5.53-8.08 mg kg^{-1} and the Cu content of Tarm-92 barley variety was 7.00 mg kg^{-1}. Other researchers determined that the Cu content of barley grain varied between 5.4-8.5 mg kg^{-1} by Altuntaş

(2012) and between 2.2-4.7 mg kg^{-1} by Demir and Sönmez (2019). On the other hand, Staugaitis et al. (2016) found that biogas waste application (4.10 mg g^{-1}) had higher Cu content in barley grain than cultivation without any fertilizer (4.26 mg g^{-1}). It is thought that climate, soil conditions and cultural practices are effective in the variation between the results of this study and the findings of other researchers.

3.3. Principal component analysis

Principal component analysis signifies the importance of the major contributor to the total variation at each axis of distinction (Sharma et al., 1998). It evaluates the significance and contribution of each factor to total variance whereas each coefficient of proper vector shows the degree of contribution of every original variable with each principal component it is related. In this study, purpose of performing PCA was carried out to explain the change of biogas waste application in barley over the years on the studied traits. As a result of PCA, it was found that the total multiple variation (PCA1 and PCA2) represented 98.28% of the total multiple variation according to the doses of biogas waste applied to barley crops. In principal component analysis, an eigenvalue greater than 1 indicates that the principal component (PC) weight values considered are reliable (Mohammadi and Prasanna, 2003), and factors with an eigenvalue less than 1 were not considered (Dunteman, 1989). PCA1 and PCA2 axis with eigenvalues greater than 1. PCA requires weights of 0.30 and above in the components, and weights of 0.50 and above are considered to be very good (Hair et al., 1998). PCA1, Ca, Mg, Cu, Fe and Mn, which contain 54.30% of the total variation, are the most important criteria that reveal the difference between biogas waste treatments with high weight values. PCA2, representing 25.38% of the available variation, included N, K, P and Zn (Table 6).

Table 6. PCA results between macro and microelements analyzed in barley grain according to biogas waste treatments

Terms	PCA1	PCA2
Eigenvalue	6.56	2.28
Percent of variance	72.89	25.38
Cumulative percent	72.89	98.28
Trait		
N	0.009	0.659
Ca	0.380	-0.121
Mg	0.388	-0.006
K	-0.306	0.399
P	-0.326	0.363
Cu	0.379	0.116
Fe	0.357	0.259
Mn	0.383	0.060
Zn	0.295	0.419

The distribution of the features analyzed as a result of principal component analysis is given in Figure 4. Cos2 indicates the importance of a component for a particular observation and is important in determining which component to infer (Adu et al., 2018). Variables with high cos2 values are close to the circumference of the correlation circle, indicating that the variable is well represented in PCA. On the other hand, when the variable is near the center of the circle, it shows a low cos2 value, indicating that the variable is not perfectly represented by PCA (Adu et al., 2018).

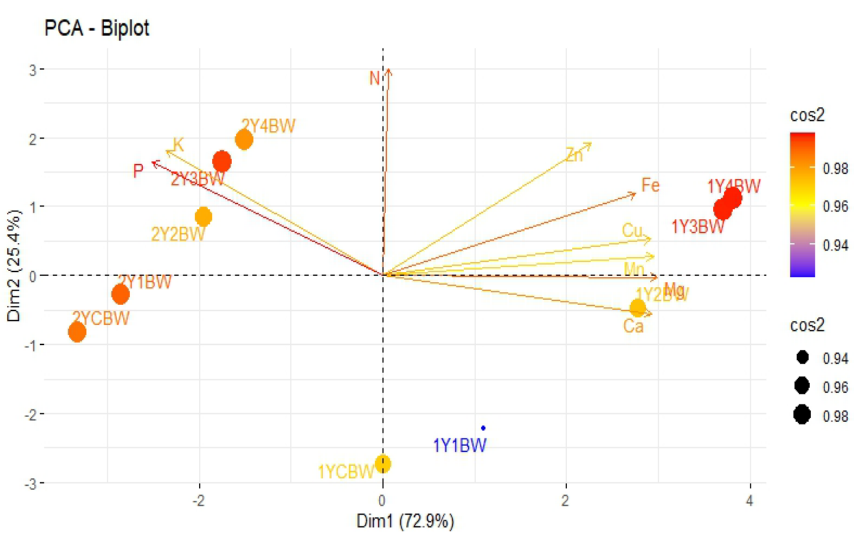

Figure 4. Biplot plot showing the relationship between biogas waste applications and macro and microelements

Among the traits examined, P and Fe content had the highest effect. When the treatments were analyzed, 30 and 40 kg ha^{-1} biogas waste doses were the highest in the first year, and the lowest was determined in 10 kg ha^{-1} biogas waste application in the first year. Since the angle between Ca, Mg, Mn, Cu, Fe, Zn and P and K elements is less than 90°, it can be said that there is a positive correlation between these traits, and since the angle between P, K elements and Ca and Mg is greater than 0°, it can be said that there is a negative correlation between these two traits. It was determined that the biogas waste applications in the second year of the study had above average values in terms of P and K elements, while the biogas waste applications in the first year had high values in terms of Ca, Mg, Mn, Cu, Fe, Zn elements (Figure 4).

4. Conclusions

The importance of studies to increase the macro and micro nutrient content of barley, which is of great importance in human and animal nutrition, is increasing day by day in terms of food safety. For this purpose, it was determined that biogas waste, which is an alternative organic fertilizer, had positive effects on the macro and micro element content of barley grain. In both years of the study, macro (N, P, K, Ca, Mg) and micro (Fe, Mn, Zn, Cu) element contents of barley grain increased with the increase in biogas waste applications. Especially 40 tons of biogas solid waste per hectare was found to be the most effective application on the nutrient content of barley grain. However, it was determined that the effect of climate and environmental conditions on the nutrient composition of barley grain was very important. Compared to the control treatment, 40 tons ha^{-1} biogas waste application increased the macroelement contents by 3.02% (maximum increase N, 7.87%) and microelement contents by 9.97% (maximum increase Cu, 22.84%). As a result of this study, it was concluded that the application of biogas waste (40 tons ha^{-1}) enriches the macro and micronutrient content of barley grain and will provide important contributions to human and animal nutrition.

Ethical Statement

The authors declare that ethical approval is not required for this research.

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Declaration of Author Contributions

The authors declare that they have contributed equally to the article. All authors declare that they have seen/read and approved the final version of the article ready for publication.

Declaration of Conflicts of Interest

All authors declare that there is no conflict of interest related to this article.

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