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Soil Studies is an international peer reviewed journal that aims to rapidly publish high-quality, novel research of studies on fertility, management, conservation, and remediation, physics, chemistry, biology, genesis, and geography of soils. In addition, the main purpose of Soil Studies is to reveal the influences of environmental and climate changes on agroecosystems and agricultural production. In this context, Soil Studies publishes international studies address these impact factors through interdisciplinary studies. In the journal, articles on hypothesis-based experimental observation of the interactions of all components of agricultural ecosystems, field trials, greenhouse or laboratory-based studies, economic impact assessments, agricultural technologies, and natural resources management will be accepted within the peer-reviewed process. Topics include, but are not limited to:

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Volume 13 *Issue 1* *JULY 2024*

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CONTENTS

Research Articles

Review Paper

Soil Studies 13(1), 1-16
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RESEARCH PAPER

Effects of humic acid and mineral Zn fertilizer on Zn uptake and maize yield in soils formed on limestone and marl parent materials

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Abstract

In this study, the effects of zinc (Zn) and humic acid (HA) applications on soils (12 Aridisol soil samples) formed on limestone and marl parent materials, which are very common in Türkiye, were tested by incubation, adsorption, and greenhouse experiments. Adsorption experiments were carried out using the batch sorption technique, and the Langmuir and Freundlich isotherm parameters were calculated. In the incubation, soils were incubated with control, HA, Zn, and HA+Zn, and the DTPA-Zn was tested in five different periods (1, 7, 15, 30, and 90th days). Maize was grown for eight weeks in pots in the greenhouse. The maximum Zn adsorption for all soils ranged between 3333 and 6250 mg kg^{-1} in marl soils and 1042 and 5263 mg kg^{-1} in limestone soils, which decreased to ranges between 2631 and 5555 mg kg^{-1} in marl soils and 1052 and 5000 mg kg^{-1} in limestone soils with HA application, respectively. The desorption rate (%) of adsorbed Zn increased as the initial Zn concentration increased in all soil series formed on marl (smectite clay mineral) and limestone (kaolinite clay mineral) parent materials. The effects of humic acid and Zn application on the fresh and dry weights of maize were found to be statistically significant at the 5% level for marl and limestone parent material. Humic acid application increased the fresh weight of maize compared with that of the control. The highest available Zn was determined in Başkuyu series (0.79 mg kg^{-1}) formed on marl parent material, while the lowest available Zn was obtained in Saraççeşme series (0.60 mg kg^{-1}) formed on limestone parent material. In the greenhouse, HA increased the fresh weight of maize in soils formed on both parent materials by 0.4 and 19.6%, respectively, compared to the control. Zn fertilization with HA further increased the fresh and dry yields, with 12 mg kg^{-1} performing better. Smax (maximum Zn adsorption of the soil) parameters of soils were negatively correlated with EC, P_{av}, K_{av}, organic matter, silt, clay, total N, and cation exchange capacity (CEC) of the samples. Although HA alone increases the availability of Zn in plants, HA + Zn applications should be applied together to obtain higher yields.

Introduction

The formation and composition of soils involve the combined effects of parent material, topography, vegetation, time, and climate (Weil and Brady, 2017; Yavitt, 2000). At a relatively large scale, climate and parent material are the most effective soil-forming factors to gain a specific character in soils. However, hilly topography causes a significant difference in soil properties even on similar types of parent material

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over a very short distance because of its control over water, heat, and vegetation. The other key soil-forming factor, parent material, regulates the speed of physical, chemical, and biological weathering processes in a specific environment (Delgado and Gomez, 2016). The parent material is also a primary source of nutrients necessary for plant growth and a habitat for soil microorganisms in natural soils (Trettin et al., 1999). The mineralogical composition of the parent material can influence the movement of fine soil particles and plant nutrients along the soil profile through water, weathering, growing vegetation types, and soil-dwelling organisms (Jacobs, 1998).

Marl is a rock containing clay-sized (<0.002 mm) clastic material and carbonate (calcite). Therefore, it is defined as a transitional rock material between clastic and chemical sedimentary rocks (Šestanović, 2001). Smectite, which predominates in the marl parent material classified as aridisol, is a phyllosilicate mineral characterized by a 2:1 (Si: Al) layer structure (Brown, 1980; Bailey et al., 2015). Smectite clays have a variable net negative charge stabilized by the outward sorption of metal cations (Na, Ca, Mg, and H) on the interlamellar surfaces. The smectite structure has numerous unique properties, including chemical and exchangeable ion structures and small crystal sizes. Furthermore, the structure of smectite is responsible for its highly active surface area, high cation exchange capacity, rare hydration properties, and ability to strongly modify the movement behavior of solutions (Mortland, 1970; Sawhney and Singh, 1997). Furthermore, Al^{3+}-saturated clays have strong water polarity associated with Al^{3+}, which leads to better adsorption by forming strong H-bonds with insecticides (Sawhney and Singh, 1997). Johnston et al., (2001) and Sheng et al., (2002) reported that some hydrated metal cations, such as Ca^{2+} and Mg^{2+}, surrounded by water molecules reduce ion-dipole bonds, preventing direct contact between exchangeable cations and polar functional groups. Furthermore, nonpolar organic compounds can interact with the siloxane surfaces of smectite (Laird and Fleming, 1999). Saturated clays with weakly hydrated cations, such as NH^{4+} and K^{+}, enhanced the adsorption of organic compounds by increasing the size of the adsorptive spheres between exchangeable cations. Marl parent materials have the most erodible surfaces in arid environments, including arid regions (Cerda 2002; Martinez-Mena et al., 2002).

Limestone is a sedimentary rock that accounts for approximately 10% of the sedimentary rocks found on Earth's surface. It is formed by the deposition of shells and shell fragments, or by the direct crystallization of calcium carbonate from water (Blatt and Tracy, 1996). The remaining components may include other carbonate minerals such as dolomite magnesite and aragonite (Jackson, 1997). Kaolinite, which predominates in the limestone parent material, is a weathering product of feldspars. Because kaolinite is electrically stable, its ability to adsorb ions is lower than that of other clay minerals. Kaolinite is a mineral commonly found in soil. It tends to be particularly abundant in weathered soils, such as Ultisols and Oxisols. Very few isomorphous substituents are present in the tetrahedral and/or octahedral layers of kaolinites. Most kaolinites were close to the ideal formula for $Al_2Si_2O_5(OH)_4$. The 1:1 layer had little or no permanent charge owing to the low amount of substitution. The cation exchange capacities and surface areas are typically low. Soils with a high kaolinite ratio are generally less fertile than soils dominated by 2:1 clay minerals (Milliken, 2003).

Illite is a closely related group of nonexpansive clay minerals. It is a secondary mineral precipitate and an example of phyllosilicates or layered aluminosilicates. Its structure is a 2:1 sandwich of silica tetrahedron (T)–alumina octahedron (O)–T layers (USGS, 2019). The formation of illite is generally favored under alkaline conditions and high Al and K concentrations. The cation exchange capacity (CEC) of illite is smaller than that of smectite, but higher than that of kaolinite, typically around 20-40 cmol kg^{-1} (Weil and Brady, 2017).

Different parent materials influence the morphology and mineralogical and physicochemical properties of soils under the same conditions, such as the biosphere, topography, and climate, especially in arid and semi-arid regions. Therefore, differences in soil properties are primarily related to the parent material (Washer and Collins, 1988). Zinc (Zn) content in soil ranges from 10 to 300 mg kg^{-1}, depending on the chemistry of the parent material and soil texture, organic matter, and pH (Mihaljevic, 1999), with an estimated global average of 64 mg kg^{-1} (Kabata-Pendias, 2011). Zn is the second most abundant transition metal in living organisms. Zn is critical for generative growth (seed formation) rather than vegetative growth. Zn may be important for pollen grain development, possibly by improving the phytohormone status of plants and protein synthesis (Brown et al., 1993).

Zinc deficiency in soils has been reported worldwide, especially in calcareous soils in arid and semiarid regions. Zinc deficiency in soils and crop plants occurs in almost all countries, especially in cereal-growing areas. Türkiye is among the countries with the most severely Zn-deficient soils. Since Zn deficiency is a major micronutrient deficiency in humans in Türkiye, increases in cereal Zn concentrations by Zn fertilization have significant impacts on human health. In Türkiye, Zn deficiency is a widespread problem in crops (Çakmak et al. 1999) and humans (Çavdar et al., 1983). Zinc concentrations in Turkish soils are some of the lowest ever recorded (Sillanpää, 1990). According to the results obtained from 1,511 soil samples using the Soil-DTPA test (Lindsay and Norvell, 1978), 49.8% of the cultivated soils in Türkiye were classified as Zn-deficient (Eyupogluet al., 1994). The prevalence of Zn deficiency in Turkish soils increased with increasing pH and decreasing organic matter levels in soils collected from different regions. Soils in different regions of Türkiye are generally deficient in Zn, which is reflected in the poor growth of plants under greenhouse conditions (Kacar, 1998). Zinc deficiency is common in plants growing in highly weathered acidic and calcareous soils. In the latter case, Zn deficiency was often associated with Fe deficiency (lime chlorosis). The low availability of Zn in calcareous soils with high pH is due to the adsorption of Zn to clay or $CaCO_3$ rather than the formation of poorly soluble $Zn(OH)_2$ or $ZnCO_3$ (Trehan and Sekhon, 1977). In addition, Zn uptake and translocation to the shoot are inhibited by high bicarbonate and HCO_3 concentrations (Dogar and van Hai, 1980).

The organic matter (OM) content controls the magnitude of Zn sorption in soil (Montalvo et al., 2016). Organic matter is composed of different fractions such as humic acid (HA) and fulvic acid. Therefore, the surface of organic colloids is dominated by negative charges at low soil pH (Stevenson, 1994). As the OM and soil pH increased, the amount of organic ligands and their charge density increased. It also increases Zn adsorption because of the increased stability of the organic complexes with HA as the pH increases (Boguta and Sokołowska, 2016). Humic acid, a pool of humic substances, tends to form complexes with zinc. However, the stability and solubility of the formed complexes depend on the Zn-HA stoichiometry, plant species, proportion of HA added to the soil, growth medium characteristics, and soil type (Olaetxea et al., 2018). Therefore, depending on the combination of these factors and soil management practices, crop Zn uptake can be improved or reduced (de Morais et al., 2021). Humic substances improve nutrient uptake and plant growth by adding HA and Zn to the soil (Justi, 2019). The effects of humic substances on plant tissues include stimulation of root proliferation, enhancement of H^+-ATPase activity in the cell membrane, and changes in the magnitude of nutrient uptake, assimilation, and utilization efficiency (Aguiar et al., 2013; Nardi et al., 2021). HA in soil can improve Zn nutrition (Boguta and Sokołowska, 2016) and plant growth by forming a Zn complex (De Morais et al., 2021). Organometallic complexes increase Zn content in the soil solution and Zn diffusion from the solution to the cell root surface. This is related to the complexation of Zn by organic ligands and the improvement in Zn uptake by plants (Justi et al., 2019). Dissolved Zn in the soil liquid phase is readily available to plants as the Zn concentration in solution contains a small fraction of the total Zn content of the soil (Montalvo et al., 2016). Therefore, HA is expected to contain organic radicals capable of complexing Zn into soluble forms. The use of HA effectively increased the Zn content in the solution, especially at a high soil pH (7.2) (Justi et al., 2019). HA can also buffer soil acidity. It maintains the pH within the optimum range required to provide crops with abundant nutrients, especially Zn, whose availability decreases as pH increases (Montalvo et al., 2016).

The buffering effect of HA on soil acidity is more frequent. When pH is in the alkaline range, less dissolved Zn is present in the soil, while low insoluble forms ($ZnOH^+$ and $ZnOH_2$) are formed in the soil (Alloway, 2009; Montalvo et al., 2016). HA buffers soil acidity and prevents oscillations in soil reaction (Aguiar et al., 2013; Rosa et al., 2018), and consequently promotes the formation of soluble Zn^{2+} free hydrated forms and soluble Zn-organic complexes (Montalvo et al., 2016). HA also depend on the structure-organic functional groups-function properties of HA (Nardi et al., 2021). It is linked to the type and concentration of oxygen, nitrogen and sulphur-containing functional groups in the HA structure (Aguiar et al., 2013; Zanin et al., 2019; Nardi et al., 2021; de Morais et al., 2021).

Materials and Methods

Materials

The taxnomy of the experimental soils

The characteristics of the experimental soils formed on marl (6 soils) and limestone parent materials belonging to the Aridisol order in the U.S. Soil Taxonomy are given in Table 1. Marl soils are classified as Xeric Hablocambic, Xeric Pedrocalcid and Typic Calciorthid and limestone soils are Vertic Calciorthid, Typic Paleorthid and Typic Calciorthid. The name of marl soils are Atınova, Hacıfakıl, Çatalca, Başkuyu, Kuyubaşı and Seyrantepe soil series and Limestone's soils are Saraççeşme, Tine, Karataş-1, Tuvem-1, Tuvem-1, Tuvem-2 and Karataş-2 soil series. The soil series is characterized by arid and semiarid climate.

Some physical and chemical properties of soils

Composite surface soil samples (0-20 cm depth) were brought to laboratory in plastic bags. Air-dried samples were then passed through 2 mm sieve to performe the following analysis: particle size distribution (sand, silt and clay contents) by a hydrometer method (Bouyoucus, 1951), pH and electrical conductivity (EC) in saturation paste (Richard, 1954) calcium carbonate equivalent (CCE) by a manametic method using the Scheibler calcimeter (Soil Survey Staff, 2014) organic matter by modified Walkley-Black method (Sparks, 1996), cation exchange capacity (CEC) by molar Na-Acetate saturation (Richard 1954), total nitrogen (N) by concentional Kjeldahl method (Bremner 1965), DTPA-extractable cationic microelements (Fe, Cu, Mn, Zn) (Lindsay and Norwel, 1978) including certain heavy metals (Ni, Cr, Pb and Cd) by ICP-OES (Perkin-Elmer, DV, 2100).

The physical and chemical properties of the experimental soils were presented in Table 2. The limestone soils had finer texture than the marl soils.

Electrical conductivity values ranged similarly in both parent materials. Soil organic matter contents were higher with limestone soils (1.61 - 2.69%) than the marl soils' (0.89 - 1.69%). The CCE contents of marl

Table 1. The soil taxonomy classification of the experimental soils

Soils	Soil Family	Soil Series	Parent material	Order
S1	Xeric Hablocambic	Atınova	Marl	Aridisol
S2	Xeric Hablocambic	Hacıfakıl		
S3	Xeric Hablocalcid	Çatalca		
S4	Xeric Hablocalcid	Başkuyu		
S5	Xeric Pedrocalcid	Kuyubaşı		
S6	Typit Calciorthid	Seyrantepe		
S7	Vertic Calciorthid	Saraççeşme	Limestone	
S8	Typit Paleorthid	Tine		
S9	Typit Calciorthid	Karataş-1		
S10	Vertic Calciorthid	Tüvem-1		
S11	Vertic Calciorthid	Tüvem-2		
S12	Typit Calciorthid	Karataş-2		

soils (27.41 - 43.40%) were higher than the limestone soils' (5.28 - 24.61%). The total nutrient element concentrations of soils were given in Table 3. The element concentrations were highly affected from the parent materials depending on the overal effects of soil forming factors and agricultural practices.

Properties of humic acid (HA)

Some chemical properties of HA used in the experiment are given in Table 4. Organic matter content

Table 2. Some chemical and physical properties of the experimental soils

Soil	Sand %	Silt %	Clay %	Texture Class	OM %	CEC cmol kg^{-1}	pH	CCE %	EC dS m^{-1}	P$_{av}$ kg ha^{-1}	K$_{av}$ kg ha^{-1}
S1	43.0	24.0	33.0	CL	1.28	24.2	7.54	27.4	0.782	7.84	134
S2	43.0	26.7	30.3	CL	0.89	23.9	7.50	35.6	0.716	4.66	96
S3	41.0	34.2	24.9	L	0.79	19.3	7.69	35.0	0.619	11.9	146
S4	39.0	33.5	27.6	CL	1.69	23.6	7.56	35.1	0.721	0.93	106
S5	42.2	31.5	26.3	L	1.50	20.9	7.49	43.4	0.656	4.27	158
S6	45.0	31.5	23.6	L	1.44	19.3	7.72	39.5	0.499	5.36	102
S7	26.2	38.2	35.6	CL	1.97	25.6	7.51	38.7	0.717	5.74	158
S8	29.0	35.5	35.6	CL	1.61	28.4	7.61	9.01	0.358	10.5	134
S9	23.0	38.0	39.0	CL	2.69	29.2	7.24	7.47	0.855	24.6	201
S10	42.2	26.2	31.6	CL	2.20	25.7	7.76	16.3	0.506	10.3	154
S11	26.6	37.8	35.6	CL	2.10	24.9	7.53	20.1	0.691	5.59	179
S12	40.2	32.2	27.6	CL	2.27	24.8	7.49	5.28	0.594	4.35	206

S1: Atınova soil series, S2: Hacıfakıl soil series, S3: Çatalca soil series, S4: Başkuyu soil series, S5: Kuyubaşı soil series, S6: Seyrantepe soil series, S7: Saraççeşme soil series, S8: Tine soil series, S9: Karataş-1 soil series, S10: Tüvem-1 soil series, S11: Tüvem-2 soil series, S12: Karataş-2 soil series, OM: Organic matter, CEC: Cation exchange capacity, pH: Soil reaction, CCE: Calcium carbonate equivalent, EC: Electrical conductivity, P$_{av}$: Available P_2O_5, K$_{av}$: Available K_2O, C: Clay, L: Loam

Table 3. Total concentration of some plant nutrients in the experimental soils

Soil Series	g kg^{-1}					mg kg^{-1}	
	P	Mn	N	K	Fe	Cu	Zn
S1	0.42	0.51	0.64	18.07	16.85	18.4	32.2
S2	0.43	0.95	0.45	15.04	17.94	30.7	83.1
S3	0.62	0.76	0.40	17.96	10.64	20.6	52.7
S4	0.69	0.97	0.85	11.75	12.93	35.1	96.1
S5	0.72	0.82	0.75	15.73	22.34	29.1	52.6
S6	0.52	0.9	0.72	1.211	18.06	29.8	97.0
S7	0.51	0.96	0.99	12.38	14.04	34.3	88.7
S8	0.55	0.79	0.81	10.36	12.57	22.8	66.1
S9	0.11	0.56	1.35	9.05	10.20	12.0	28.0
S10	0.17	0.91	1.10	14.72	10.20	26.4	78.7
S11	0.52	0.82	1.05	11.43	19.67	35.4	58.9
S12	0.24	0.80	1.14	8.42	10.21	29.3	68.0

S1: Atınova soil series, S2: Hacıfakıl soil series, S3: Çatalca soil series, S4: Başkuyu soil series, S5: Kuyubaşı soil series, S6: Seyrantepe soil series, S7: Saraççeşme soil series, S8: Tine soil series, S9: Karataş-1 soil series, S10: Tüvem-1 soil series, S11: Tüvem-2 soil series, S12: Karataş-2 soil series

was 43.3%, total humic acid value was 20.8% and electrical conductivity was 0.27 dS m^{-1}. The HA was highly acidic with a pH of 3.3 and its heavy metal contents were at trace amounts below the detection limits of ICP-OES.

Table 4. Chemical properties of the humic acid

Parameters	Results
Organic matter (%)	43.3
Σ Humic acid (%)	20.8
Σ Nitrogen (%)	0.17
pH	3.3
Electrical conductivity (dS m^{-1})	0.27
Σ Phosphorus (%)	1.71
Σ Potassium (mg kg^{-1})	395
Σ Calcium (mg kg^{-1})	83.5
Σ Magnesium (mg kg^{-1})	2125
Σ Iron (mg kg^{-1})	3.12
Σ Zinc (mg kg^{-1})	1.87
Σ Manganese (mg kg^{-1})	<0.02
Σ Nickel (mg kg^{-1})	<0.02
Σ Chromium (mg kg^{-1})	<0.02
Σ Lead (mg kg^{-1})	<0.02
Σ Cadmium (mg kg^{-1})	<0.02

Method

Adsorption and desorption experiments

Triplicate scoops of 2 g of the soils were equilibrated with 25 mL of Zn solutions containing of 0, 6.5 - 32.5 - 65 - 162.5 - 325 - 487.5 - 650 mg L^{-1} prepared in 0.01 M $Ca(NO_3)_2$ background solution to keep ionic strength constant. The suspentions were shaken for 24 h at 25°C on an end-over-end shaker. Then the solution phase were separated by sequential centrifugation at 3000 rpm for 10 min and filtering through Whatman 2 filter paper. Immediately after adsorption, the desorption batches were performed by equilibrating the Zn-loaded-soils with 20 mL of 0.01 $Ca(NO_3)_2$ solutions for 24 h at 25°C. Then, the Zn concentration of the supernatants obtained from the adsorption ad desorption batches were determined by ICP-OES. The amounts of adsorbed and desorbed Zn was calculated from the difference in the equilibrium and initial Zn concentrations (Alumaa, 2001). The sorption data were then tested for the comformation of linear Langmuir and Freundlich isotherms as given below:

$$\frac{Ce}{S} = \frac{1}{k\,Smax} + \frac{1}{Smax}$$

Where S amount of Zn adsorbed (mg kg^{-1}), Ce Zn concentration of the equilibrium solution (mg L^{-1}), Smax maximum Zn adsorption of the soil (mg kg^{-1}), k bonding energy coefficient (mg mL^{-1}).

The exponential forms to the Freundlich model is:

$$S= K_F\ Ce^{1/n}$$

Where K_F Freundlich constant and n constant.

In order to reduce the deviation from the Langmuir model, the total amounts of the Zn was included into the S. This improved the determination coefficient ($R^2 \geq 0.948$) of the regression line without ommiting any sorption data point at the lower-end.

Clay mineralogy

In order to carry out clay analyses in soils, carbonates, oxide minerals and organic matter were sequentially removed by the following methods: carbonates by 1 N acetate buffer (pH. 4.5-5), organic matter by 30% H_2O_2 on a hot plate, sesquioxides by citrate-bicarbonate-dithionite on a hot plate at 80°C.

The X-ray diffractograms of the soil samples were obtained to determine clay types (Whittig and Allardice, 1986). The semi-quantitative percentages of the minerals were calculated by the ratio of the individual peaks to total peak area. The results were presented in Table 5. The content of smectite clay minerals varied between 37.18% and 29.75%, kaolinite clay minerals between 59.08% and 43.87% and illite clay minerals between 18.95-11.17%. The dominance of the clays in the soils were smectite 42.86 %, kaolinite 35.71% and illite 21.43%. The smectite clays were dominant in the limestone soils whereas kaoline was dominant in the marl soils. Illite however were present at equal amounts in soils developed on both parent materials.

Table 5. Semi-quantitative clay contents (%) of the experimental soils

Soil	Dominance	Smectite	Illite	Kaolinite
S1	Smectite > Kaolinite > Illite	41.6	21.9	36.5
S2	Smectite > Kaolinite > Illite	45.4	11.5	43.2
S3	Smectite > Kaolinite > Illite	58.2	4.2	37.6
S4	Smectite > Kaolinite > Illite	55.2	8.2	36.6
S5	Kaolinite > Smectite > Illite	31.6	12.4	55.9
S6	Kaolinite > Illite > Smectite	16.2	32.7	51.0
S7	Kaolinite > Illite > Smectite	5.33	44.1	50.6
S8	Kaolinite > Illite > Smectite	20.4	20.9	58.6
S9	Kaolinite > Smectite > Illite	31.8	3.53	64.7
S10	Smectite > Kaolinite> Illite	50.6	16.4	32.9
S11	Kaolinite > Smectite > Illite	29.7	11.2	59.1
S12	Kaolinite > Smectite > Illite	37.2	18.9	43.9

S1: Atınova soil series, S2: Hacıfakıl soil series, S3: Çatalca soil series, S4: Başkuyu soil series, S5: Kuyubaşı soil series, S6: Seyrantepe soil series, S7: Saraççeşme soil series, S8: Tine soil series, S9: Karataş-1 soil series, S10: Tüvem-1n soil series, S11: Tüvem-2 soil series, S12: Karataş-2 soil series

Incubation experiments

According to the differences in adsorption isotherms (lime, composition, etc.), four soils (S2 and S4 soil series on marl parent material and S7 and S8 soil series on limestone parent material) were selected to represent both marl and limestone parent materials. Theses soils were used to test time-dependent effects of HA acid treatments on the DTPA extractability of Zn over 90 days. The experiment consisted of HA, Zn chemical fertiliser ($ZnSO_4$), humic acid+Zn chemical fertiliser, and the control (without HA and Zn) treatments in triplicates. The experiment was set up in completly-randomised design. The soil were incubated at constant moisture content in the field capacity and 25±2°C. Soil samples were taken on the 1, 7, 15, 30 and 90th days of incubation and analysed for DTPA-Zn (Lindsay and Norwel, 1978).

Greenhouse experiments

A representative soil samples were selected from each parent material by taking into account the results of adsorption/desorption and incubation experiments. The greenhouse experiment was conducted in triplicates with two soils (Başkuyu soil series (S4) on marl parent material and Tine soil series (S8) on limestone parent material), two doses of humic acid (0% and 2%) and 5 levels of $ZnSO_4$ (0 - 4 - 8 - 12 - 16 mg Zn kg^{-1}). Soil samples were passed through a 5-mesh sieve and 2 kg soil was filled into plastic pots on dry weight basis. Plant nutrient solutions were prepared and sprayed on the soil and mixed thoroughly to maintain homogeneity. Maize seeds (*Zea mays* var. *indentata*) were sown after soaking 24 hours before sowing. The plant were irrigated in field capacity. At the end of the vegetation period of 8 weeks, they were harvested just above the soil and their heights and fresh weights were determined and then washed with distilled water and dried at 65°C to a constant weight and dry weights were determined. Plant samples were then ground and homogenized to a particle size of ≤0.5 mm and prepared for analysis.

Plant analysis

Scoops of 0.5 g plant samples were digested in a microwave oven in HNO_3/H_2O_2 mixture (8/2, v/v). Then the plant nutrient concentration of the digests were analysed for plant nurients by means of ICP-OES. The total nitrogen was determined by the conventional Kjeldahl method.

Statistical analysis

Data were analyzed using SPSS 19.0 statistical software. The differences between the treatment means were tested using the Duncan's multiple range test. The underlying coherence between the investigated parameters were revealed by Pearson's correlation (SPSS 19.0, SPSS Inc. 2011). The incubation data were subjected to repeated measure analysis procedures to simultanously test the between (treatment effects) and within effects (the time-effect) and the mean separation was performed by Bonferroni test at p≤0.05.

Results

Zn adsorption isotherms

Adsorption isotherms of 12 soil samples without and with humic acid application are given in Figure 1. Zn adsorption data were characterized at acceptable

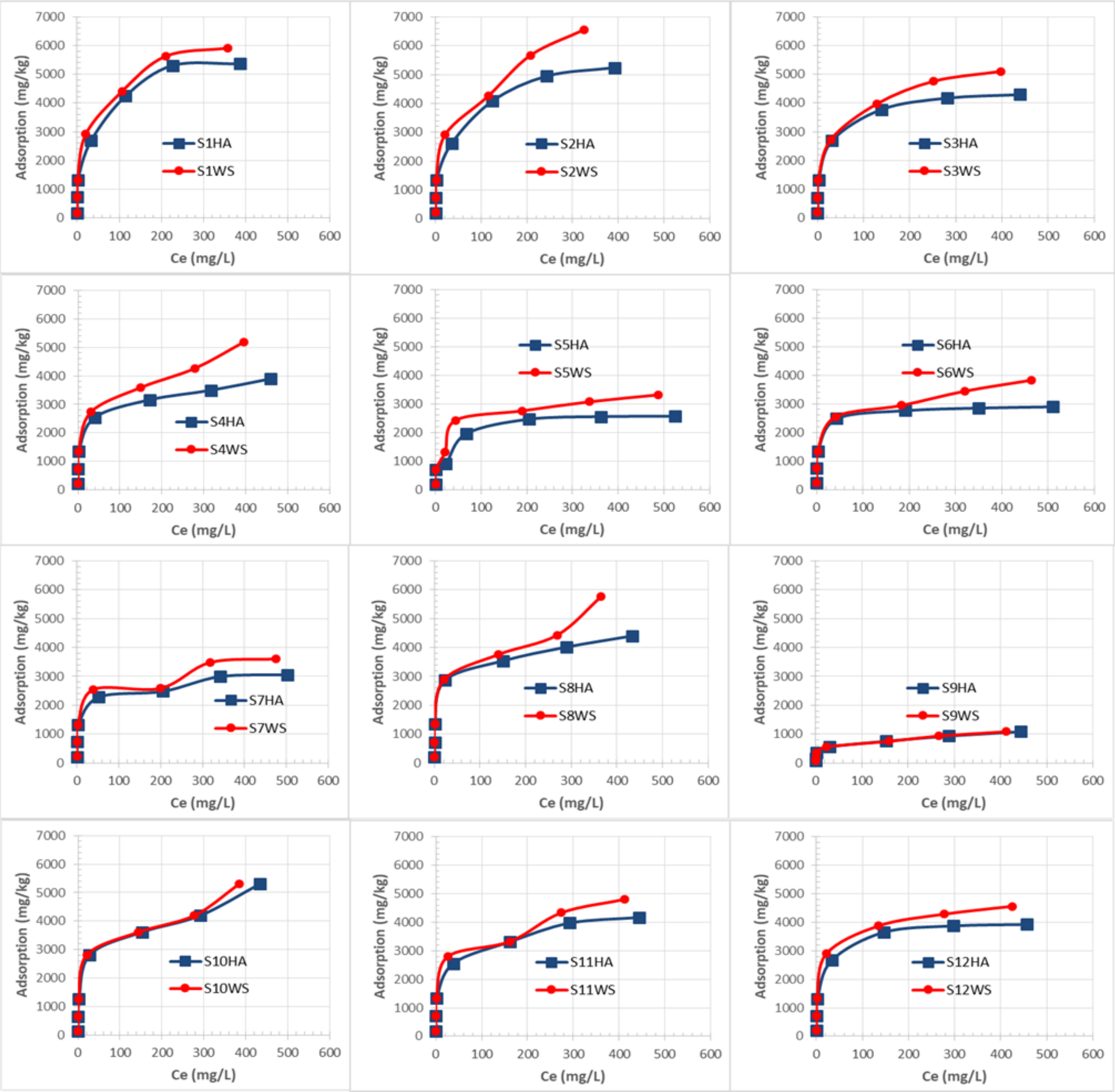

Figure 1. The adsorption isotherms of the experimental soils with and without humic acid treatment. Soils numbered 1-6 are marl soils and 7-12 are limestone soils

levels with both isotherms. The adsorption maximum values of Langmuir isotherm (b) without and with humic acid application ranged between 1042-6250 mg kg^{-1} and 1052-5555 mg kg^{-1}, respectively. The maximum adsorption values were significantly reduced by the HA treatment. This was apparent at higher Zn loadings (Figure 1). The binding energy (k) varied between 0.061-0.137 and 0.056-0.267 in soils without and with humic acid application, respectively. In the Freundlich isotherms, the adsorption power (n) varied between 0.171-0.231 and 0.225-0.384 in soils without and with humic acid treatment, respectively. K_f values varied between 326-1564 and 550-2019 in soils without and with humic acid application, respectively. The regression coefficients for the Langmuir isotherm without and with humic acid application were R^2=0.958-0.997 and R^2=0.990-0.999, while the regression coefficients for the Freundlich isotherm were R^2=0.472-968 and R^2=0.653-0.968, respectively.

Zn desorption isotherms

In general, the amount of Zn desorbed increased with increasing initial Zn concentration and HA treatment (Table 6). In the non-HA treatments in the marl parent material in the Kuyubaşı series Xeric Pedrocalcid soil (S5), 16.9% of the highest amount of Zn adsorbed was desorbed and this rate increased to 25.6% with humic acid application. In general, the apercentages of desorbed Zn remained constant after 325 mg L^{-1} Zn treatment. At the 650 mg L^{-1} initial concentration, 22.2% of the Zn amount was desorbed in the limestone parent material in the Saraççeşme series Vertic Calciorthid soil (S7), and this rate increased to 28.7% with the application of humic acid.

Incubation period

During incubation, Zn contents of the soil samples were taken on 1, 7, 15, 30 and 90 days. In the Zn incubation experiment, the difference between soils (formed on marl and limestone parent materials) and treatments (humic acid, chemical fertilizer, humic acid + chemical fertilizer application and the control) was statistically significant at 1% level (Table 7). Soil and treatment interaction was found to be significant at 1% level. The

Table 6. Desorption ratio (%) of the adsorbed Zn as a function of the initial Zn concentrations, humic acid treatments and parent material

	Init. Zn (mg L^{-1})	S1		S2		S3		S4		S5		S6	
		Humic acid treatments											
		(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)
Marl soils	6.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	32.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	65	0.34	0.63	0.91	1.10	1.94	4.67	1.31	2.40	2.00	2.27	2.22	2.42
	162.5	2.19	3.48	3.73	4.63	2.93	5.51	4.80	6.61	5.29	7.19	6.07	6.62
	325	3.76	6.57	6.82	7.96	6.96	10.1	7.26	10.2	9.88	12.1	10.1	11.0
	487.5	3.05	10.6	7.20	9.77	7.49	12.2	9.22	14.9	14.2	18.6	16.0	17.6
	650	3.18	10.6	8.49	13.5	10.3	19.4	9.54	17.2	16.9	25.6	16.1	17.6

	Init. Zn (mg L^{-1})	S7		S8		S9		S10		S11		S12	
		Humic acid treatments											
		(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)	(-)	(+)
Limestone soils	6.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	32.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	65	2.02	2.22	0.90	0.98	1.51	1.65	1.59	1.75	1.24	1.74	1.59	1.37
	162.5	5.48	6.68	3.78	5.60	5.53	6.33	4.43	5.07	4.37	6.96	5.24	5.03
	325	12.8	14.6	7.69	11.2	7.81	8.13	7.39	9.59	5.69	11.0	8.48	10.1
	487.5	20.5	26.1	11.0	14.2	15.9	18.1	11.6	15.1	10.6	15.3	13.0	15.6
	650	22.2	28.7	10.2	16.5	18.0	22.6	13.3	19.2	10.6	18.9	14.7	19.4

S1: Atınova soil series, S2: Hacıfakıl soil series, S3: Çatalca soil series, S4: Başkuyu soil series, S5: Kuyubaşı soil series, S6: Seyrantepe soil series, S7: Saraççeşme soil series, S8: Tine soil series, S9: Karataş-1 soil series, S10: Tüvem-1 soil series, S11: Tüvem-2 soil series, S12: Karataş-2 soil series

Table 7. Time-dependent DTPA-Zn concentrations (mg kg^{-1}) of the experimental

Soils	Treatments	Incubation periods (Days)					Treat.mean	Soil mean	Grand mean
		1	7	15	30	90			
S4	WS	0.08	0.09	0.19	0.09	0.12	0.12 b	0.79 A	0.68
	WS + Zn	1.17	1.51	1.30	1.58	1.13	1.34 a		
	WS + HA	0.08	0.11	1.57	0.08	0.14	0.40 b		
	WS + Zn + HA	1.17	1.42	1.27	1.49	1.20	1.31 a		
	Incubation mean	0.63	0.78	1.08	0.81	0.65			
S2	WS	0.08	0.15	0.14	0.08	0.12	0.12 b	0.70 B	
	WS + Zn	1.23	1.52	1.33	1.20	0.28	1.11 a		
	WS + HA	0.07	1.13	0.13	0.07	0.12	0.30 b		
	WS + Zn + HA	1.15	1.46	1.33	1.19	1.26	1.28 a		
	Incubation mean	0.63	1.07	0.73	0.64	0.44			
S7	WS	0.06	0.08	0.15	0.07	0.11	0.10 b	0.60 C	
	WS + Zn	1.05	1.55	1.19	1.19	1.16	1.23 a		
	WS + HA	0.06	0.10	0.13	0.06	0.10	0.09 b		
	WS + Zn + HA	1.04	1.41	1.17	0.17	1.15	0.99 a		
	Incubation mean	0.55	0.79	0.66	0.37	0.63			
S8	WS	0.06	0.08	0.19	0.06	0.12	0.10 b	0.62 C	
	WS + Zn	1.06	1.31	1.13	1.11	1.10	1.14 a		
	WS + HA	0.05	0.08	0.12	0.06	0.11	0.08 b		
	WS + Zn + HA	1.08	1.30	1.13	1.10	1.08	1.14 a		
	Incubation mean	0.56	0.69	0.64	0.58	0.60			
	Grand mean of incubation periods	0.59 b	0.83 a	0.78 a	0.60 b	0.58 b			

F_i	12.028	P_i	0.000**
F_t	375.859	P_t	0.000**
F_{pm}	8.128	P_{pm}	0.000**
$F_{t \times pm}$	2.293	$P_{t \times pm}$	0.018*

S4: Başkuyu soil series, S2: Hacıfakıl soil series, S7: Saraççeşme soil series, S8: Tine soil series, WS: Whole soil, S7: Saraççeşme soil series, i: Incubation periods, t: treatments, pm: parent material

effects of Zn on soils formed on marl and limestone parent materials due to humic acid application were insignificant. Humic acid applications increased the available Zn content compared to the control in the soil formed on marl parent material. The highest available Zn content was determined in Başkuyu series (0.79 mg kg^{-1}) formed on marl parent material, while the lowest DTPA-Zn content was obtained in Saraççeşme series (0.60 mg kg^{-1}) formed on limestone parent material. The highest Zn content of the soils (1.34 mg kg^{-1}) was increased by humic acid application in Başkuyu series formed on marl parent material, while the lowest available Zn content (0.08 mg kg^{-1}) was determined in chemical fertilizer application in Tine series formed on limestone parent material. Humic acid and humic acid + chemical fertilizer applications statistically affected at the same level the available Zn content of the soils. In addition, control and only chemical fertilizer applications had statistically increased the available Zn content of soils.

Greenhouse Experiment

Maize performance on the marl soil

The effect of humic acid and Zn applications on the fresh and dry weights of maize was found to be statistically significant at the 5% level (Table 8). Humic acid applications (HA 2%) increased the fresh weight of maize compared to the control (HA 0%). The lowest fresh and dry weights of maize for marl parent material were 58.0 and 24.3 g for the S4, 65.5 and 26.4 g for the 2% HA obtained from the control treatment, whereas the highest fresh and dry weights of maize were 82.2 and 34.9 g for the marl parent material (S4), 86.3 and 35.7 g for the 2% HA obtained from the 2% HA + 12 mg kg^{-1} Zn treatment, respectively.

Maize performance on the limestone soil

The effect of humic acid and Zn applications on the fresh and dry weights of maize was statistically significant (p≤ 5%) (Table 8). Humic acid applications increased the fresh weight of maize compared to the control. The lowest fresh and dry weights were 65.8 and 24.2 g for the limestone parent material soil (S8), 78.7 and 26.2 g for the 2% HA obtained from the control treatment; whereas the highest fresh and dry weights were 86.0 and 34.6 g for the the limestone parent material soil (S8), 84.8 and 35.0 g for the 2% HA obtained from the 2% HA + 12 mg kg^{-1} Zn treatment, respectively.

Discussion

In soil, Zn availability is controlled by the intensity of adsorption and precipitation reactions. Zn sorption increases as the soil pH are higher due to the rise of negative charges on soil colloid surfaces and the increased presence of adsorbed and precipitated Zn forms in soil (Montalvo et al., 2016). Langmuir and Freundlich adsorption models were applied in Zn adsorption study, and adsorption parameters were determined from these models (Table 9). Langmuir and Freundlich adsorption isotherms of 12 soil samples without and with humic acid application were determined. In these soils, adsorption data for applications are described at acceptable levels with both isotherms. The adsorption data of all the soils were better described by the linear Langmuir model compared with the Freundlich model. For all soils, the Langmuir isotherm showed significant results both in the control soils without humic acid and in the soils with 2% humic acid. Freundlich isotherms showed significant results only in soils with humic acid. Regarding the physical and physicochemical properties of the soil, texture (clay content), organic matter and pH were the factors that sharply influenced soil Zn availability. Organic matter content controls the magnitude of Zn sorption in soil (Montalvo et al., 2016). Organic matter is composed of different fractions, including humic acid and fulvic acids, which are organic matter pools characterized by low isoelectric points; thus, even at low soil pH levels, negative charges prevail on the surface of organic colloids (Stevenson, 1994). Soil properties can modulate Zn interaction, adsorption and precipitation with soil components, including organic matter pools (Broadley et al., 2012; Alloway, 2009; Montalvo et al., 2016). When associated with organic ligands, Zn availability for crops depends on the chemical stability, solubility and reactivity of the bonds formed between the humic matrix and the metal in the complexes formed (Boguta and Sokołowska, 2016; Rose et al., 2014).

In this study, soils formed on marl and limestone parent material showed differences in the desorption rates of adsorbed Zn at initial Zn concentrations (6.5-32.5-65-162.5-325-487.5-650 mg L^{-1}). These differences in soil properties (Table 2 and 3) may have caused differences in the effects of humic acid application on sorption isotherm parameters. As a function of initial concentrations, the soil scavange the Zn by variety of sorption/precipitation reactions that each has different irreversibility and bounding strength. The desorption rate (%) of adsorbed Zn increased as the initial Zn concentration increased in the all soil series formed on marl (smectite clay mineral) and limestone (kaolinite clay mineral) parent material (Table 6). An increase in clay content is a key factor to increase Zn adsorption in soils. However, the density of negative charges in tropical clay minerals and Al and Fe oxides is lower than those in organic colloids (Alloway, 2009; Broadley et al., 2012; Montalvo et al., 2016). Moreover, Zn availability to plants is controlled by soil type, minerals associated with clay and Fe and Al oxides, soil parent material, total Zn content, soil pH, concentrations of organic

Table 8. The effects of humic acid (HA) and Zn treatments on the fresh and dry biomasses of maize grown on the marl (S4) and limestone soil (S8) in the greenhouse experiment

Zn treatments, mg kg^{-1}	Marl parent material (S4)				Limestone parent material (S8)			
	Fresh biomass, g pot^{-1} HA (0%)	Fresh biomass, g pot^{-1} HA (2%)	Dry biomass, g pot^{-1} HA (0%)	Dry biomass, g pot^{-1} HA (2%)	Fresh biomass, g pot^{-1} HA (0%)	Fresh biomass, g pot^{-1} HA (2%)	Dry biomass, g pot^{-1} HA (0%)	Dry biomass, g pot^{-1} HA (2%)
0	58.0 e	65.5 d	24.3 d	26.4 e	65.8 d	78.7 b	24.2 d	26.2 e
4	71.2 d	74.3 c	29.2 c	29.0 d	82.2 b	83.5 a	28.4 c	28.6 d
8	78.3 b	77.5 b	32.2 b	32.1 c	82.5 b	84.7 a	31.7 b	31.9 c
12	82.2 a	86.3 a	34.9 a	35.7 a	86.0 a	84.8 a	34.6 a	35.0 a
16	75.3 c	79.5 b	33.0 b	34.1 b	75.2 c	75.5 c	31.8 b	33.5 b

Different letter in the same column indicate a significant difference at p≤0.05

Table 9. The effects of humic acid treatment on the sorption isotherm parameters

		Langmuir isotherm			Freundlich isotherm		
Soil	Treatment	S_{max} (mg kg^{-1})	k	R^2	K_F (mg kg^{-1})	1/n	R^2
S1	HA	5555	0.069	0.991	674	0.384	0.898
	WS	5882	0.090	0.990	1482	0.231	0.886
S2	HA	5263	0.066	0.990	769	0.342	0.901
	WS	6250	0.065	0.969	1564	0.222	0.905
S3	HA	4347	0.116	0.998	804	0.304	0.873
	WS	5000	0.087	0.991	1383	0.213	0.896
S4	HA	3846	0.090	0.992	883	0.256	0.890
	WS	5000	0.064	0.973	1414	0.196	0.902
S5	HA	2631	0.060	0.995	550	0.258	0.816
	WS	3333	0.061	0.993	1077	0.173	0.845
S6	HA	2857	0.267	0.999	845	0.225	0.842
	WS	3704	0.083	0.988	1259	0.174	0.886
S7	HA	3030	0.095	0.993	790	0.233	0.853
	WS	3571	0.075	0.979	1213	0.171	0.875
S8	HA	4348	0.106	0.993	795	0.311	0.892
	WS	5263	0.072	0.959	1469	0.210	0.901
S9	HA	1052	0.059	0.979	2019	0.264	0.935
	WS	1042	0.069	0.976	326	0.183	0.947
S10	HA	5000	0.056	0.970	766	0.326	0.880
	WS	5000	0.071	0.948	1249	0.227	0.872
S11	HA	4167	0.084	0.976	832	0.282	0.871
	WS	4762	0.071	0.976	1336	0.202	0.890
S12	HA	4000	0.153	0.999	840	0.283	0.888
	WS	4545	0.137	0.997	1386	0.203	0.895

S1: Atınova soil series, S2: Hacıfakıl soil series, S3: Çatalca soil series, S4: Başkuyu soil series, S5: Kuyubaşı soil series, S6: Seyrantepe soil series, S7: Saraççeşme soil series, S8: Tine soil series, S9: Karataş-1 soil series, S10: Tüvem-1 soil series, S11: Tüvem-2 soil series, S12: Karataş-2 soil series, HA: Humic acid, WS: Whole soil, Smax: Maximum Zn adsorption of the soil, k: Bonding energy coefficient, K_F: Freundlich K, n: Constant

matter, Ca, calcite, bicarbonate, and phosphate found in the soil, solution or in labile forms prone to be solubilized and to react with zinc with subsequent formation of precipitates and high-stability organometallic complexes (Alloway, 2009; Boguta and Sokołowska, 2016; Broadley et al., 2012; Montalvo et al., 2016). Smectite is one of the largest and most important classes of the phyllosilicate clay-mineral group. They are common in temperate soils and tend to dominate the cationic adsorption chemistry of these soils due to their cation exchange capacity and very high specific surface (Kloprogge and Frost, 1999). Desorption is an important property that determines the mobility of adsorbed elements or metals in contaminated areas. The amount of desorption varies depending on the nature of the adsorption event, i.e. whether the binding is by physical, electrostatic bonds or covalent bonds. Physically adsorbed cations are usually capable of being readily replaced or desorbed by other cations present in the soil solution. On the other hand, ions or molecules bound by covalent bonds are not easily desorbed because they bind to the adsorbent with high energy and usually released back to the solution phase with the complete breakdown of the adsorbent. In soil 9, none of the Zn absorbed at the lowest concentration was desorbed. At the 650 mg L^{-1} initial concentration, 18.0% of the Zn amount was desorbed in the limestone parent material in the Karataş-1 series Typit Calciorthid soil family (S9) in the Aridisol and this rate increased to 22.6% with the application of humic acid. The amount of Zn that could be desorbed or replaced by Ca was calculated from the adsorbed Zn at each initial concentration applied. Accordingly, at the lowest concentrations applied, almost none of the absorbed Zn was desorbed. The amount of absorbed Zn was almost not desorbed at the lowest concentrations applied (6.5 - 32.5 - 65 mg L^{-1}). This shows that especially Zn adsorbs with a high energy and is retained with a high energy even at high concentrations. The other point is that the adsorption or precipitation mechanisms of Zn cause the release of 2 H$^+$ ion on a stochiomeric base (Uygur and Rimmer, 2000). This reduces the pH of equilibrium solution below 6.5, in turn, the physisorption processes take place that increase the desorption rate. In addition, humic acid application showed that desorption was higher than the application without humic acid because of chelation reaction between the HA and Zn and possible blockage of specific sorption site on the colloidal surfaceses (Spark et al., 1997). This suggests that Zn may be highly immobilized in these soils, especially at high concentrations. The fact that Zn is not desorbed at low concentrations indicates that Zn deficiency is a key fact in soils with poor organic matter content and high pH under insufficient fertilization practices, to limit plant performance. The release of trace elements over time (desorption rate) is important for plant nutrition. In general, desorption of soils increased Zn mobility due to humic acid application.

Bivariate Pearson correlations coefficients between the soil properties and the sorption parameters were given in Table 10. Smax parameter was negatively correlated with soil EC, P_{av}, K_{av}, OM, silt, clay, total N and CEC. The properties negatively correlated with Smax indicates that the property function a reduced sorption site, co-input of Zn by previously applied agricultural practices and chelate with it. The parameters such as pH, CCE, sand, total K, P, Fe, Zn, Cu, Mn and CEC positively correlated with has a primary rol over accumulation or fixation of Zn in the soil. Regarding the soil's physical and physicochemical properties, the texture (clay content), organic matter and pH were the factors that sharply influenced soil Zn availability. Soil properties are capable of modulating Zn interaction, adsorption, and precipitation with soil components, including organic matter pools (Alloway, 2009; Broadley et al., 2012; Montalvo et al., 2016). When associated with organic ligands, the Zn availability to crops relies on the chemical stability, solubility, and reactivity of the bonds formed between the humic matrix and the metal in the complexes formed. Generally, Fe and Al oxides have a larger and stronger sorption sites due to a chemisorption process take place on their surface, can coat relatively lesser soil component such as carbonates and sand sized fractions (Uygur and Rimmer, 2000). Smax parameter was significantly and positively correlated with K_F (0.940, $p < 0.01$) and n (0.755, −0.47, $p < 0.01$) values.

The DTPA-Zn measured troughout the entire incubation period of 90-day are given in Table 7. The availability of plant nutrients during the growth period ensures a good performance along with a desirable yield and yield quality. The release of trace elements retained by sorption sites is required to sustainably meet the trace element needs of the plant (Uygur and Rimmer, 2000). In this study, HA+Zn application increased the DTPA-Zn concentration of the soils compared to only HA application in all soil series formed on marl (smectite clay mineral) and limestone (kaolinite clay mineral) parent material during the incubation period. When Zn was mixed with HA, free sulfates were

Table 10. Bivariate Pearson correlations between the soil properties and the sorption parameters

Parameters	Smax	k	K_F	n
k	0.110			
K_F	0.940^{**}	0.206		
n	0.755^{**}	0.154	0.514	
EC (dS m^{-1})	-0.301	-0.136	-0.413	-0.114
pH	0.559	0.038	0.628^{*}	0.314
CCE (%)	0.137	-0.408	0.259	-0.323
P_{av} (kg ha^{-1})	-0.584^{*}	-0.107	-0.761^{**}	0.017
K_{av} (kg ha^{-1})	-0.541	0.421	-0.551	-0.171
OM (%)	-0.619^{*}	0.138	-0.629^{*}	-0.300
Sand (%)	0.526	0.213	0.530	0.339
Silt (%)	-0.582^{*}	-0.101	-0.439	-0.631^{*}
Clay (%)	-0.252	-0.252	-0.397	0.080
ΣN (%)	-0.620^{*}	0.139	-0.629^{*}	-0.300
ΣK (%)	0.459	-0.240	0.359	0.410
ΣP (%)	0.277	-0.338	0.449	-0.267
ΣFe (%)	0.117	-0.373	0.196	-0.255
ΣZn (mg kg^{-1})	0.279	-0.085	0.453	-0.202
ΣCu (mg kg^{-1})	0.313	-0.076	0.504	-0.248
ΣMn (mg kg^{-1})	0.250	-0.219	0.404	-0.223
CEC (cmol kg^{-1})	-0.210	-0.069	-0.352	0.149

Σ: Total, k: Bonding energy coefficient, K_F: Freundlich K, n: Constant, EC: Electrical conductivity, pH: Soil reaction in saturation paste, CCE: Calcium carbonate equivalent, P_{av}: Available P_2O_5, K_{av}: Available K_2O, OM: Organic matter, CEC: Cation exchange capacity retained in the complex formed. In addition, bonds related to sulfone groups were formed, which are indicative of the interaction of HA with $ZnSO_4$ and the synthesis of Zn-HA complexes. Sulfur groups present in the HA+$ZnSO_4$ mixture are indicative of Zn-HA complexation. This is probably due to the presence of functional groups containing oxygen, nitrogen and sulfur on the HA surface (Aguiar et al., 2013; Nardi et al., 2021; Zanin et al., 2019). There was no statistical difference between Zn treatment and Zn+HA, treatment in terms of DTPA-Zn concentrations of soils in both soil series (Başkuyu, Hacıfakıl, Saraççeşme and Tine) regardless the parent material during the incubation period. The DTPA-Zn concentration of the soils was higher in the soil series formed in the marl parent material dominated by smectite clay mineral than in the limestone parent material, especially in Başkuyu soil series. The mechanisms and processes of Zn interaction with HA include ionic or uncoordinated forms, undefined complexes, bidentate chelates and bidentate bridging coordination bonds (Boguta and Sokołowska, 2016). The interaction of organic ligands with Zn is beneficial for providing Zn to plants, considering that free Zn ions are prone to react with soil constituents through sorption and precipitation, which are the main processes regulating Zn availability in soil (Montalvo et al., 2016; Olaetxea et al., 2018). Organic matter is also a source of soluble organic compounds that can bind micronutrients through the formation of soluble organo-metal complexes (Wang and Xing, 2005). In this study, S4, which had a higher Zn content than S2, S7 and S8, presented a higher soil Zn-DTPA content in the Başkuyu soil series formed on the marl parent material with smectite clay mineral during the incubation period.

The effects of humic acid (HA) and Zn treatments on the fresh and dry biomasses of maize grown on the marl (S4) and limestone soil (S8) in the greenhouse experiment were given in Table 8. The highest fresh and dry weight of maize was 86.3 and 35.7 g from 2% HA+12 mg kg^{-1} Zn application in the Başkuyu soil series formed on the marl parent material with smectite clay mineral, respectively. Humic acid applications in soil formed on marl (smectite clay mineral) and limestone (kaolinite clay mineral) parent material increased the fresh weight of maize compared to the control. Humic substances are formed by the chemical and biological breakdown of plant and animal residues and provide an important source of organic carbon in soil. The most prominent biostimulant is humic acid, which has direct and indirect effects on the morpho-physiological growth of plants (Peña-Méndez et al., 2005). HA is mainly derived from humic substances and the final decomposed material contains 60% of the organic matter in the soil (Muscolo et al., 2013). On the other hand, application of HA to soil not only improves various soil properties (such as structural stability, biological activity and affecting soil pH), but also promotes better root development, water holding capacity, carbon sequestration, cation exchange capacity and nutrient availability in the rhizosphere (Gümüş and Şeker, 2015). Solution cations have an influence on the rate and amount of HA sorbed onto smectite. The adsorption of HA by mineral surfaces is mostly influenced by solution pH, ionic strength and the type of exchangeable cations. These factors also influence the structure conformation of HA (Essington, 2015). HA and clay complexes contribute to soil structure and water holding capacity and play an important role in the cycling of various nutrients and pollutants by taking part in reductive and oxidative reactions (Sparks, 2003). The presence of Ca^{2+} improves the binding between the mineral surface and HA. Ca^{2+} is more effective than K^+ in eliminating the repulsive charges between the smectite surface and weathered humates and fulvates. Furthermore, the Ca^{2+} ions reduce the HA solubility (Li et

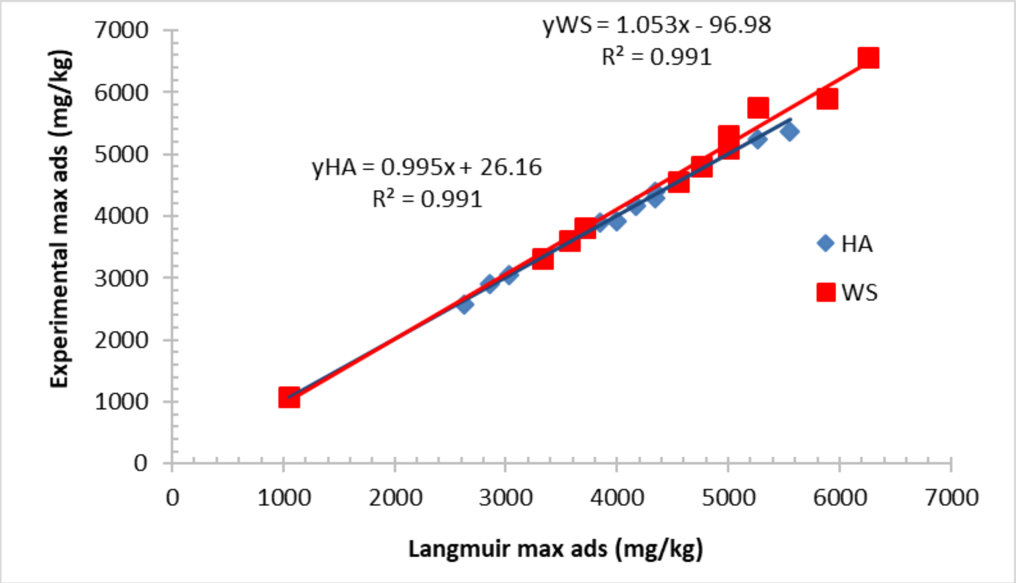

Figure 2. Scatter diagram for the experimental max adsorption vs. predicted ones with (HA) and without (WS) humic acid (HA) treatment

al., 2004) by bridging clay and surfaces. This infact further decreases the efficiency of potentially high energy sites for Zn sorption by changing the nature of colloidal surfaces. Therefore, higher calcium carbonate containing Başkuyu soil (S4, 35.1%) had higher DTPA-Zn in overall than the Tine soil series (S8, 9.01%) due to apparent drawback the effect of excessive soil carbonates in the soil. Similarly, the heavy fraction of soil organic corbon such as HA accumulated twice as much SOC at the $CaCO_3$-bearing site, in Ca prevalent soils than the soils with less Ca (Rowley et al., 2021).

Conclusion

It was determined that the clay types were different in 12 different soil samples with two different parent materials belonging to the Arisol order. While the dominant clay mineral in the soils formed on marl parent material was smectite, the dominant clay mineral in the soils formed on limestone parent material was kaolinite. Because of adsorption analysis, the parameters of Langmuir and Freundlich models were determined. Langmuir model was found to be more suitable for Zn adsorption than Freundlich model. There was no significant difference between Langmuir and Freundlich isotherm parameters in soils formed on marl and limestone parent material with and without humic acid. The desorption rate (%) of adsorbed Zn increased as the initial Zn concentration increased in the all soil series formed on marl (smectite clay mineral) and limestone (kaolinite clay mineral) parent material. In the incubation study, humic acid applications increased the available Zn content in soils formed on both parent materials compared to the control. Humic acid applications increased the fresh weight of maize compared to the control. The highest available Zn was determined in Başkuyu series (0.79 mg kg^{-1}) formed on marl parent material, while the lowest available Zn was obtained in Saraççeşme series (0.60 mg kg^{-1}) formed on limestone parent material. In the greenhouse experiment, humic acid applications increased the fresh weight of maize in soils formed on both parent materials by 0.4 and 19.6% compared to to the control. Zn fertilization with HA further increased the fresh and dry yield that 12 mg kg^{-1} performed better. The lowest wet and dry weight values of maize were obtained from the control in the soil formed on marl parent material, while the highest wet and dry weight values were obtained from 2% humic acid + 12 mg kg^{-1} Zn treatment. Smax (maximum Zn adsorption of the soil) parameter of soils were negatively correlated with EC, P_{av}, K_{av}, organic matter, silt, clay, total N and cation exchange capacity (CEC) of the samples. Although humic acid alone increases the plant availability of Zn, HA + Zn applications should be applied together in order to obtain higher yields. It is necessary to improve the results obtained by conducting studies for soils with different parent material and soil families.

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Author Contribution

M.K.: Conceptualization, investigation, methodology, validation, software, validation, formal analysis, investigation, resources, data curation, writing-original draft preparation, writing-review and editing, visualization, supervision, statistical analysis, project administration. **G.D. and N.G.:** methodology, formal analysis. **S.U., V.U. and M.O.A.:** Methodology, validation, software, validation, formal analysis, investigation, resources, data curation, writing-original draft preparation, writing-review and editing, visualization, supervision, statistical analysis. **Z.D.:** Writing-original draft preparation, writing-review and editing, visualization, statistical analysis, supervision, resources, data curation, all authors reviewed the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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RESEARCH PAPER

Development of yield prediction model for wheat by using AquaCrop model with different nitrogen dose applications in Central Anatolia Region (semi arid) conditions

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Abstract

In this study, yield prediction was made for Tosunbey and Bayraktar bread wheat varieties under rainfall conditions and 4 different fertilizer ratios with AquaCrop model, one of the plant growth models. In this experiment conducted at Haymana Ikizce Research Farm, actual field observations and model predicted grain yield, biomass, and green area coverage ratio were evaluated. Mean deviation (α), standard error (RMSE), and model efficiency coefficient (E) tests were used to determine the performance of the model. The AquaCrop model was calibrated in the first year and validated based on observational data collected in the first and second years of the experiment, respectively. Based on the results obtained, it was observed that the AquaCrop model simulated grain yield at different levels of nitrogen fertilizer applications with higher precision for Bayraktar variety. For Bayraktar variety, grain yield E = 0.93 in the first year and 0.99 in the second year for grain yield, and E = 0.83 in the first year and 0.98 in the second year for biomass, indicating excellent agreement between model and observation was found. In Tosunbey variety, first-year grain yield E=0.66 and 2nd year grain yield 0.76 were found. The 2nd year RMSE value for grain yield of Bayraktar variety was 0.266, and the 2nd year RMSE value for the grain yield of Tosunbey variety was 0.664 and found to be statistically compatible. Grain yield, biomass, and percent cover (CC) values obtained from the model were found to be highly consistent with field observations.

Introduction

Determining the effects of soil, plant, and climate components on plant growth and yield is possible with plant simulation models. While these models serve the purpose of comparing potential and actual yields, they can also predict how far yields can be increased. One of the most important advantages of the models is that they save time and are also economical. It is also possible with models to analyze the extent and how the atmospheric parameters and soil will affect plant development, and to determine the most appropriate times for fertilization, spraying, and other activities. Many researchers in the world and our country use "Plant Growth Models" to examine the effects of climate factors on crops. These models are used to solve a wide range of problems encountered during plant development, to predict yields, and to realize decision mechanisms to ensure the continuity of maximum yield (Korkmaz et al., 2000; Köksal and Kanber, 2003).

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The AquaCrop model can be used by FAO as a planning tool in field studies. Particularly useful topics include understanding plant response to environmental conditions, estimating irrigation water requirements, comparing actual yield values with achievable yield values for a field or a whole region, identifying factors limiting crop production and water productivity, developing methods to maximize water productivity under water shortage, irrigation strategies (full irrigation, deficit irrigation, etc.), plant and land practices (planting date, variety selection, fertilization, organic mulch, etc.) (Raes et al., 2009).

Guo et al. (2020) evaluated the performance of the Aquacrop model for different irrigation depths and different nitrogen applications for maize crops. They estimated the performance of the model based on grain yield, biomass and plant coverage ratios and compared it with actual field values.

A field experiment was conducted with three nitrogen levels of 0, 150 and 300 kg N ha^{-1} (N_1, N_2 and N_3) with four irrigation depths corresponding to 60, 80, 100 and 120 cm of soil water. The AquaCrop model was calibrated in maize planted as a complete block according to the randomized plots experimental design with three replications between 2002 and 2004 and then validated based on field data collected from the first and second years of the study, respectively. Based on the results obtained, the AquaCrop model simulated the grain yield of maize with high accuracy under different levels of nitrogen fertiliser and irrigation depths (Ebrahimi et al., 2015).

Abedinpour et al. (2012) calibrated the model using different water regimes and nitrogen applications using two years (2009-2010) of maize data. In order to determine the performance of the model, they used the model efficiency (E), coefficient of determination (R2), standard error (RMSE), and mean deviation error (MDE) tests. The most accurate prediction was obtained from the scenario with full irrigation at field capacity (W4) and 150 kg ha^{-1} (N3) nitrogen application, while the lowest prediction was obtained from the scenario with no nitrogen and irrigation water application. The AquaCrop model was predicted with acceptable accuracy for all scenarios created in this study.

In another study, Abedinpour (2021) carried out a comparison between DSSAT-CERES and AquaCrop models to simulate wheat growth under different irrigation and nitrogen levels on the basis of accurate prediction. For this purpose, four irrigation treatments (rainfall-based, irrigation at 50% and 75% of field capacity and 100% irrigation) were considered as the main subject and the experiment was conducted with three nitrogen fertilizer levels (no fertilizer, 100 kg Nha $^{-1}$ and 200 kg N ha^{-1}) as sub-main subjects. Model efficiency (E), Wilmott fit index (d), Root Mean Square Error (RMSE) and Normalized Root Mean Square Error (NRMSE) were used to test model performances. The AquaCrop model was calibrated to simulate grain and biomass yields with prediction error statistics of $0.87 < E < 0.90$, $0.24 < RMSE < 0$. The DSSAT-CERES model was calibrated and its performance was found to be $0.88 < E < 0.93$, $0.92 < d < 0.96$, $0.19 < RMSE < 0.34$ t ha $^{-1}$ and $5.7 < NRMSE < 5.8$, then -1, $6 < NRMSE < 7.2\%$ and $0.90 < d < 0.93$, respectively.

In general, the simulation results of the DSSAT model were relatively more accurate than those of the AquaCrop model. However, considering that the data required for the DSSAT model would be difficult to obtain in developing and undeveloped countries, the Aqucrop model was considered to be more advantageous because it makes accurate calculations in less time using less input data.

Saab et al. (2015) compared the performance of AquaCrop and Cropsyst to simulate barley growth in a study conducted in Southern Italy. In this study, under three water treatments (full irrigation, 50% irrigation and sprinkler) and two nitrogen levels (high and low), in a 3-year study (2006-2008), they calibrated in the first year and validated in the following two years. Accordingly, they concluded that AquaCrop was superior to CropSyst. In terms of biomass, they found AquaCrop RMSE (0.09 to 0.15) lower than CropSyst (0.15 to 0.17). Similarly, in the case of yield, AquaCrop had a lower RMSE value than Cropsyst (from 0.16 to 0.23). Similarly, in the case of yield, AquaCrop had a lower RMSE value than Cropsyst (from 0.16 to 0.23).

Ghanbbari and Tavassoli (2013) simulated the effect of different irrigation and fertilisation practices on yield with AquaCrop in their study conducted in Iran. The researchers reported that the model predicted cover area percentage, biomass and grain yield well, but could not simulate water use efficiency.

Zhang et al. (2013) evaluated the performance of the FAO-AquaCrop model for winter wheat in the southern Loess Plateau of China. In this study, data obtained from experimental fields between 2004 and 2011 were used to estimate biomass, percent vegetation cover, soil water content and grain yield under non-aqueous conditions and to calibrate and validate the model. In general, the model predicted percent cover and yield better than biomass and soil water content. The results showed that AquaCrop is able to simulate winter wheat under water-free conditions. It is concluded that more progress is needed by applying different fertilisation and irrigation levels for this region.

In this study, the Aquacrop model was used to plant and observe 2 wheat varieties at different fertilizer ratios and the yield predictions of the model were compared with actual field trials. AquaCrop uses atmospheric, plant, soil, and management (irrigation, fertilisation, etc.) as inputs to estimate crop water consumption and yield. The model separates transpiration from the plant and evaporation from the soil in the estimation of plant water consumption and uses the percent cover (CC) parameter instead of leaf area index (LAI) to simulate plant growth.

Material and Methods

Description of the Research Site

The experiment was conducted at the Research and Application Farm of the Central Research Institute of Field Crops Directorate İkizce/Haymana. The experiment area is between 39' 12''- 43' 6'' north latitude and 35' 58'' - 37' 44'' east longitude. The experiment area is located in the south of Ankara province, within the borders of Haymana district center, at the 22nd km of Haymana-Gölbaşı State Highway, with Topaklı village in the northwest and İkizce village in the southwest of the farm and covers an area of 968.3 ha. The slope of the land varies between 2-15 % (Dengiz and Yüksel, 2001). Considering the topographical characteristics of the location of the research area, the altitude is between 820-1470 m and the altitude of the experiment area is 1069 m (Figure 1).

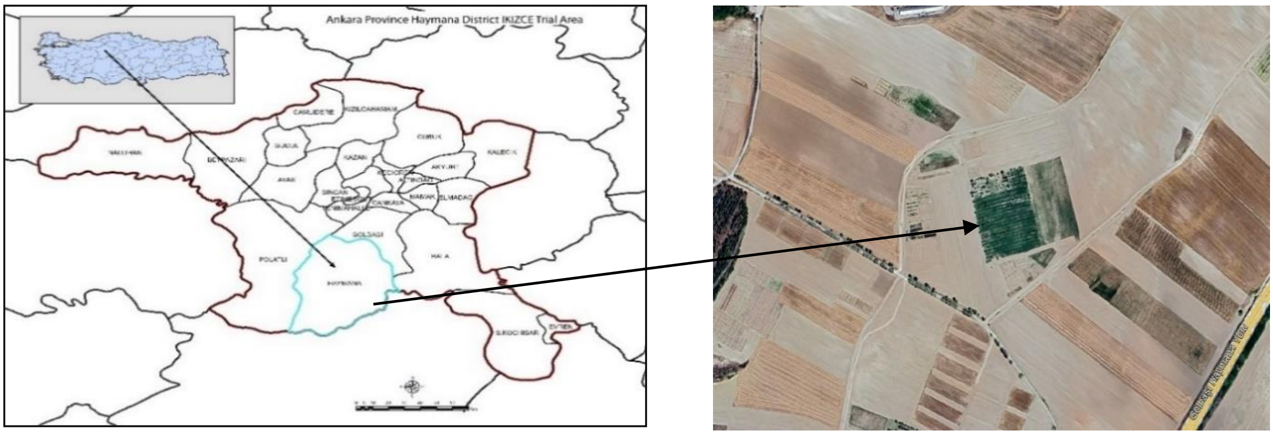


Figure 1. Experimental area (İkizce-Haymana/ANKARA)

Climatic Characteristics of The Research Site

Haymana İkizce Research Farm is located in a region where the typical steppe climate of Central Anatolia prevails in terms of climatic characteristics. Summers are hot and dry and winters are cold (Table 1).

Table 1. Climatic data of the experiment area

	Average of Monthly Rainfall Total (mm)			Average monthly temperature (°C)			Average monthly min. temperature (°C)			Average monthly max. temperature (°C)		
	2017-2018	2018-2019	Long Years mean	2017-2018	2018-2019	Long Years mean	2017-2018	2018-2019	Long Years mean	2017-2018	2018-2019	Long Years mean
October	9.8	68.4	27.9	9.9	12.1	11.9	5	6.4	0.2	16.5	19.3	25.7
Kasım	11.2	15.4	31.7	4.7	6.5	5.6	0.2	1.9	-7.5	10.7	12.2	19.4
Aralık	26.2	53	44.1	2.1	1	0.8	-1.5	-1.3	-10.1	7.3	4	14.9
January	19.2	36.2	39.7	0.9	-0.8	-1.2	-1.8	-3.3	-13.8	4.3	2.3	11.7
February	39.6	36.4	35.1	4.1	2.2	1.1	-0.2	-1.4	-12.3	10	7.3	13.6
March	74.6	20.6	39.1	7.9	4.7	5.1	3.2	-0.9	-8.3	13.3	11.2	20.5
April	2.6	23.4	41.9	12.2	7.9	9.5	4.6	2.5	-2.2	19.9	14	23.3
May	122.8	3.8	51.8	15.3	15.1	14.3	9.8	8.5	2.4	22.2	21.9	27.5
June	27	15	34.3	18.7	18.7	18.5	11.9	13.2	6.9	25.9	25.9	31.6
July	4.2	7.2	13.5	22	17.8	22.2	14.7	12.5	9.7	29	26	35.8

Wheat Varieties Used in the Study and Their Characteristics

In the research area, an experiment design was established by using Tosunbey and Bayraktar bread wheat varieties.

Agricultural Characteristics:

BAYRAKTAR 2000

Institute: The Field Crops Central of Research Institute

Grain Yield (kg/da): 350-400

1. Alternative developmental nature and early,
2. Resistant to cold, drought and lodging,
3. High reaction to fertilizer,
4. Evergreen and good threshing ability

(https://arastirma.tarimorman.gov.tr/tarlabitkileri/Belgeler/cesit_katalogu.pdf)

TOSUNBEY

Institute: The Field Crops Central of Research Institute

Grain Yield (kg/da): 300-400

1. Alternative developmental nature,
2. Good cold resistance,

3. Good drought and lodging resistance,
4. Good reaction to fertilizer.

(https://arastirma.tarimorman.gov.tr/tarlabitkileri/Belgeler/cesit_katalogu.pdf)

Establishment of Experimental Design and Nitrogen Applications

Two varieties of bread wheat were planted in the experiment area in 2017-2018 and 2018-2019. These are the Tosunbey and Bayraktar varieties. On 24.10.2017, the first year planting took place and on 11.10.2018, the second year planting took place. Sowing was done in two blocks and each block was treated with 4 different Nitrogen ratios, including two different variety controls. Nitrogen Dose Applications in the experiment N_0: Sowings, one of which is control plot (without fertilizer), N_{12}: Normal fertiliser application (12 kg/da), N_6: 50% reduced fertiliser application (6 kg/da.), N_{18}: 50% increased fertiliser application (18 kg/da.) was applied. Parcel length was calculated as 26.50 m. and parcel width as 9.45 m. Total parcel area is calculated as 26.5 m* 9.45 m = 250 m^2. Plot spacing was determined as 5 m. Parcel length was calculated as 30.0 m and parcel width as 3.0 m. Total parcel area is calculated as 30.0 m* 3.0 m = 90 m^2. Plot spacing was determined as 1.5 m (Figure 2). Physical analyses of soil samples taken from the project area at 0-30, 30-60, 60-90 cm depths are given in Table 5. These data were entered into the "Soil characteristics" section of the programme (Table 2).

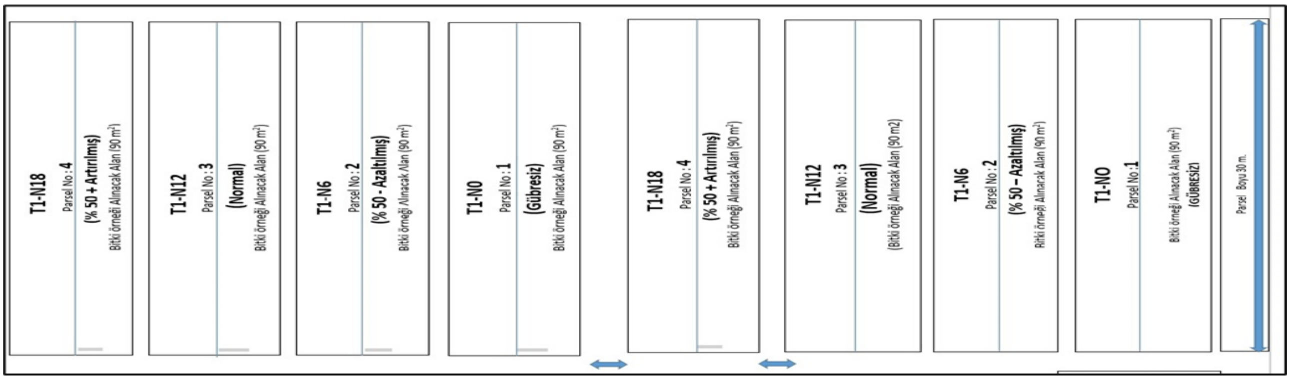


Figure 2. Experiment pattern

Table 2. Soil physical analysis results of the experiment area

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	Texture	Field Capacity (%)	Wilt Point (%)	Volume Weight (g cm^{-3})	Hydraulic Conductivity (cm h^{-1})
0-30	15.8	41.5	42.7	SİC	32.90	14.76	1.22	0.05
30-60	9.8	37.7	52.5	C	38.55	18.42	1.17	0.76
60-90	10.8	33.9	55.3	C	39.08	18.84	1.17	0.71

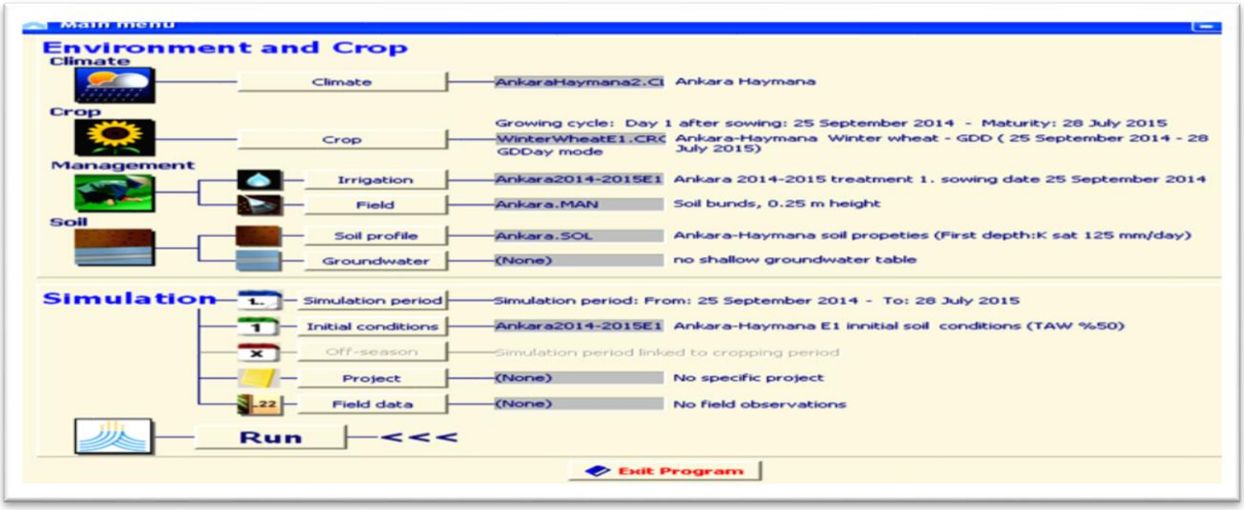
AquaCrop Plant Simulation Model

This study used the AquaCrop model, a plant-climate model developed by the Food and Agriculture Organization of the United Nations (FAO). The scientific basis of this model was has been described by Steduto et al. (2009), Raes et al. (2009) and Hsiao et al. (2009). AquaCrop is a water-oriented model developed to see the response of plants to water and its effect on yield and requires fewer parameters and input data than other simulation models. Most researchers around the world prefer the AquaCrop model because it is simpler and more reliable than other models. In this study, version 5.0 of the AquaCrop Model from the FAO official website (http://www.fao.org/nr/water/aquacrop.html) was downloaded and run (Figure 3).

After running the AquaCrop Model, there are sections on the main menu screen where environmental and plant related data are entered, simulation is performed and project and field data are entered (Figure 4).

It consists of climatic data, soil and plant characteristics and input data related to plant management practices that help define the environment in which the plant will be grown. Inputs are stored in climate, crop, soil and management files and can be easily modified by the user (Raes et al., 2011).

The AquaCrop model incorporates water balance from the soil component; plant growth, development and yield process from the plant component; thermal



Climate: AnkaraHaymana2.Cl — Ankara Haymana

Crop: WinterWheatE1.CRC — GDDay mode — Growing cycle: Day 1 after sowing: 25 September 2014 - Maturity: 28 July 2015 — Ankara-Haymana Winter wheat - GDD (25 September 2014 - 28 July 2015)

Irrigation: Ankara2014-2015E1 — Ankara 2014-2015 treatment 1. sowing date 25 September 2014

Field: Ankara.MAN — Soil bunds, 0.25 m height

Soil profile: Ankara.SOL — Ankara-Haymana soil propeties (First depth:K sat 125 mm/day)

Groundwater: (None) — no shallow groundwater table

Simulation period: Simulation period: From: 25 September 2014 - To: 28 July 2015

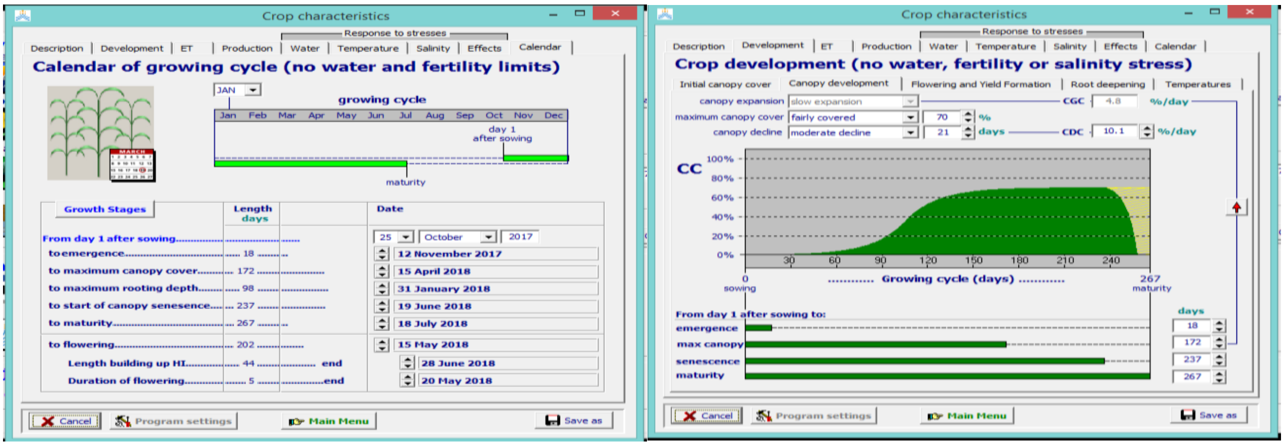
Initial conditions: Ankara2014-2015E1 — Ankara-Haymana E1 innitial soil conditions (TAW %50)

Off-season: Simulation period linked to cropping period

Project: (None) — No specific project

Field data: (None) — No field observations

Figure 3. AquaCrop 5.0 software boot window



Calendar of growing cycle (no water and fertility limits)

JAN

Growth Stages	Length days		Date
From day 1 after sowing			25 October 2017
to emergence	18		12 November 2017
to maximum canopy cover	172		15 April 2018
to maximum rooting depth	98		31 January 2018
to start of canopy senesence	237		19 June 2018
to maturity	267		18 July 2018
to flowering	202		15 May 2018
Length building up HI	44	end	28 June 2018
Duration of flowering	5	end	20 May 2018

Crop development (no water, fertility or salinity stress)

canopy expansion: slow expansion — CGC 4.8 %/day

maximum canopy cover: fairly covered — 70 %

canopy decline: moderate decline — 21 days — CDC 10.1 %/day

From day 1 after sowing to:	days
emergence	18
max canopy	172
senescence	237
maturity	267

Figure 4. Inputting the plant phenological values of the Aqucrop program into the program, Canopy cover (CC%) calculations, running the simulation

balance, evaporation, precipitation and CO_2 concentration from the atmosphere component (Raes et al., 2009). It also incorporates soil-plant-atmosphere components as well as agricultural activities such as irrigation and fertilisation that affect these components and yield (Raes et al., 2009). As given in the AquaCrop application guide (Raes et al., 2009), some parameters are conservative and environmental and climatic conditions do not affect the change of these parameters. These parameters include vegetation cover (Figure 5) and the coefficient of vegetation decline, the plant coefficient for transpiration when the surface is completely covered by vegetation, water use efficiency or water productivity (WP) for biomass, and the threshold of soil water content at a level that inhibits leaf growth, stomatal conductance and accelerates yellowing of the vegetation surface. These parameters are assumed to be acceptable over a wide range except in very specific cases. The fixed parameters used in the simulation for the Aquacrop model are given in Table 3.

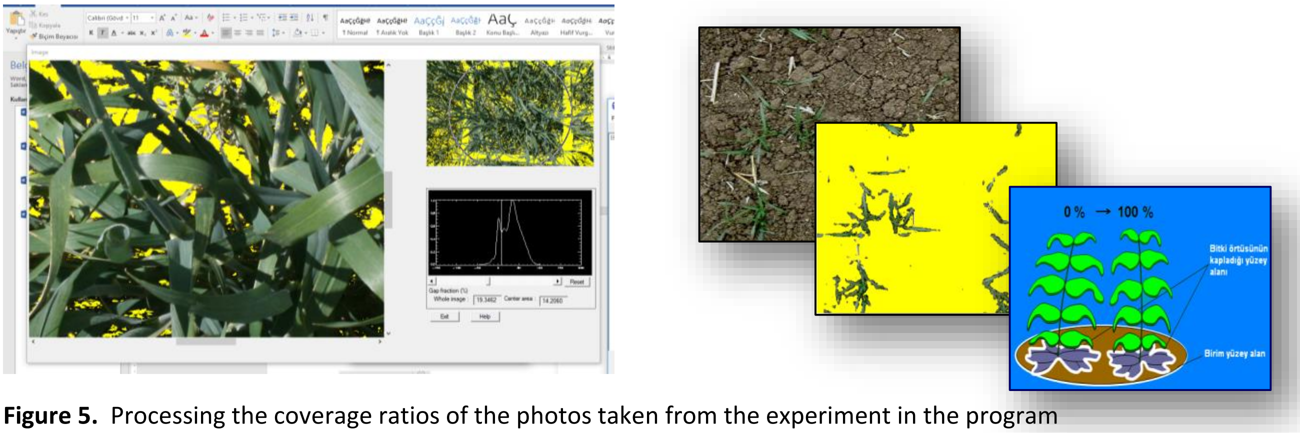


Figure 5. Processing the coverage ratios of the photos taken from the experiment in the program

Table 3. Fixed (conservative) parameters used in simulation (Raes et al., 2009)

Describing	Value	Unit and Description
The temperature at which the yield begins to decrease	26	*C
Covering (CCo) at 90% output	7.16	cm^2
Cover development coefficient (CGC)	2.4	Coverage development rate in each GDD %
Maximum cover percentage (CC%)	95	A function of plant density %
Plant coefficient for transpiration at 100% cover level	1.10	Full coverage transpiration for relative ETo
Cover % reduction coefficient (CDC) in the dough setting period	0.39	Relative little % in CCx per CC reduction per GDD
Water efficiency	15	g (biomass) m^{-2}, atmos. A function of CO_2
Leaf growth threshold p-top	0.20	A function of soil water content
Leaf growth threshold p-sub	0.65	The point at which leaf growth completely stops
Leaf growth stress coefficient slope shape	5.0	Medium convex curve
Stoma conductivity threshold p-top	0.65	The point where the stomata begin to close
Stoma stress coefficient slope shape	2.5	Highly convex curve
Yellowing stress coefficient p-top	0.70	Below this value, early yellowing begins.
Yellowing stress coefficient slope shape	2.5	Medium convex curve

*GDD, growing degree days

In addition to these fixed parameters, variable (non-conservative) parameters are added to the model by the user as variable (non-conservative) parameters for special tillage, some management and environmental conditions, and applications that are not widely used. These parameters are usually established using data measured in the field during the plant growth period. Phenological parameters of Tosunbey and Bayraktar bread wheat varieties for two years (2017-2018 and 2018-2019) for Aquacrop model are given in Tables 4 and 5.

Table 4. Phenological parameters for Bayraktar varieties

Observations	2017-2018	2018-2019
Seed rate	18 kg/da	18 kg/da
Planting date	24/10/2017	11/10/2018
First germination	25/01/2018	27/01/2019
Jointing time	22/03/2018	28/03/2019
Tillering time	25/04/2018	25/04/2018
Flowering time	15/05/2018	13/05/2019
Flowering Time	5	7
Physiological maturity time	20/06/2018	22/06/2019
The date the yellowing started	27/06/2018	25/06/2019
Harvest time	18/07/2018	20/07/2019

Table 5. Phenological parameters for Tosunbey variety

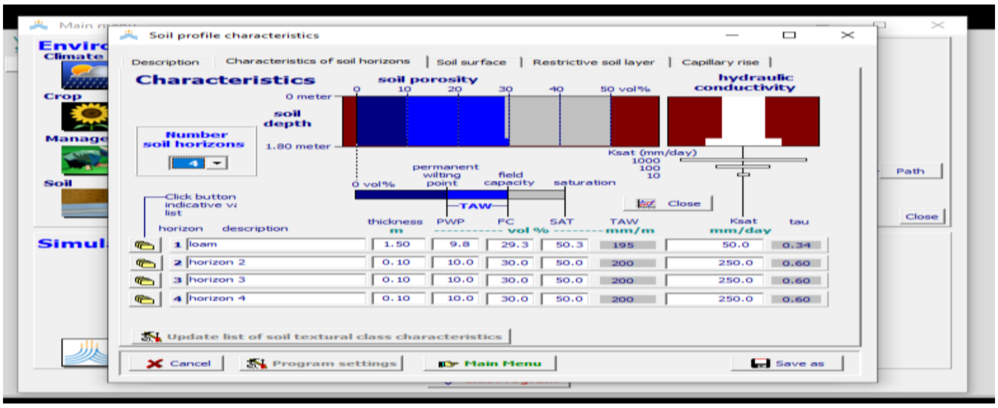
Observations Taken	2017-2018	2018-2019
Planting date	24/10/2017	11/10/2018
First germination	25/01/2018	27/01/2019
Jointing time	22/03/2018	28/03/2019
Tillering time	25/04/2018	25/04/2018
Flowering time	18/05/2018	13/05/2019
Flowering period	7	5
Physiological maturity time	25/06/2018	22/06/2019
The date the yellowing started	01/07/2018	25/06/2019
Harvest time	18/07/2018	20/07/2019

Phenological observations taken for each variety depending on the nitrogen ratio applied during the plant growth period are entered into the "Crop characterictics" section of the programme to make separate calculations.

In this study, grain yield, dry biomass, and plant coverage ratio (CC) were used to determine the accuracy of the model. Statistical evaluation of the validity of the model was done by comparing observed and predicted biomass and grain yield values. Mean absolute deviation (α), standard error (RMSE) and model efficiency coefficient (E) were used to determine the relationship between measured and predicted values (Janssen and Heuberger, 1995; Lyman, 1993; Nash and Sutcliffe, 1970). For the accuracy of the model's predictions, the value of E (Model efficiency coefficient) should be between 0.5 and 1.0. The value of E is from negative infinity to 1. An E value is close to 1, it indicates that there is a perfect fit between the model and observation values, while E value close to 0, indicates that the model should not be used. Using the Green Crop Tracker program, the percentage of plant green area coverage (CC%) observed in the field is calculated. The results obtained can be compared with the simulation observations calculated by the Aquacrop model. The Green Crop Tracker (GCT) program is a software developed in Canada for processing digital photographs of agricultural crops. This program calculates the vegetation coverage in green areas based on photographs taken by a digital color camera at certain angles and heights. For this purpose, the percentage of green vegetation cover (CC%) is calculated by the program with the help of photographs taken at a certain height and angle with a digital color camera from each plot during plant growth periods (Sandhu et al., 2019).

Results

Inputs related to climate, soil, different fertilizer ratios, plant and environmental parameters of the experimental area where the project was carried out for 2 years in 2017-2018 and 2018-2019 were entered into the model. Parameters of plant phenological periods such as sown seed quantity, flowering, yellowing and ripening periods recorded during the plant development period were used as plant inputs in the program. Soil properties of the experimental area were entered into the model (Figure 6).



horizon	description	thickness m	PWP vol %	FC vol %	SAT vol %	TAW mm/m	Ksat mm/day	tau
1	loam	1.50	9.8	29.3	50.3	195	50.0	0.34
2	horizon 2	0.10	10.0	30.0	50.0	200	250.0	0.60
3	horizon 3	0.10	10.0	30.0	50.0	200	250.0	0.60
4	horizon 4	0.10	10.0	30.0	50.0	200	250.0	0.60

Figure 6. Aquacrop model soil characteristics section

Estimates based on rainfall without irrigation in the experiment. Daily climate data from Haymana Climate station were used. Simulations were made according to fertilization subjects and the predicted grain yield and biomass yield results were compared with the actual values measured in the experimental field (Table 6, 7, 8, 9, 10, 11).

Table 6. Coverage percentage (%) values of varieties by growing periods (Haymana 2017-2018 Growth Period)

Period (Dates)	Coverage percentage (%) values (Tosunbey-Bayraktar)							
	Tosunbey				Bayraktar			
RATIOS	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
31.01.2017	14.0	16.0	33.0	32.0	26.0	14.0	15.0	8.0
01.03.2018	43.10	49.10	33.86	56.23	54.05	40.01	63.89	38.05
22.03.2018	41.61	64.23	52.95	64.25	44.32	50.76	68.63	41.74
10.04.2018	75.88	67.65	83.90	76.47	69.52	84.25	85.94	62.00
25.04.2018	79.69	83.59	82.78	84.49	77.82	70.68	77.03	81.29
08.05.2018	71.87	83.63	84.61	86.66	80.89	77.45	85.21	61.89
28.05.2018	74.92	78.23	79.60	74.29	80.01	77.32	80.91	93.96
13.06.2018	65.65	69.86	69.64	78.78	68.55	70.03	64.76	70.47

Table 7. Biomass-dry weight values of varieties by growing periods (g /0.25 m^{2}) (Haymana 2017-2018)

Period (Dates)/ Does	Biomass (Dry weight) (g/ 0.25 m^{2})							
	Tosunbey				Bayraktar			
	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
22.03.2018	131.98	79.35	105.16	117.03	71.83	77.82	115.51	82.39
10.04.2018	287.52	156.80	160.32	126.08	202.88	197.92	377.60	379.36
25.04.2018	159.60	185.16	199.0	131.48	84.08	105.36	102.48	87.32
08.05.2018	219.80	250.40	193.12	254.84	152.64	170.52	115.68	131.04
28.05.2018	335.16	215.96	397.04	247.44	289.20	215.96	250.20	210.60
13.06.2018	683.72	458.08	429.64	589.60	812.28	299.20	909.96	541.84
18.07.2018	662.12	513.82	460.23	692.77	558.91	484.15	693.55	587.62

Table 8. Haymana harvest data (2017-2018)

Yield / Harvest Index	Variety name (Harvest date: 18.07.2018)							
	Tosunbey				Bayraktar			
Ratios	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
Dry Biomass (g/0,25 m^{2})	662.12	513.82	460.23	692.77	558.91	484.15	693.55	587.62
Grain Yield (kg/da)	560	320	240	560	320	400	720	400
Harvest Index	25.19	25.00	29.73	30.54	24.90	27.66	30.75	29.44

Table 9. Coverage Percentage (%) Values of Varieties by Growing Periods (Haymana 2018-2019)

Period (Dates)	Variety name (Percent coverage values) (%)							
	Tosunbey (II. Block)				Bayraktar (I. Block)			
Ratios	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
27.11.2018	10.0	8.0	11.0	17.0	17.0	11.0	12.0	16.0
20.02.2018	24.0	21.0	34.0	38.0	27.0	34.0	27.0	31.0
28.03.2019	45.12	49.28	34.79	57.73	55.02	42.24	64.56	39.44
30.04.2019	81.67	86.14	85.36	86.72	78.65	72.87	81.04	84.35
15.05.2019	71.87	83.63	84.61	86.66	80.89	77.45	85.21	61.89
30.05.2019	76.63	60.25	71.54	64.42	56.80	58.04	65.07	63.23
18.06.2019	70.20	65.56	59.98	62.39	65.20	57.92	52.80	51.33
25.06.2019	77.77	72.84	70.79	70.39	74.92	76.30	71.66	70.39

Table 10. Biomass-dry weight values of varieties by growing periods (g /m^{2}) (Haymana 2018-2019)

Period (Dates)	Varety name (Biomass-Dry Weight (g/ m^{2})							
	Tosunbey (II. Block)				Bayraktar (I. Block)			
Ratios	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
20.02.2018	64.32	45.76	50.40	47.36	24.16	48.64	33.28	54.88
28.03.2019	97.60	60.96	96.96	132	176.16	231.20	193.28	183.68
30.04.2019	21.08	14.67	56.54	41.57	89.33	44.66	34.71	60.52
15.05.2019	879.20	1001.60	772.48	1019.36	610.56	682.08	462.72	524.16
30.05.2019	411.36	888.16	1707.52	1316.80	1845.28	1996.16	3206.56	1851.68
18.06.2019	487.36	490.24	1472.48	2559.20	1840.64	2617.92	2544.0	2745.12
25.06.2019	742.24	747.52	904.64	1263.20	2361.28	1818.88	1964.16	2046.08

Table 11. Haymana Harvest Data (2018-2019)

Period (Dates)	Variety name (Harvest data: 20.07.2019)							
	Tosunbey (II. Block)				Bayraktar (I. Block)			
Ratios	N_0	N_6	N_{12}	N_{18}	N_0	N_6	N_{12}	N_{18}
Dry Biomass (g/ m^{2})	3045.40	1909.96	3126.0	3374.12	2739.80	1972.24	2365.40	3342.88
Grain Yield (kg/da)	148.89	155.0	218.89	347.78	307.78	287.22	330.56	306.67
Harvest Index	14.55	11.81	25.17	29.78	3.55	12.49	22.37	22.79

Simulation Evaluation Results of Yield Parameters

The model was calibrated by evaluating the data measured from the trial area between 2017 and 2018. Validation is an important step in determining the accuracy of the model. Validation is the comparison of independent data measured in the field with data predicted by the model (Andarzian et al., 2011). The performance of the calibrated model was validated using data from the 2018-2019 growing period. The Aqucrop model processes the data entered into the program, such as plant, soil, irrigation, fertilization, etc. and produces its own simulated results using daily climate data. These results are statistically compared with the actual yield, biomass, coverage percentage (CC%) values obtained from the field. Accordingly, the comparisons of the observations made between the 2017-2018 and 2018-2019 periods with the model are summarized in the figures below (Figures 7, 8, 9, 10).

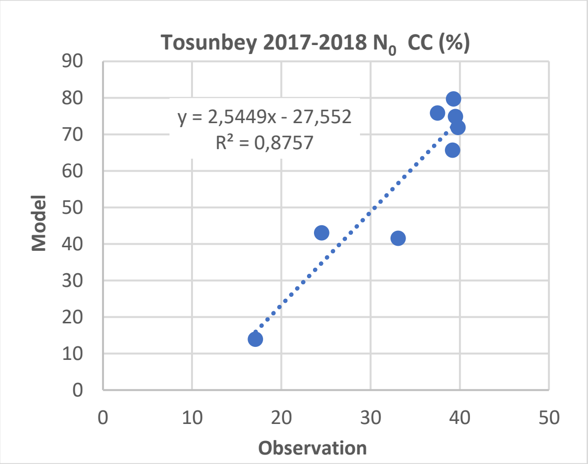


Figure 7. The relationship between the observation-model and the N_0 ratio of vegetation (CC%) percentages (Tosunbey, 2017-2018)

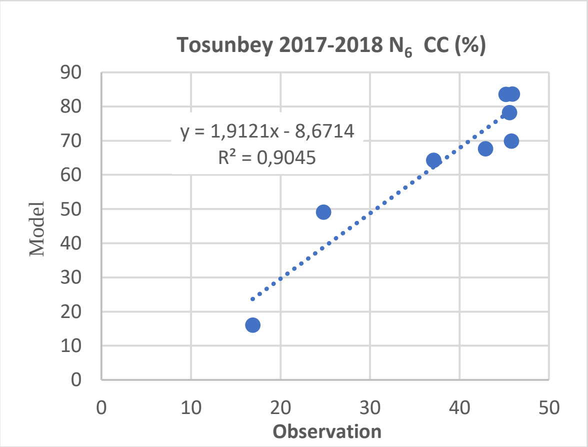


Figure 8. The relationship between the observation-model and the N_6 ratio of vegetation (CC%) percentages (Tosunbey, 2017-2018)

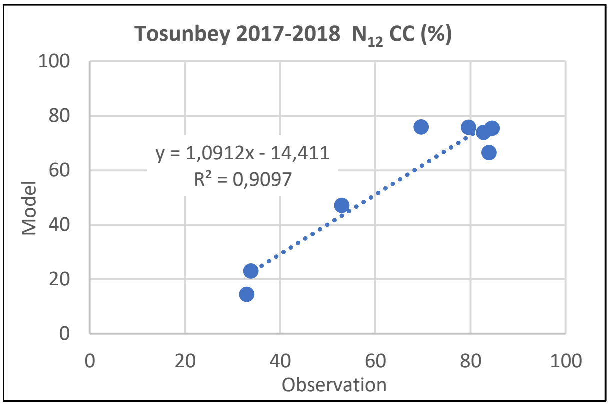


Figure 9. The relationship between the observation-model and the N_{12} ratio of vegetation (CC%) percentages (Tosunbey, 2017-2018)

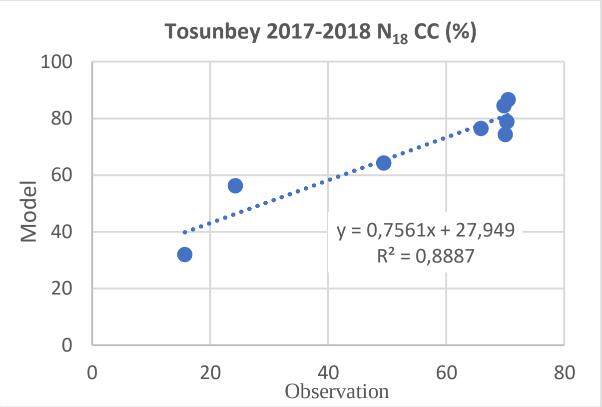


Figure 10. The relationship between the observation-model and the N_{18} ratio of vegetation (CC%) percentages (Tosunbey, 2017-2018)

In the 2017-2018 experimental year, the experiment conducted in the field with the N_{12} ratio gave the lowest grain yield value and the highest yield levels were the yield levels corresponding to the N_0 and N_{18} ratios. When the statistical evaluations between model and observation are analyzed, the relationships between grain yields model and observation for Tosunbey variety are given in Table 11, Table 12 and Table 13, and the relationships between grain yields model and observation for Bayraktar variety are given in Table 14 and Table 15. Bayraktar variety biomass yield model observation comparisons (2017-2018, 2018-2019) are also given in Table 16 and Table 17. Tosunbey variety biomass yield model observation comparison (2018-2019) is given Table 18. The efficiency coefficients for grain yield and biomass were calculated for Bayraktar and Tosunbey for the years 2017-2018 and 2018-2019 (Table 19).

Table 12. Model and observation comparison for grain yield (Tosunbey, 2017-2018)

Growing Year	Application	Grain Yield (t ha^{-1})	
		Observation	Model
	N_0	5.60	2.37
	N_6	3.20	2.81
2017-2018	N_{12}	2.40	4.32
	N_{18}	5.60	4.00
α		1.785	
RMSE(t ha^{-1})		2.051	
E		0.66	

Table 13. Model and observation comparison for grain yield (Tosunbey, 2018-2019)

Growing Year	Application	Grain Yeald (t ha^{-1})	
		Observation	Model
	N_0	1.49	1.79
	N_6	1.55	1.95
2018-2019	N_{12}	2.19	2.21
	N_{18}	3.47	2.24
α		0.353	
RMSE(t ha^{-1})		0.664	
E		0.91	

Table 14. Model and observation comparison for grain yield (Bayraktar, 2017-2018)

Growing Year	Application	Grain Yield (t ha^{-1})	
		Observation	Model
	N_0	3.20	3.17
	N_6	4.00	4.11
2017-2018	N_{12}	7.20	5.32
	N_{18}	4.00	5.55
α		0.893	
RMSE(t ha^{-1})		1.220	
E		0.93	

Table 15. Model and observation comparison for grain yield (Bayraktar, 2018-2019)

Growing Year	Application	Grain Yield (t ha^{-1})	
		Observation	Model
2018-2019	N_0	3.08	2.66
	N_6	2.87	2.73
	N_{12}	3.31	3.30
	N_{18}	3.07	3.36
α		0.216	
RMSE(t ha^{-1})		0.266	
E		0.99	

Table 16. Model and observation comparisons for biomass yield (Bayraktar, 2017-2018)

Growing Year	Application	Biomass (t ha^{-1})	
		Observation	Model
	N0	4.60	4.73
	N6	4.54	4.81
2018-2019	N12	4.91	5.87
	N18	5.11	5.97
α		0.555	
RMSE (t ha^{-1})		0.662	
E		0.98	

Table 17. Model and observation comparisons for biomass

Growing Year	Application	Biomass (t ha^{-1})	
		Observation	Model
	N_0	8.12	5.74
	N_6	11.97	7.14
2017-2018	N_{12}	9.1	9.29
	N_{18}	5.42	9.23
α		2.803	
RMSE (t ha^{-1})		3.299	
E		0.83	

Table 18. Model and observation comparisons for biomass yield (Tosunbey, 2018-2019)

Growing Year	Application	Biomass (t ha^{-1})	
		Observation	Model
	N_0	2.19	4.58
	N_6	2.51	4.86
2018-2019	N_{12}	3.68	5.70
	N_{18}	6.37	5.78
α		1.838	
RMSE(t ha^{-1})		1.979	
E		0.76	

Table 19. Model Efficiency Coefficient (E) comparisons by trial years

Growing Year	Model Efficiency Coefficient (E)	Tosunbey	Bayraktar
2017-2018	Grain Yield	0.66	0.93
	Biomass		0.83
2018-2019	Grain Yield	0.91	0.99

Discussion

In the project, in order to determine the effectiveness of the Aquacrop model, grain yield, biomass, and canopy cover (canopy cover-CC) values were evaluated at 4 different nitrogen ratios and dry conditions for 2 years (2017-2018, 2018-2019) to compare the results obtained from the model with the real field trial results. However, some of the problems encountered also affected the results. In the first year of the project, 2017-2018, biomass measurements could not be measured properly, especially in the plots with Tosunbey variety due to the rye effect in the trial area. The plots were cleaned especially at the end of the emergence and spike periods because weeds and foreign species of rye were mixed between the plots. Rye was cut at the level of the wheat spike with the help of garden shears to reduce the negative effect on yield. Accordingly, when the model and observation results were evaluated together for the first year grain yield, the model efficiency coefficient E for Tosunbey variety was found to be 0.66 and 0.91 (Table 19). For Bayraktar variety, and it is seen that the model is compatible with field observations and predicts correctly. For Bayraktar variety, when the results between the model and observation were compared in the biomass value, E=0.83 was found (Table 17) and it was concluded that the model was quite compatible with the real field observations. Similar results showing that the grain yield and biomass values obtained in winter wheat in case of sowing on normal sowing date were correctly predicted by the model were also found by some researchers such as; Araya et al., (2010), Zeleke et al., (2011), Iqbal et al., (2014), Kale Çelik et al., (2018) and Sırlı Alsancak et al., (2023). In addition, Abedinpour, (2021) conducted a comparison between DSSAT-CERES and AquaCrop models to simulate wheat growth under different irrigation and nitrogen levels and found that the simulation results of DSSAT model were relatively more accurate than AquaCrop model. However, considering that it would be difficult to obtain the necessary data for the DSSAT model in undeveloped and developing countries, it was accepted that the Aqucrop model is more advantageous because it requires less input and makes accurate calculations in less time. Phenological observations were taken during the experiment period and entered into the model. In addition, photographs of plant coverage areas were taken from the same height and with a good quality digital camera throughout the growth period and then processed in GreenCrop Tracker programme to determine green area canopy coverage rates (CC%). Again, although the weed effect in the first year negatively affected the result in determining the coverage area, photographs were taken from clean plots to prevent this. The canopy coverage (% CC) rates determined were compared with the canopy coverage values on the days predicted simultaneously by the model. Accordingly, the coefficients of determination (R^2) for N_0, N_6, N_{12} and N_{18} fertiliser treatments in terms of percent plant cover (% CC) of Tosunbey wheat variety between 2017-2018 were found to be 0.88, 0.90, 0.91 and 0.89, respectively, and were found to be compatible with the model (Figures 7, 8, 9, 10). In the software used to determine the percent cover values with the observation values obtained from the field, there may be deviations in the actual values due to the fact that the grasses in the sampling area outside the wheat are also within the calculation area, albeit very slightly, since the percentage of green area coverage is calculated (Table 6). In this study, canopy coverage percentage (CC%) values obtained in 2018-2019 for Tosunbey variety were statistically close to each other when evaluated as model and observation. Similarity was found between the percentage of green vegetation cover predicted by the model and observed in the field. The correlation (R^2) values between the percentage coverage values (CC%) obtained for Tosunbey wheat variety and the observed values were calculated for different fertilizer application ratios for the years 2018-2019 and were found to be 0.95, 0.89, 0.89, 0.89 and 0.82 for N_0, N_6, N_{12} and N_{18} values, respectively (Figures 11, 12, 13, 14). Studies on winter wheat and various other crops have also shown that the model accurately predicted the percent cover (CC%) values (Heng et al., 2009, Hsiao et al., 2009, Farahani et al., 2009; Tavakoli et al., 2015).

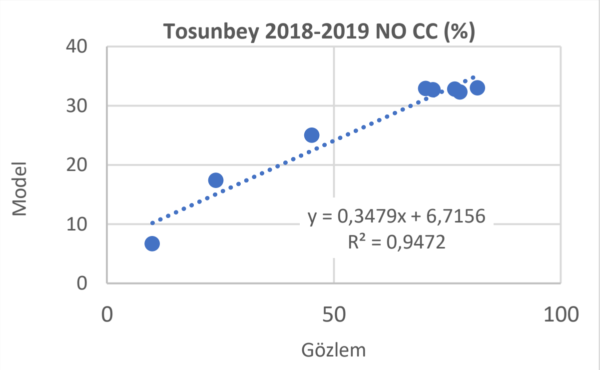


Figure 11. The relationship between the observation-model and the N0 ratio of vegetation (CC %) percentages (Tosunbey, 2018-2019)

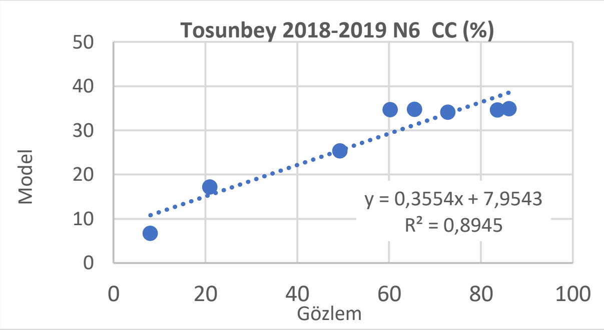


Figure 12. The relationship between the observation-model and the N_6 ratio of vegetation (CC%) percentages (Tosunbey, 2018-2019)

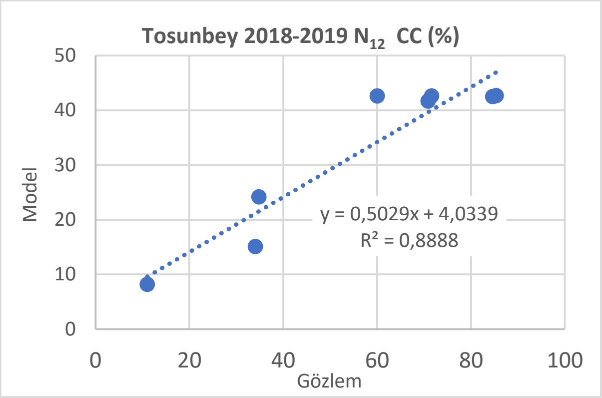


Figure 13. The relationship between the observation-model and the N_{12} ratio of vegetation (CC%) percentages (Tosunbey, 2018-2019)

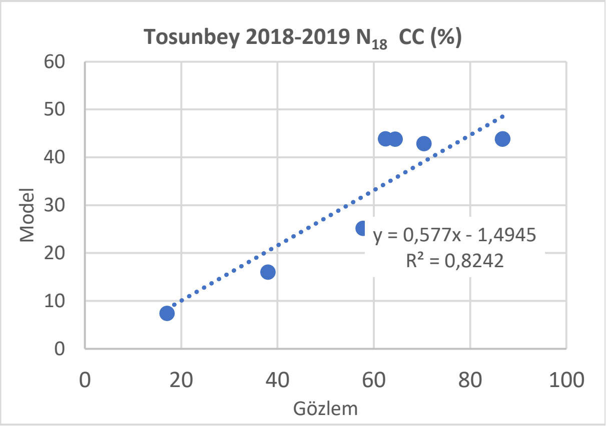


Figure 14. The relationship between the observation-model and the N_{18} ratio of vegetation (CC%) percentages (Tosunbey, 2018-2019)

The coefficients of determination (R^2) between the values observed in the field and the values predicted by the model in the first year of the experiment (2017-2018) for the Bayraktar variety were obtained for different fertiliser treatments N_0, N_6, N_{12} and N_{18}. These values were found to be 0.79, 0.91, 0.63 and 0.81, respectively (Figures. 15, 16, 17,18). These values were found to be 0.87, 0.87, 0.74 and 0.82 for the years 2018-2019, respectively (Figures. 19, 20, 21, 22). Accordingly, for Bayraktar variety, the value of N_6 fertiliser trial had the highest R^2 value in the first year (Figure 16), while N_6 trial had the highest value in the second year (Figure 20).

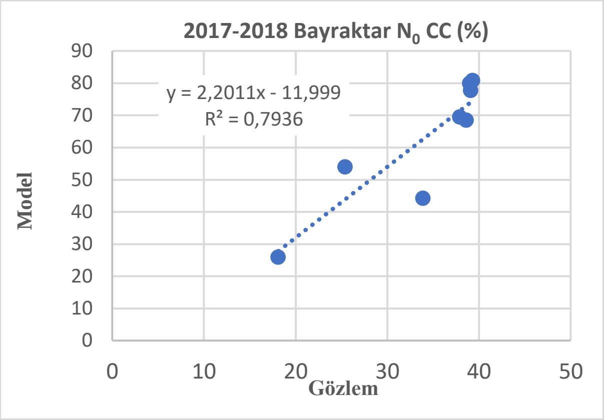


Figure 15. The relationship between the observation-model and the N_0 ratio of vegetation (CC%) percentages (Bayraktar, 2017-2018)

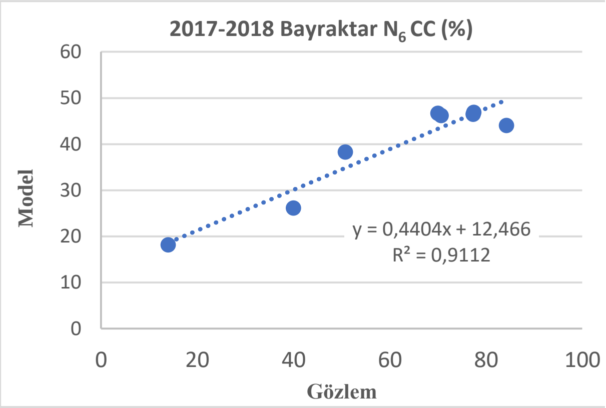


Figure 16. The relationship between the observation-model and the N_6 ratio of vegetation (CC%) percentages (Bayraktar, 2017-2018)

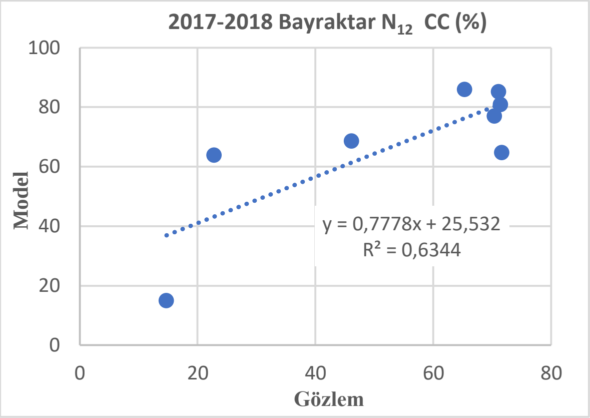


Figure 17. The relationship between the observation-model and the N_{12} ratio of vegetation (CC%) percentages (Bayraktar, 2017-2018)

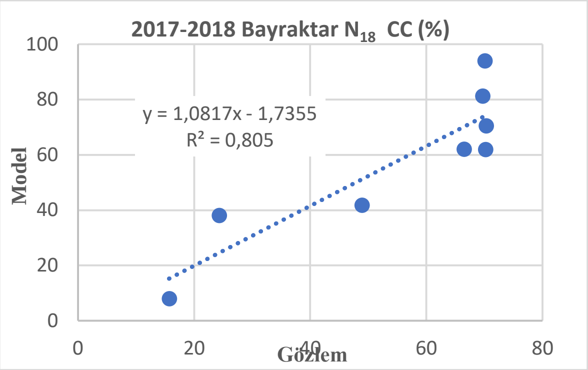


Figure 18. The relationship between the observation-model and the N_{18} ratio of vegetation (CC%) percentages (Bayraktar, 2017-2018)

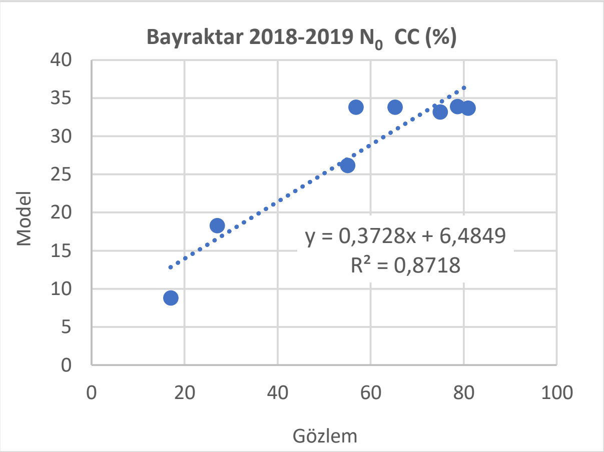


Figure 19. The relationship between the observation-model and the N_0 ratio of vegetation (CC%) percentages (Bayraktar, 2018-2019)

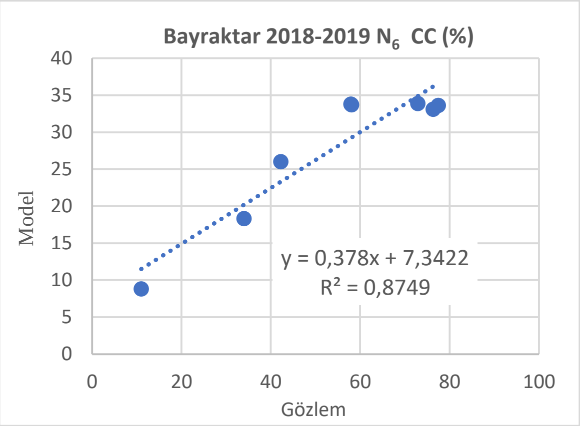


Figure 20. The relationship between the observation-model and the N6 ratio of vegetation (CC %) percentages (Bayraktar, 2018-2019)

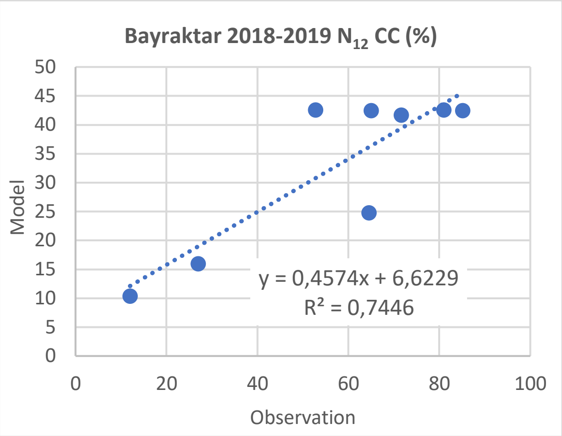


Figure 21. The relationship between the observation-model and the N12 ratio of vegetation (CC %) percentages (Bayraktar, 2018-2019)

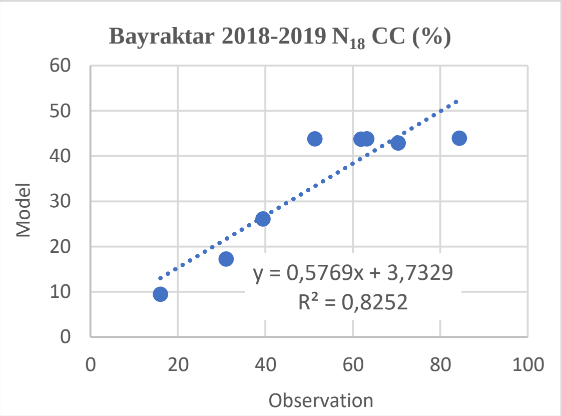


Figure 22. The relationship between the observation-model and the N_{18} ratio of vegetation (CC%) percentages (Bayraktar, 2018-2019)

Conclusion

In the studies conducted in 2018-2019, the second year of the experiment, Tosunbey variety grain yield was calculated as E=0.91 and Bayraktar grain yield was calculated as E=0.99, and an excellent agreement was found between the model and observation Considering the biomass evaluations, Tosunbey variety E=0.76 and Bayraktar variety E=0.98, and a very high agreement between the model and observation was found.

The Aquacrop model is intended for annual plants only. However, compared to other models, it provides much simpler and more reliable results. In such plant simulation models, the more accurately the data is entered, the more smoothly the model runs. These models constitute an important basis for yield estimation studies. With the Aquacrop model, it will be possible to reveal the yield deficit in a certain area or a region, to reveal the effects of inadequate fertilisation effects on yield, to evaluate the water-fertiliser interaction, to analyse future climate scenarios, to facilitate decision-makers in water distribution and other water policy-related events.

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that might appear to influence the work reported in this paper.

Author Contribution

BA: Idea/Hypothesis, Material, Method, Research, Data Processing, Data-Analysis, Visualization, Executive/Consultant, Thesis Management, Original Drafting, Writing- Reviewing & Editing; **HY:** Data processing, Executive/Consultant, Writing-Reviewing & Editing. **MA:** Data processing, Executive/Consultant, Writing-Reviewing & Editing. All authors have read and agreed to the published version of the manuscript.

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RESEARCH PAPER

Spectroscopic, thermic and metal binding properties of commercial humic acid and leonardite

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Abstract

Humic acids are formed from a combination of variable chemical groups found in natural sources containing partially aromatic groups in an amorphous structure. These substances have been shown to significantly impact plant biomass, affecting nutrient distribution through direct interaction with the plant and nutrient supply and regulation through indirect interaction. The lack of a regular and repeating molecular structure in humic substances makes them challenging to determine. Humic substances used in agriculture commercially are humic and fulvic acid or combinations of both in different proportions. In our research, we used spectroscopic and thermal methods to understand the structures of commercial samples. We conducted FT-IR (Fourier Transform Infra-Red) spectroscopy to analyze the structure's bonds, thermal analysis to comprehend its thermal properties, and NMR (Nuclear Magnetic Resonance) analysis to obtain information about the carbon content. By combining, comparing, and interpreting all these methods, we can predict commercial samples' spectroscopic and thermal properties during the production stage. This can serve as a foundation for researchers studying or utilizing humic acid.

Introduction

Humic substances have been used in agriculture for a long time due to their beneficial effects on plant nutrition. Humic acid is composed of a large and complex structure consisting of carbon, hydrogen, nitrogen, and oxygen. These substances, which are the source of humic acid, are amorphous, partially aromatic, and naturally occurring. Humic substances are categorized into humin, humic acid, and fulvic acid (Chen and Avnimeleek, 1986). The main benefits of humic substances are that they affect the distribution of nutrients by direct interaction and provide and regulate nutrients through their indirect effects (Schnitzer and Khan, 1978). Humic acids are macro-organic molecules containing polymeric phenolic compounds that can form complexes with metal cations (Schnitzer and Khan, 1978).

Humic substances have large supramolecular structures, which can cause their properties to vary depending on their source. Therefore, characterization and content determination are of great importance. Studies on this subject have continued increasingly in recent years. Like this “For instance, five coal samples from China were oxidized with hydrogen peroxide to obtain humic acids (HAs). These HAs were characterized by physical and chemical methods, showing differences in yield, ash content, aromaticity, molecular weight, and functional groups (Shuangdui et al., 2021). In the study aimed at researching the molecular characterization of organic matter in the soil, the fractions of humic matter, humic substances, fulvic acids, humic acids, and humins were investigated and broad spectrum spectroscopic (UV-VIS and VIS - near IR) analyses were performed. In addition, electrochemicals (zeta potential, particle size diameter, and polydispersity index were examined. All data were brought together to investigate the relevant differences in behavior, formation, and composition, and it was determined that humic substances differ in terms of behavior, formation, composition, and sorption properties (Ukalska-Jaruga A. et al., 2021).

Additional studies have employed spectroscopic methods (FT-IR/ATR and CP/MAS 13C-NMR - Carbon 13 Nuclear Magnetic Resonance) and elemental composition analysis to evaluate the thermal decomposition and quality of humic acids from various sources, revealing differences in the degree of humification. Moreover, spectroscopic methods (FT-IR/ATR and CP/MAS ^{13}C -NMR) and elemental composition analysis were used to determine the effect of humic acids extracted from peat and lignite on the thermal decomposition of HA and to evaluate the quality of humic acid in this article, which examined the thermal decomposition of ammonium nitrate and humic acid mixtures Analysis of the spectra revealed differences in the degree of humification of humic acids extracted from various raw materials (Nieweś et al., 2023).

Sodium humate samples were isolated from soil, compost, and South Moravian lignite, and FT-IR, fluorescence spectroscopy, and ^{13}C- NMR analyses were performed on the samples. The density of chemical groups decreases in the order of compost, soil, lignohumate, and lignite. It is observed that sodium humate samples isolated from soil, compost, and lignite are more polycondensed (Enev et al., 2014)

Humic substances have many beneficial properties. In addition to agriculture, it is also used in medicine and animal husbandry. Humic acid has been found to reduce damage caused by the retention of heavy metals and pesticides when taken orally in animals. In recent years, the use of humic acids in medicine has been investigated in the solution of very common problems such as asthma, bronchitis, flu, stomach disorders, kidney stone disorders, hemorrhoids, skin cancer, stopping bleeding, anemia, excessive sleep, and oversleeping. Sleepiness accumulation, pollution and residue problems caused by chemical fertilizers and regulators do not apply to humic acids.

Certain humic acid derivatives, once purified from humate substances, are found to possess similar molecular structures and chemical characteristics. However, a study conducted with humic acids extracted from different types of soils revealed significant variations. Humic acid obtained from andisol soils was found to be rich in carboxyl and carbonyl groups with a high C ratio, while being poor in hydroxyl, and low in H and N. Conversely, humic acid obtained from entisol soils exhibited low carboxyl and carbonyl groups. Furthermore, aquatic humic acids were found to have higher H and N values compared to terrestrial humic acids (Yonebayashi and Hattori, 1988). Additionally, humic acid extracted from lignite humate contains more nitrogen, carbohydrates, and aromatic compounds than those obtained from non-lignite sources. Moreover, humic acid extracted from domestic wastes contains more carbon, exhibits a more aliphatic structure, contains fewer oxygen groups, and is more heterogeneous than those extracted from peat and leonardite (Aşık, 2008).

In Türkiye, the use of humic acid is increasing, but its application often overlooks source variations and soil-plant characteristics. The Ministry of Agriculture and Forestry regulates commercial humic acid products, classifying them as organic according to the Ministry's 2018 directive (Anonymous, 2018). To use humic acid resources more efficiently and healthily, their structures need to be characterized in detail.

The study conducted thorough final characterization analyses on humic acid and leonardite products, commonly used in the market, uncover their molecular properties. This research marks the first time that the spectroscopic and thermal properties of various commercial humic acid products have been collectively examined at a national level.

Material and Method

Humic acid and Leonardite samples

The samples analyzed in this study were selected from commonly used products in the market to ensure compliance with relevant regulations. Among the samples, three were identified as leonardite, one as liquid potassium humate, and four as solid potassium humate.

Characterization of Materials

^{13}C-NMR analyses targeted within the scope of the project were carried out at the Middle East Technical University Central Laboratories. FT-IR and Thermogravimetric analyses (TGA) were performed at Bilkent University National Nanotechnology Center. Elemental analyses of the samples were performed with the ICP-OES device at the Soil, Fertilizer, and Water Resources Central Research Institute. In addition, total humic acid + fulvic acid percentage, organic matter percentage, total nitrogen percentage, amount of Na and S, moisture, pH, and EC parameters were determined in the laboratories of the Central Research Institute of Soil, Fertilizer and Water Resources.

The moisture content of the samples was determined by subjecting them to 70°C after initial wet weighing. pH and EC values were measured by diluting the samples 1/10 using potentiometric methods. Organic matter analysis was conducted for 5 hours at 550°C using a modified AOAC method. Total carbon, nitrogen, and sulfur analyses were performed in duplicate using the TruSpec-Leco brand elemental analysis. Total potassium, water-soluble potassium, and total phosphorus analyses were carried out following the Kacar &Kutuk -2009 method. Additionally, total sodium analyses were performed using a Jenway brand flame photometer. The total phosphorus analysis was conducted using the coloring method with a Libra-Biochrom brand UV-visible spectrophotometer.

All measurements were conducted twice, and the average value was considered as the result. Analysis of calcium, magnesium, iron, copper, manganese, zinc, cadmium, lead, cobalt, chromium, and nickel additives involved three repeated readings using the Varian 720-ES ICP-OES device. The Merck brand ICP multi-element standard solution IV served as the reference standard. Statistical evaluation of the results was deemed unnecessary.

Elemental Analysis

The device used in elemental analysis can simultaneously detect carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in the structure of inorganic and organic substances in solid, liquid, or gas samples. With the elemental analyzer, microanalysis of all homogeneous organic compounds such as petrochemical industry (oils and derivatives), industrial chemistry (polymer), environment (soil, sediment, water), and drug and protein analysis can be performed. The sample was prepared by precise weighing between 0.10 - 0.20 g and analyzed with an instrumental analyzer (Leco TruSpec NHC-S). Because of these analyses, the percentages of carbon, hydrogen, and nitrogen, which form the main skeleton of the molecules of our samples, were determined.

FT-IR Analyze

Fourier transform infrared (FT-IR) spectroscopy is a method frequently used in basic sciences, health sciences, and engineering by detecting the bonds in the structure of molecules. This method is based on the absorption of infrared rays falling on intramolecular bonds by the vibration and rotational movements of the bonds. However, this phenomenon is observed only in polar molecules with dipole moments. IR spectra can be obtained by pelleting solid samples with potassium bromide (KBr) or analyzing them directly with an ATR unit with IR spectrometry. Direct IR spectra of liquid and gas samples can be obtained with ATR (Attenuated Total Reflection unit). The IR spectrometer, an indispensable device for both academic and industrial studies, can be applied in almost every field. It is often used to determine organic and inorganic molecules (Yildiz et al., 1997). In this study, an FT-IR/Thermo device with a diamond-tipped ATR unit was used at Bilkent University National Nanotechnology Research Center (UNAM) laboratories. As sample number 9, Acros Organics brand powder humic acid salt produced as a laboratory chemical with a purity of 50-60 % was used.

^{13}C- NMR Analyze

NMR is the most powerful technique for determining the structures of organic compounds. It can be used to examine a wide variety of nuclei: ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P are examples. All atoms with an odd atomic number and/or mass number have nuclear spin. The nucleus (proton, ^{1}H, etc.), which rotates around itself (rotational motion) and has an electric charge, creates its magnetic field. When spinning protons are placed in an external magnetic field, they rotate under the influence of this magnetic field. The magnetic fields of these rotating protons tend to be either in the same direction as the external field or in the opposite direction to the external field.

When the energy of a photon with the right amount of energy is absorbed, the direction of its magnetic field changes. The energy difference between the two states is corrected by the strength of the magnetic field (strength of the magnet). If all protons absorbed the same amount of energy in the same magnetic field, not much information would be obtained. Protons protect them from the influence of the external magnetic field. Spinning electrons reduce the effect of the external field by creating an excited magnetic field in the opposite direction to the external magnetic field. Protons in molecules depend on chemical environmental conditions.

They are preserved in varying amounts. The signal number indicates how many different types of protons there are. The position of the signals (chemical shift) indicates how protected the proton is. The intensity of the signals tells you how many protons there are. The division of signals shows how many protons are in neighboring atoms (Erdik, 1998).

TG/DTG/DTA Analysis

Thermal methods are based on the study of the dynamic relationship between temperature and some properties of the system, such as mass, reaction rate, or volume. There are about twelve methods of thermal analysis; the methods we used in the project are as follows; Thermo Gravimetric Analysis (TGA/DTG) and Differential Thermal Analysis (DTA).

Thermo Gravimetric analysis (TGA)

In Thermo Gravimetric Analysis, the mass (weight) of the sample is continuously monitored as the temperature is heated from ambient conditions to temperatures reaching 1200°C. The mass-temperature graph is called a "thermogram" and is used in qualitative/quantitative determinations. The thermogravimetric analyzer consists of a precision analytical balance, an oven, an oven temperature controller and programmer, and a recorder. The logger plots the mass of the sample versus the temperature. In an inert atmosphere, auxiliary systems are also needed to provide this when necessary. With TGA, the purity, degradation behavior, and chemical kinetics of the sample are examined.

Differential thermal methods are used to determine the composition of natural or artificial substances. The thermal behavior of inorganic compounds such as silicates, ferrites, clay, oxides, ceramics, and glasses can be monitored by differential thermal measurements. The monitoring processes consist of melting, dissolution, hydrogen removal, oxidation, reduction, adsorption, degradation, and solid-state reactions. The most important applications are drawing phase diagrams and investigating phase transitions.

Thermal analyses were performed in Bilkent University National Nanotechnology Research Center (UNAM) laboratories. Analyzes were carried out with TA Instruments Q500 device in a dry air environment at a heating rate of 10°C min^{-1}, using sintered α-Al_2O_3 as a reference, in a platinum crucible at a temperature range of 20-900°C and using 5-10 mg of sample. Sample number 9 was used as the standard. It is an Acros Organics brand powdered humic acid salt, produced as a standard laboratory chemical with 50-60% purity.

Differential Thermal Analyze (DTA)

In Differential Thermal Analysis, the heat absorbed or emitted by the system is observed by measuring the temperature difference between a chemical system (sample) and an inert reference compound (can be aluminum, silicon carbide, or glass particles). In operation, the temperatures of the system and reference are increased at a constant rate. The temperature difference between the sample and the reference is monitored as a function of temperature (Yıldız et al., 1997).

The sample is prepared for analysis by placing it in an inert micro crucible with precision weighing in the thermal analyzer. Because of the analysis, thermograms, differential thermal graphs, and differential thermal analysis graphs are interpreted.

ICP-OES Analyze

Metal contents of samples prepared by licking in a microwave oven will be determined by ICP-OES. The ICP-OES instrument is an analytical technique that analyzes many different elements in metal, sediment, soil rock, industrial waste, anode sludge, aluminum and magnesium anode, coal ash, ore, and pre-treated beneficiation products. ICP stands for Inductively Coupled Plasma and is an optical emission spectrometer. This technique involves the excitation of the sample with argon plasma reaching temperatures of 10.000 K by electromagnetic induction and identification of the excited elements according to the specific wavelengths they emit. Plasma is obtained by electromagnetically exciting argon gas in induction windings with a radio frequency (RF) generator. This happens when the hot plasma ionizes the incoming gas and the process continues continuously. The fundamental principle of inductively coupled plasma spectroscopy is to measure the emission emitted by the excitation of atoms and ions in the plasma, an electrically conductive gaseous medium containing a high concentration of equivalent amounts of cations and electrons.

Results and Discussion

Analyzes

Physical and chemical analyses

Analyzes were carried out on eight commercial samples 3 of the samples are products originating from leonardite, 1 is liquid potassium humate and 4 are solid potassium humate. Study findings show that products originating from leonardite exhibit high organic matter and humic + fulvic acid content. Additionally, the analysis revealed that the liquid humic acid was particularly rich in potassium. Although the analysis results of the selected samples vary, the results of leonardite-derived products and potassium humate-labeled products are similar in most parameters. When the organic matter amounts were examined, high values such as 50.63% and 54.2% in the first 2 products and 95.93% in the third product were found in the leonardite-derived products. It was determined that the liquid sample had the lowest organic matter content at 4.05%. Potassium humate samples have 35.8-34.41-66.86-44.51% organic matter, respectively. Leonardite-derived products have much higher moisture content than humate-derived products, between 20.90-48.94% moisture values and 3.54-13.13% moisture values. While humate-derived products have more basic pH values of 9.97-10.34, leonardite-derived products have more acidic values of 7.58-7.63-8.04. Total nitrogen values were determined slightly higher in humate-based products. While it is 1.03% in leonardite products, it is 1.44% in Humate-based products. When the parameters of total potassium, water-soluble potassium, and total phosphorus are compared, it is seen that the values of humate-derived products are 15-20 times higher than the others.

The interaction of a molecule with metal elements that have electropositive properties, such as plant nutrients, is measured by the electronegativity characteristics of that molecule. Electronegativity is the tendency of an atom in a compound to attract bond electrons. If the molecule contains more than one covalent bond, the bond dipole moments have a vector result. Polar molecules with a net dipole moment interact electrostatically with each other and with other molecules. The vector direction and magnitude of the net dipole moment are determining factors in these interactions.

The humic + fulvic acid ratio, which is the most important analysis parameter of the samples, is 72.23-64.10-50.14%, respectively, in leonardite-origin products. The rate in the liquid sample was determined as 13.97%. For humate derivative products, it is 67.97-68.38-71.89-64.16%, respectively. When the ratios of the elements contained in the samples are examined, it can be said that calcium, magnesium, chromium, lead, and sulfur are more in leonardite-sourced products, while sodium and zinc elements are more in humate-sourced products. Since the amounts of other elements vary from sample to sample, no correlation can be established between sample sources. While cadmium and cobalt remained below the detection limit in all samples, manganese, nickel, lead, and copper elements could not be measured in some samples when they remained below the detection limit (Table 1-2).

Table 1. Analysis of selected commercial humic acids (1)

Analyzes	Analysis method	Leonardit-1	Leonardit-2	Leonardit-3	Liquid Humic Acid
Organic matter (%)	AOAC 967.03-04-05	50,63	54,22	95,93	4,05
Humidity (%)	AOAC 1995	48,94	37,90	20,90	--
pH	1/10 Potansiyometry	7,58	7,63	8,04	12,1
EC (mS cm^{-1})	1/10	2,06	1,96	3,05	26,00
Total nitrogen (N) (%)	TS EN 15478	1,089	1,080	0,92	0,31
Total carbon (C) (%)	Elemental analysis device	34,05	34,15	22,10	6,33
Total potassium (K) (%)	Kacar and Kutuk, 2009	0,04	0,06	0,19	3,9
Water-soluble Potassium (K) (%)	Kacar and Kutuk, 2009	0,05	0,05	0,09	2,28
Total (H+F) acid (%)	TSE 5869	72,23	64,10	50,14	13,97
Total phosphorus (P) (%)	Kacar and Kutuk, 2009	0,44	0,46	0,20	0,002
Total calcium (Ca) (mg L^{-1})	ICP-OES	93140	79470	45330	15466
Total magnesium (Mg) (mg L^{-1})	ICP-OES	3777	4940	18443	1411
Total iron (Fe) (mg L^{-1})	ICP-OES	5871	126830	37040	396,80
Total manganese (Mn) (mg L^{-1})	ICP-OES	32,89	45,08	277,10	1,78
Total copper (Cu) (mg L^{-1})	ICP-OES	6,68	129,30	53,00	UDL
Total zinc (Zn) (mg L^{-1})	ICP-OES	1,44	14,57	UDL	0,62
Total cadmium (Cd) (mg L^{-1})	ICP-OES	UDL	UDL	UDL	UDL
Total lead (Pb) (mg L^{-1})	ICP-OES	UDL	UDL	UDL	UDL
Total chromium (Cr) (mg L^{-1})	ICP-OES	57,81	67,00	95,80	14,2
Total cobalt (Co) (mg L^{-1})	ICP-OES	UDL	UDL	UDL	UDL
Total nickel (Ni) (mg L^{-1})	ICP-OES	7,65	35,97	324,00	4,56
Total sulfur (S) (%)	Elemental analysis device	2,55	4,32	6,07	1,11
Total sodium (Na) (%)	Flame photometry	0,04	0,02	0,13	0,07

UDL: Under Detection Limit, Cu<0,015 ppm, Pb <0,09 ppm, Cd<0,03 ppm, Co<0,01 ppm, Zn<0,01 ppm

Table 2. Analysis of selected commercial humic acids (2)

Analyzes	**Analysis method**	**Humat-1**	**Humat-2**	**Humat-3**	**Humat-4**
Organic matter (%)	AOAC 967.03-04-05	35,89	34,41	66,86	44,51
Humidity (%)	AOAC 1995	7,82	7,98	13,13	3,54
pH	1/10 Potansiyometry	10,16	10,34	9,97	10,32
EC (mS cm^{-1})	1/10	16,50	15,44	11,91	21,8
Total nitrogen (N) (%)	TS EN 15478	1,37	1,38	1,53	1,47
Total carbon (C) (%)	Elemental analysis device	46,02	43,90	46,55	41,05
Total potassium (K) (%)	Kacar and Kutuk, 2009	6,05	6,82	5,62	13,26
Water-soluble Potassium (K) (%)	Kacar and Kutuk,2009	11,93	9,36	2,81	9,59
Total (H+F) acid (%)	TSE 5869	67,97	68,38	71,89	64,16
Total phosphorus (P) (%)	Kacar and Kutuk, 2009	3,24	3,41	3,97	0,61
Total calcium (Ca) (mg L^{-1})	ICP-OES	8517,00	7511,00	9124,00	13766,00
Total magnesium (Mg) (mg L^{-1})	ICP-OES	1093,90	1280,40	1358,404	4687,00
Total iron (Fe) (mg L^{-1})	ICP-OES	17139,00	13201,00	16415,00	5274,00
Total manganese (Mn) (mg L^{-1})	ICP-OES	UDL	0,22	40,00	128,89
Total copper (Cu) (mg L^{-1})	ICP-OES	46,60	43,97	14,85	22,92
Total zinc (Zn) (mg L^{-1})	ICP-OES	23,00	272,00	74,34	49,92
Total cadmium (Cd) (mg L^{-1})	ICP-OES	UDL	UDL	UDL	UDL
Total lead (Pb) (mg L^{-1})	ICP-OES	5,84	11,65	6,40	0,56
Total chromium (Cr) (mg L^{-1})	ICP-OES	12,88	11,48	9,75	UDL
Total cobalt (Co) (mg L^{-1})	ICP-OES	UDL	UDL	UDL	UDL
Total nickel (Ni) (mg L^{-1})	ICP-OES	30,43	23,26	27,40	UDL
Total sulfur (S) (%)	Elemental analysis device	UDL	UDL	UDL	UDL
Total sodium (Na) (%)	Flame photometry	2,36	2,42	2,42	0,84

UDL: Under Detection Limit Mn<0,03 ppm, Pb <0,09 ppm, Cd<0,03 ppm, Co<0,01 ppm, Ni<0,14 ppm

FT-IR Analyzes

When the spectra of all samples are evaluated, it is seen that they give very close peaks at very close wavelengths. The peaks in the middle range between 3400-3200 cm^{-1} are O-H stress peaks. Bending peaks of C-H bonds are the most common bonds in the strong peak structure. Because of the overlap of O-C and C-N peaks, slightly shouldered peaks are observed between 1000-900 cm^{-1}. The weaker peaks below 800 cm^{-1} belong to N-H peaks.

Table 3. Observable ranges of some intramolecular vibration types in the IR region

Vibration type	Wave number range, cm^{-1}
C-H strain	2700-3300
C-H bending	1300-1500
O-H strain	3000-3700
O-H stretch (overtone)	6700-7100
N-H strain	3000-3700
N-H stretch (overtone)	6300-7100
N-H bending	700-900
C-O strain	900-1300
C-N strain	900-1300
C=C stress	1600-1700
C=O stress	1600-1900

The IR spectrum of the liquid potassium humate sample shown in Figure 1(d) only displays peaks related to O-H stretching and H-O-H shift, indicating the presence of water. After heating the liquid sample at 100°C for 10 hours, solid humic acid was obtained, and the IR spectrum was taken again. This time, IR peaks consistent with other solid samples were observed, as depicted in Figure 1(f).

Upon examining the overlaid graph in Figure 1(k), it is evident that all samples exhibit a consistent correlation, displaying peaks and shoulders at the same wavelength (Figure 1).

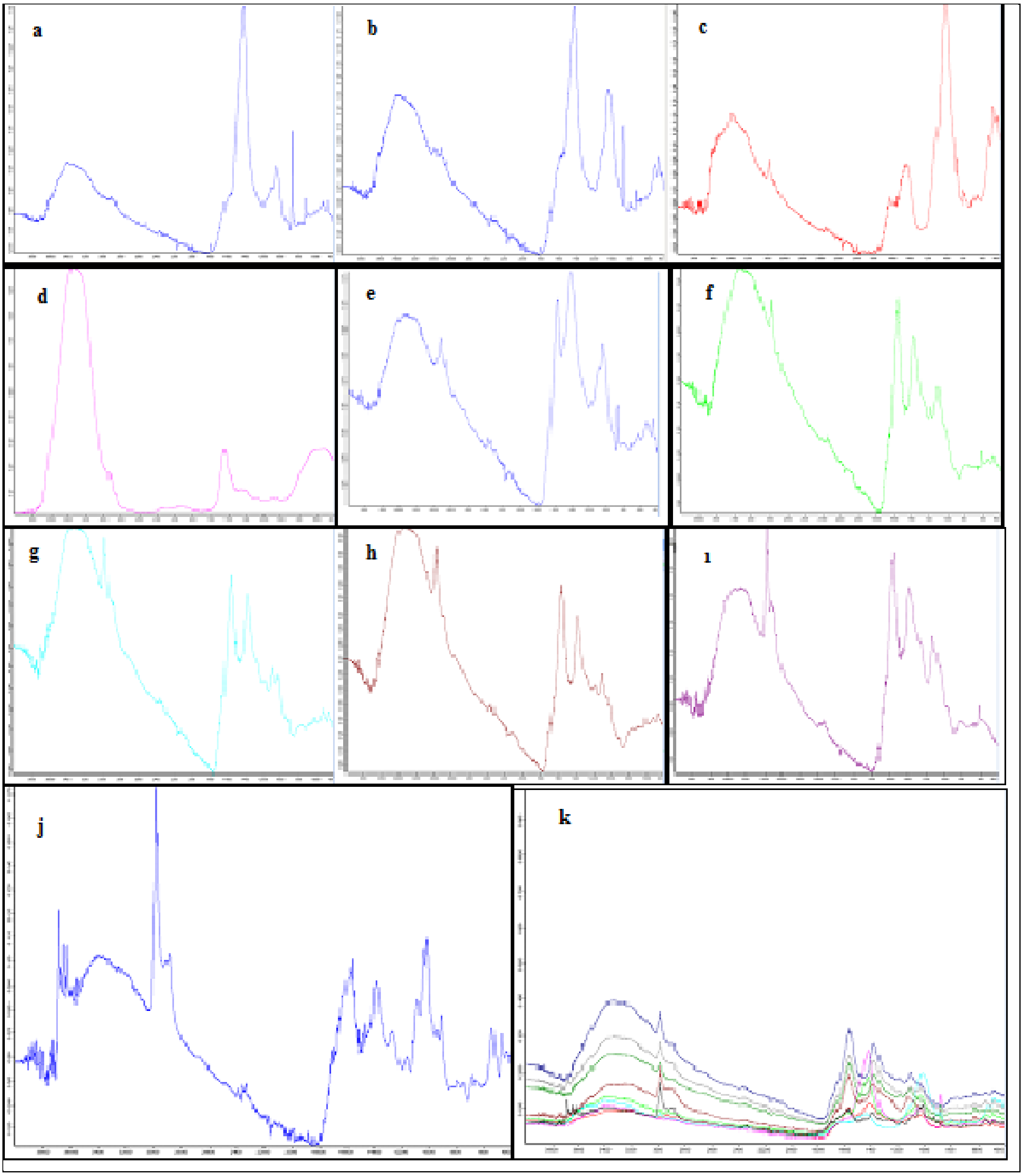

Figure 1. FT-IR spectrums of all samples a) Leonardite No. 1 b) Leonardite No. 2c) Leonardite No. 3 d) Liquid potassium humate No.4 (liquid phase IR) e) Liquid potassium humate no.4 (solid phase IR) f) Potassium humate No. 5 g) Potassium No. 6 humat h) potassium humate no. 7 i) potassium humate no. 8 j) humic acid standard k) Superimposed IR spectra of all samples. In all FTIR tables, the x-axis is given from left to right between 4000-4000 cm$^{-1,}$ and the y-axis is given between 0-0.900 A from bottom to top.

Thermal analysis curves

When the thermal analysis graphs are interpreted, it is clear that the 10-15% mass loss observed at 100°C is water. A mass loss of 7-10% is observed between 100-350°C and 35-40 % between 350-950°C. At 950°C, 35-50% of the mass of the structure is still solid.

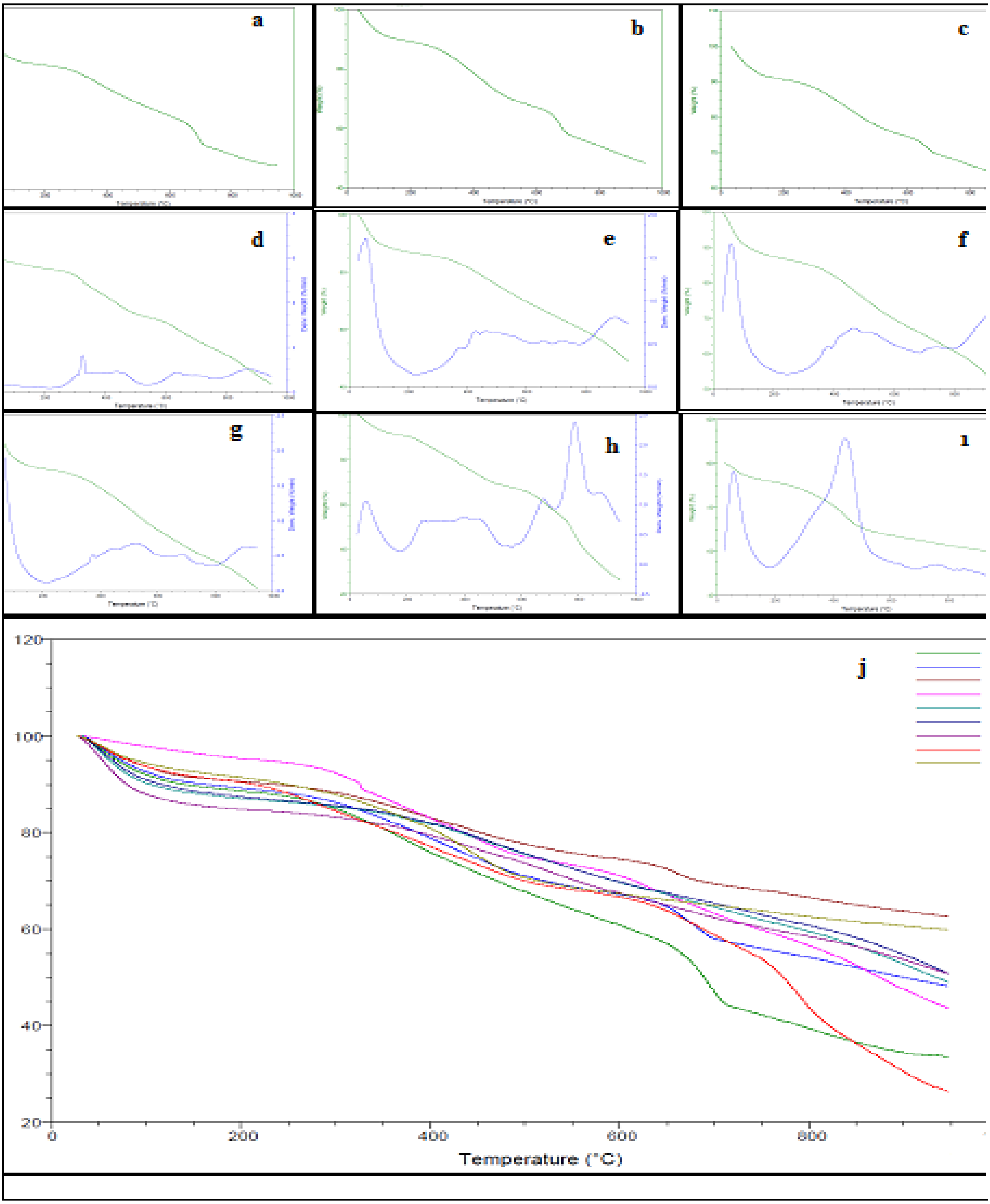

Figure 2. TGA curves of all samples a) Leonardite No. 1 b) Leonardite No. 2 c) Leonardite No. 3 d) Liquid potassium humate No. 4 e) Potassium humate No. 5 f) Potassium No. 6 humat g) potassium humate no. 7 h) potassium humate no. 8 i) humic acid standard j) the same axis representation of all TGA curves

When the thermal analysis graphs are interpreted, it is clear that the 10-15% mass loss observed at 100°C is water. A mass loss of 7-10% is observed between 100-350°C and 35-40 % between 350-950°C, at 950°C, 35-50 % of the mass of the structure is still solid.

^{13}C-NMR spectra

^{13}C-NMR analyses were carried out in the central laboratories of the Middle East Technical University with a 300 MHz Solid State High Power Bruker Avance device, using a 4 mm MAS probe and at least 500 mg of powder samples, with a rotation speed of 8500 Hz in approximately 8 hours.

As expected, mixed signals were observed in the ^{13}C-NMR spectra due to the high number of carbons in our samples. However, we observe that the same signals among these signals reinforce each other and form a peak. The divisions cannot be observed due to the large number of C peaks caused by the strong signals. Despite the confusion of the signals, it is seen that the signals become stronger at close points where the samples give very similar spectra in all spectrum shapes.

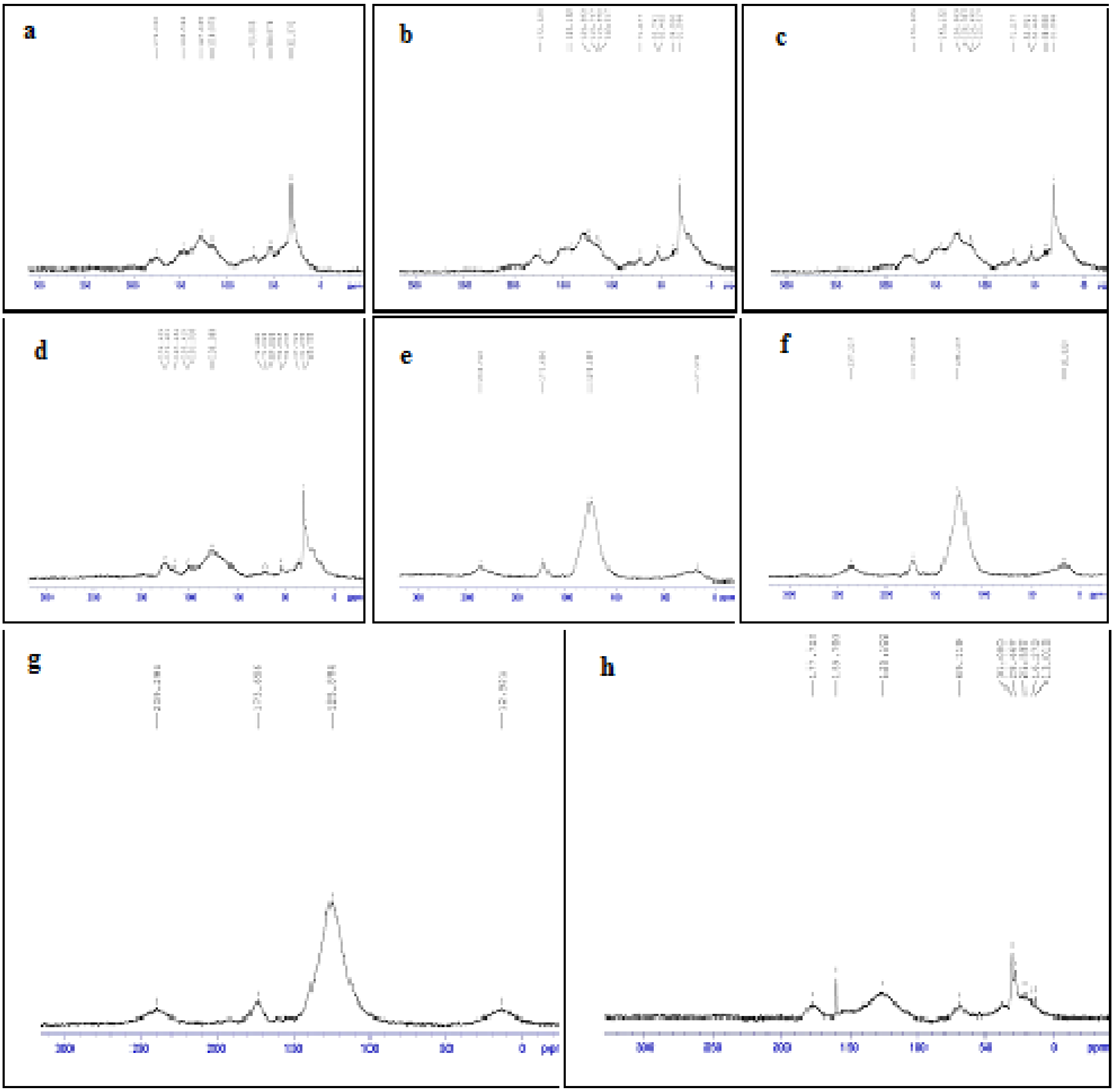

Figure 3. The carbon NMR spectra of the samples a) Leonardite No. 1 b) Leonardite No. 2 c) Leonardite No. 3 d) Liquid potassium humate No. 4 e) Potassium humate No. 5 f) Potassium No. 6 humat g) potassium humate no. 7 h) potassium humate no. 8. In all NMR tables, the x-axis is from left to right from 300 to 0 ppm.

Conclusions

Eight commercial products selected within the scope of the study were examined primarily with their chemical and physical properties. In the analysis of humate substances, it is common to look for a proportional relationship between the analysis of humic and fulvic acids and the analysis of organic matter. The humic acid + fulvic acid analysis result is the total percentage of both acids in the humate substance. Organic matter is an analysis that yields results based on the amount of the carbon element in the structure. In addition to carbon, humate substances also contain oxygen, hydrogen, nitrogen, and small amounts of metal elements. Humate substances are known to have different compositions depending on their source. Therefore, the amount of humic acid + fulvic acid is often greater than the amount of organic matter. However, a fixed correlation cannot be established between the two analysis results.

When the FT-IR spectra are evaluated, it is seen that they give very similar intensity peaks at very close wavelengths. The intermediate intensity peaks between 3200-3400 nm are O-H stress peaks. C-H stress peaks overlap with these peaks, creating flatter and more variable peaks. Because of the overlap of O-C and C-N peaks, peaks with slight shoulders are observed between 1000 and 900 nm. The weaker peaks below 800 nm belong to N-H peaks. When looking at the graph where the spectra are combined, it is seen that all samples show a suitable correlation with peaks and shoulders at the same wavelength. The IR spectrum of the liquid humic acid sample shows only O-H stretching and H-O-H shift peaks. Thus, only the spectrum of water was obtained. When the liquid sample was kept at 100°C for 10 hours, solid humic acid was obtained and the IR spectrum was taken again and IR peaks compatible with the other samples were observed. When FT-IR analysis is evaluated, it can be interpreted that the sample is not a homogeneous liquid humic acid solution, but a liquid suspension.

The general characteristics of the samples in the thermal analysis graphs can be summarized as follows; Samples contain an average of 10-15% moisture. 35-55% of the sample content became gas at 950 °C. The remaining 35-50% remains in solid form. The fact that most of it remained solid because of the analysis indicates a high carbon content and a multi-ring supramolecular structure.

It can be seen that mixed signals are collected in the ^{13}C-NMR spectrum due to the high number of carbons. However, we see that the same signals among these signals reinforce each other and form a peak. Due to the high number of C in the peaks, the breaks cannot be observed clearly due to strong signals. Despite the confusion of the signals, it is seen that the signals become stronger at points close to each other where the samples give very similar spectra. This situation shows that the number of C in the molecule is high.

All chemical and physical analyses carried out within the scope of the project show that humic acids are large macrocyclic supra molecules with high organic matter, and low solubility, but capable of interacting with elements with electropositive properties. They display these properties in different intensities depending on the humic acid content in natural humin sources.

In many studies conducted in our country and around the world, humic acid applications not only increase plant productivity but also transfer N, P, K, Ca, Mg, Fe, Cu, Mn, Zn, etc. from the soil to the plant. It provides the transfer of substances. It increases the transition speed of elements. Greater penetration of the elements affects the plant's nutrient uptake and thus its productivity. The findings we obtained within the scope of the project confirm that humic acid and humic substance applications will increase especially the yield and plant nutrient uptake. ^{13}C- NMR results show the abundance of the carbon element in the structure, i.e., high levels of organic matter.

Within the scope of these findings, it would be very beneficial to use natural humic sources, especially leonardite, or products prepared by adding humic substances by taking into account soil and plant analyses. The use of organic fertilizers containing less humic substances, such as animal manure and compost, by further enriching them is important for increasing organic matter, which is the most important effect of organic fertilizers.

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

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Author Contribution

AE: selection of samples, preparation of samples for analysis, interpretation of analyzes, writing of the final report EK: preparation of samples for analysis, interpretation of analyzes KA: selection of samples, preparation of samples for analysis RMP: selection of samples preparation of samples for analysis.

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RESEARCH PAPER

Sunflower-nitrogen calibration based on the amount of mineral nitrogen in soil under rainfed conditions in thrace region

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Abstract

Sunflower is grown under both rainfed and irrigated conditions in all regions to meet the vegetable oil needs of Türkiye, however, in the Thrace region, it is the main rotation crop grown under rainfed conditions after wheat. This study was conducted in the Thrace Region between 2013 and 2016 in order to evaluate the parameters that can be used as an index for nitrogen fertilization recommendations for sunflower plant. For this purpose, organic matter and saturation were determined in soil samples taken from 0-20 cm depth before the experiment and ammonium and nitrate contents were determined in soil samples taken from 0-30 cm, 30-60 cm, and 60-90 cm depths. Within the scope of the study, 27 field trials were conducted over four years. Nitrogen levels of 0 (control), 3, 6, 9, and 12 kg da^{-1} were implemented in the trials conducted in a Latin square experimental design. In this study, $\log(279.9\text{-}y) = \log 279.9\text{-}0.090b_1\text{-}0.117x$ Mitscherlich calibration equations were determined based on 0-30 cm ammonium+nitrate content in the soil.

Introduction

Soils naturally have different yield potential, which is related to the mineral matter and organic matter content of the soil. Soil texture and organic matter are two important factors affecting water retention capacity. Organic matter is an important source of nitrogen as well as having important effects on water holding capacity. However, since the properties of soils vary according to their parent material and formation conditions, the yield and fertilizer requirements are also different. The amount of mineral nitrogen forms in the soil is influenced by organic matter, the previous plant in rotation, the amount of nitrogen fertilizer applied, drought or humidity, and the addition of plant residues to the soil. In a dryland farming system, dry periods after N fertilization applied to the previous crop can cause an excess of N, which reduces N use efficiency (Angaás et al., 2006).

More than half of the sunflower cultivation in Türkiye is in the Thrace Region, where rainfall-dependent cereal-sunflower alternation is practiced in ¾ of the agricultural lands. Soil analysis laboratories, which provide soil analysis services for farmers, take the results of soil analysis as a basis for phosphorus and potassium fertilization recommendations, while the amount of organic matter in the soil is taken into account in nitrogen fertilization recommendations (Güçdemir, 2006), but the main factor determining the recommendation is the results of local nitrogen fertilization trials. The data obtained from these experiments cause contradictory results. (Arslan, 1989) obtained the quadratic equation $Y = 143.95+37.793x-$

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$1.929x^2$ for the relationship between sunflower yield and nitrogen fertilizer in a study carried out to determine the nitrogen fertilizer requirement of sunflower under rainfed conditions in the Thrace Region and determined that 90 kg ha^{-1} N should be applied for the economic optimum yield according to 1987 fertilizer-crop prices. In a similar study in Edirne province, Süzer (1998), stated that the equation $[Y = 1.988+4.86x-0.032x^2 \ (R = 0.804^{**})]$ can be used to determine the nitrogen fertilizer requirement of sunflower. Considering the year 1997, fertilizer, and crop prices, the economic optimum fertilizer level was determined as 50 kg ha^{-1} N. Studies have reported that the amount of NO_3^-N can be taken into account instead of the amount of soil organic matter in determining the nitrogen need of plants (Korkmaz et al., 2021; Gokmen Yilmaz et al., 2021). Besides mineral nitrogen forms, there are other chemical methods to determine the soil's capacity to provide nitrogen to plants. In studies conducted in the dry farming areas of Central Anatolia, it was determined that the phosphate-borate buffer method and the acid $KMnO_4$ method were the best methods, and the total hydrolyzable ammonium content showed a strong correlation with biological methods (Elkarim and Usta, 2001).

Ayla (1984) applied nitrogen (0, 6, and 12 kg N da^{-1}) before sowing in 1974-1977 in a study conducted to determine the water consumption, amount, time, and number of irrigation water and nitrogen-water relations of sunflower under Central Anatolian conditions. As a result of the study, at 6 kg da^{-1} nitrogen implementation, when 5% of the available capacity was reached, 640 mm irrigation water was applied 5 times from sowing to harvest and the annual water consumption of the plant was 815 mm and the highest daily water consumption was determined in July with 11.79 mm. In this case, 235 kg da^{-1} yield was obtained, while 226 kg da^{-1} yield was obtained in the implementation with no fertilizer at the same irrigation amount. At 12 kg da^{-1} nitrogen level, 235.5 kg yield was obtained. This indicates that the addition of nitrogen fertilizer does not cause a very significant increase in sunflower yield increase when the water requirement of the plant is met.

Currently, nitrogen recommendations for most states, such as North Dakota, South Dakota, Nebraska, and Kansas, are based on expected yield formulas. The formulas include a reduction in nitrogen recommendations due to nitrate content in the soil, organic matter level, fertilization, and gains from the previous crop. The formula is expected yield per decare x 0.05. However, when recent nitrogen rate studies were evaluated, yields responded less than expected to nitrogen in other countries (Darby et al., 2013; Scheiner et al., 2002).

In a study investigating the effects of environmental conditions (temperature, rainfall) and nitrogen applications on sunflower phenological indicators and water use efficiency in at two locations in Mexico, plant growth, yield and yield components, and water use efficiency were significantly affected by environment, nitrogen application and environment-nitrogen interaction. Nitrogen positively affected other traits (Olalde et al., 2001).

Considering the amount of nitrogen removed from the soil by plants, Chapman (1960) stated that if the amount of NO_3^-N in the soil for plants is less than 5 mg kg^{-1}, it is deficient, and if it is more than 20 mg kg^{-1}, it is high.

Mortvedt et al., (1996) stated that the amount of nitrogen fertilizer to be applied should be determined by taking into account the expected sunflower yield for each field. The researchers published a table in which the amount of nitrogen to be applied can be determined according to the amount of nitrate and organic matter in the soil based on the expected yield.

Kansas State University, in their report, interpretation of soil analysis results and fertilization recommendations, it is accepted that 1% of the organic matter of the soil will provide mineralized nitrogen for the expected crop yield of sunflower and other crops grown in summer. The nitrogen requirement of the plant is determined by taking into account the previous crop in the rotation and the amount of nitrate in the soil and irrigation water (Meyer, 1997). The formula used for this purpose is given below.

N Rec^{2*} *= (Yield Goal × 0.075) - (% SOM × 20) - Profile N - Manure N - Other N Adjustments + Previous Crop Adjustments*

^{*2}: It will be useful to give 3.5 kg ha^{-1} of nitrogen in the early period for adequate development of the plants.

Gürbüz and Kardeş (2017) applied 0 (control), 3, 6, 9 and 12 kg da^{-1} (N) levels in Thrace Region in order to investigate the parameters that can be used as an index in nitrogen fertilization recommendations for sunflower plants. Correlation coefficient between nitrogen requirement and the amount of soil organic matter was 0.72, the correlation coefficient for saturation was 0.63, the correlation coefficient for 0-30 cm nitrate nitrogen was 0.62, the correlation coefficient for ammonium+nitrate content in 0-30 cm was 0.71 and correlation coefficient for ammonium+nitrate content in 0-60 cm was 0.72.

It has been reported that the Mitscherlich-Bray equation $[\log(A-y) = \log A – c_1b_1-c_x]$ can be used for the Mitsherlich calibration equation, depending on the relationships between the KCl-extractable NO_3-N content in the soil and the yield (Bray, 1945; Afzal et al., 2014, Sonar and Babhulkar, 2002, Ali et al., 2022). In this study, it was aimed to obtain the relationship between the amount of $NH_4^+NO_3^-N$ extracted with KCl and the yield for the sunflower plant under rainfed conditions in Thrace Region, using the Mitscherlich-Bray equation.

Materials and Methods

Thrace Region, located in the northwest of Turkey, has an area of 2 372 000 ha and constitutes 3.1% of the total area of Türkiye. In the region, the wide flat lands between the Istranca and Ganos Mountains, forming the partially undulating Thracian peneplain, are largely suitable for agriculture (Anonymous, 1971).

Although the region is characterized by different climate types, Edirne, Tekirdağ and Kırklareli are characterized by a continental climate. This climate is characterized by hot and dry summers and cold and rainy winters Some meteorological data of these three provinces where the experiments were carried out as the average of long years are given in Table 1 (Anonymus, 2024c; Anonymus, 2024d; Anonymus, 2024e).

Table 1. Some meteorological data of the provinces in Thrace

Province	Period	Annual precipitation mm	Average temperature °C	Highest temperature °C	Lowest temperature °C
Edirne	1930-2023	601.0	13.8	44.1	-19.5
Kırklareli	1959-2023	583.7	13.3	42.5	-15.8
Tekirdağ	1940-2023	580.0	14,1	40.2	-13.5

The month with the highest rainfall is December and the month with the lowest rainfall is August. The number of frost days in the region is between 30-90. The prevailing winds are the northeaster and the stellar and the average wind speed is 2.6 m s^{-1}.

In the study, the experimental areas were distributed to Kırklareli, Edirne and Tekirdağ considering major soil groups and especially different soil textures. Trial locations were determined as Kırklareli, Pınarhisar, Kaynarca, Lüleburgaz (Sarmısaklı Farm), Edirne, Orhaniye (Keşan), Boztepe (Keşan), Tekirdağ, Çorlu (Velimeşe), Hayrabolu (Figure 1).

Figure 1. Locations of the trial areas

In the trials, the Tunca variety, which is intensively cultivated in the region due to its resistance to orobanche and high oil content, was used as sunflower plant. Ammonium nitrate fertilizer containing 33% N was used for nitrogen fertilization during seeding and top fertilization.

The field trials were conducted under rainfed conditions and N_0=0, N_1=3 kg da^{-1} N, N_2=6 kg da^{-1} N, N_3=9 kg da^{-1} N, N_4=12 kg da^{-1} N levels were applied as nitrogen fertilizer. Ammonium nitrate fertilizer containing 33% N was applied at planting (1/2) and top dressing (1/2). No microelement fertilization was applied to the sunflower plant in the trials. The experiment was conducted in a Latin square experimental design with 5 replications (Yurtsever, 1984). The plot size was 5.6x7=39.2 m^2 at planting and 2.8x5=14 m^2 at harvest. A gap of 1.0 m was left between the plots. For sunflower planting, the seedbed was plowed in the fall after the wheat harvest and made ready for planting by harrowing in the spring. In all treatments, half of the nitrogen fertilizer was applied before planting and the other half before hoeing.

Soil and Plant Analysis Methods

Before planting, soil samples were taken from 0-20 cm depth for fertility analysis and 0-30, 30-60, and 60-90 cm depths with a soil auger in order to determine mineral nitrogen forms.

Saturation (%) was determined by saturating the soil with water, soil reaction (pH) was measured by using a pH meter in water-saturated soil (Jackson, 1958), Electrical conductivity (EC) was measured with an EC meter in soil-water suspension (Richards, 1954), Lime (%) determined by the Scheibler Calcimeter method (Tüzüner, 1990), Organic matter (%) determined by the Modified Walkley-Black Method (Tüzüner, 1990). Available phosphorus was determined by sodium bicarbonate method (Olsen, 1954), available potassium determined by ammonium acetate method (Tüzüner, 1990), available boron (B) for plants was extracted according to Berger and Troug (1939) and determined by Spectro Arcos SOP ICP-OES device (Kacar, 2009), available manganese, iron, copper and zinc for plants determined by DTPA extraction method and determined by Spectro Arcos SOP ICP-OES (Lindsay and Norvell, 1982).

Table 2. Soil analysis results of the trial areas

Year	Location	Sat. %	pH	EC %	Lime %	OM %	Contents of plant available nutrients						
							P_2O_5 kg da^{-1}	K_2O kg da^{-1}	B mg kg^{-1}	Mn mg kg^{-1}	Fe mg kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}
2013	Kırklareli	64	7.44	0.03	17.5	0.83	8.49	53.0	0.50	21.59	7.83	5.49	1.95
	Edirne	29	4.60	0.02	0.0	0.99	22.07	46.5	0.51	110.6	66.44	2.16	1.19
	Tekirdağ	53	7.50	0.06	9.0	1.57	4.86	86.0	0.53	12.56	7.28	9.05	0.63
	Boztepe	99	7.50	0.07	1.0	0.54	8.93	86.0	0.52	14.57	7.50	1.08	0.57
	Sarımsaklı	63	7.54	0.09	5.5	1.07	11.47	146.0	0.68	10.44	7.90	1.60	0.29
	Pınarhisar	46	7.44	0.06	13.5	1.65	8.93	95.0	0.49	19.58	9.02	2.06	0.32
2014	Kırklareli	49	7.55	0.02	5.78	1.33	15.70	76.65	0.82	7.19	4.70	3.54	1.07
	Edirne	45	5.60	0.03	0.0	0.96	22.20	56.90	0.44	79.39	33.90	1.72	0.57
	Tekirdağ	59	7.74	0.04	6.80	0.87	7.21	29.07	0.43	2.17	3.36	3.16	0.15
	Keşan	64	7.56	0.06	5.44	1.45	11.33	93.98	0.68	6.84	5.42	0.93	0.34
	Sarımsaklı	89	7.82	0.08	6.20	1.49	10.10	137.1	1.56	8.19	9.26	1.15	0.19
	Pınarhisar	65	7.23	0.06	0.0	1.23	12.01	98.71	1.25	15.02	7.40	1.48	0.26
2015	Kırklareli	51	7.79	0.042	17.5	1.22	9.65	54.85	0.72	22.35	6.02	4.36	1.26
	Edirne	39	5.46	0.028	0.2	0.48	27.40	68.75	0.46	136.9	29.47	1.83	0.88
	Tekirdağ	57	7.51	0.053	15.0	0.77	9.12	92.00	0.71	11.02	8.20	11.1	0.46
	Keşan	66	7.59	0.063	3.7	1.54	11.40	101.5	0.65	27.50	12.28	2.00	0.39
	Sarımsaklı	64	7.41	0.086	7.5	1.05	16.00	115.5	0.86	11.29	8.67	1.36	0.38
	Pınarhisar	75	7.33	0.074	5.5	1.46	7.52	123.3	0.67	16.87	5.97	1.80	0.37
	Kaynarca	50	4.82	0.013	-	0.65	18.20	31.30	0.27	68.24	29.76	0.58	0.44
	Velimeşe	38	5.09	0.007	-	0.33	22.80	37.10	0.22	73.60	23.27	0.72	0.57
	Boztepe	61	7.43	0.068	5.5	1.03	12.54	57.10	0.56	17.48	7.35	0.90	0.52
	Hayrabolu	55	4.69	0.016	-	0.91	33.10	46.20	0.42	104.7	69.64	1.46	0.37
2016	Kırklareli	42	7.60	0.018	38	1.42	17.10	39.8	0.66	9.28	4.88	4.52	4.20
	Edirne	39	5.46	0.017	0.0	0.49	18.60	37.4	0.32	37.8	30.92	1.56	0.66
	Tekirdağ	57	7.83	0.043	17.5	1.02	11.30	42.8	0.64	7.68	10.4	5.4	0.41
	Keşan	58	7.85	0.041	9.0	1.93	10.10	60.0	0.68	15.08	7.52	1.98	2.34
	Pınarhisar	63	7.77	0.042	53	1.52	13.70	44.3	0.40	20.92	4.52	2.02	0.60

Soil samples were air-dried in the shade and sieved through a 2 mm sieve for inorganic nitrogen ($NH_4^+NO_3^-N$) analysis as stated by Bremner (1965). Then, 10 g of soil sample for analysis was placed in a 250 ml Erlenmeyer and 100 ml of 2M KCl (1/10 ratio) was added. The flask was sealed with a rubber stopper and shaken for 1 hour and waited for about half an hour until the soil settled to the bottom. The ammonium and nitrate nitrogen amounts were determined by distillation method by taking 30 ml of the upper clear liquid. For $NH_4^+NO_3^-N$, 0.2 g MgO and 0.2 g Devarda alloy were added to the extract. Then 30 ml of the extract was taken and 0.2 g MgO was added to determine NH_4-N nitrogen. The amount of NO_3-N is determined by subtracting NH_4-N from $NH_4^+NO_3^-N$. The amount of nitrite was neglected due to very low content in soils (Bremner, 1965).

Nitrogen Fertilization Calibration Based on the Amount of Mineral Nitrogen in Soil

The Mitscherlich equation "$\log (A-Y) = \log A - c_1 b_1 - c_x$" modified by Bray (Yurtsever, 1969) was used for the collective evaluation of nitrogen fertilizer trials, and c_1 values were found for soil nitrogen (b_1) and c values were found for fertilizer nitrogen (x_1+x_2) x represents N levels.

Calculation of the Maximum Yield

The equation “$A = \frac{Y_k - Y_0}{k-1}$” was used to determine the amount of N that should be supplied to the soil in order to reach different levels of maximum yield (90%, 92%, 94%, 96%, 98%). The calculation methods of calibration values can be briefly summarized as follows.

a) Calculation of the Impact Value of Soil Nitrogen (c_1)

By using the equation log(A-Y_0) = logA-c_1b_1, c_1 was calculated for each trial.

*The average yield of the plots with the highest yield (9 kg da^{-1} N application) is A, the average yield of the control plots is Y_0, the soil analysis value is b_1

b) Calculation of the Impact Value of Fertilizer Nitrogen (c)

By using the equation log (A-Y) = log A-c_1b_1-c_x, c was calculated for each trial.

By the formulas given above, c_1 and c values were calculated for each trial and nitrogen level, their averages were taken and c_1 and c values were obtained for sunflower grown in the climate and soil conditions of the Thrace region.

c) Calculation of Maximum Yield

The formula "$A = \frac{Y_k - Y_0}{k-1}$" was used.

A = Maximum yield
Y_0 = Yield of control plot
Y = Average crop yield for each nitrogen level
k = antilogarithm of cx
x = Nitrogen dose
c = Effect value of fertilizer nitrogen

Maximum yield is found for different nitrogen levels (x_1, x_2) in each trial and evaluated by taking the average.

d) Calculation of Baule Units

One baule unit of nutrient (nitrogen) increases yield by 50% of the difference between the present yield and maximum possible yield. Baule unit for soil nitrogen is obtained by solving the equation *log (A-Y_0)=log A - c_1b_1* in terms of b, by substituting 100 for maximum yield A, 50 for Y_0, and the calculated average value for c_1.

Baule unit of fertilizer nitrogen is obtained by the equation log (A - Y_0) = log A - c_x, by substituting 100 for maximum yield A, 50 for Y_0, and the calculated average value for c.

e) Determination of Crop %

The ratio of other nitrogen levels to the highest nitrogen level is determined and multiplied by 100. The smaller the % values, the higher the nitrogen requirement.

Crop%= (Y_0/Y_3) x 100
Y_0: Sunflower yield obtained in control
Y_3: Sunflower yield obtained in x_3 (the highest average yield)

f) Classification of Sufficiency Percent in Terms of Nitrogen Content of Soil

In the equation log (100-Y_0) = log100-c_1b_1, the previously known value of c_1 was substituted and Y_0 is found by giving b_1 increasing values starting from 2. This value has been determined based on the consideration that significant results can be obtained from every additional 2 kg ha^{-1} of N in the soil, taking into account the NH_4+NO_3 amount in the trial soils (3.95-21.8 kg da^{-1}).

g) Determination of the amount of nitrogen to be applied

By substituting the previously determined parameters b_1, c_1, c_1, and c in the equation log (100-Y_0) = log100-c_1b_1-c_x, the amount of nitrogen (x) to be applied for the targeted levels of maximum yield (such as 90%, 92%, ... 98%) for the parameter Y_0 was calculated by substituting the previously determined parameters b_1, c_1, and c. The 20 kg da^{-1} NH_4+NO_3-N in the soil, which is determined in Boule units and is sufficient to take more than 98% of the crop, a classification was made for sunflower by dividing into five parts (0-4), (4-8), (8-12), (12-16) and (16-20).

h) Calculation of Economic Fertilizer Amount

Mitscherlich equation was used and the theoretical maximum product level of all trials was used for A in the equation, c_1, b_1, and c parameter values were substituted and fertilizer levels such as 1, 2, 3, 4 ... were written for x and Y values were determined for each fertilizer level. To perform the economic analysis, both marginal product and marginal fertilizer amounts were determined by using the current fertilizer marginal revenue values.

Results and Discussion

Soil Characteristics of the Experimental Area

In this study, 6 field trials were conducted in 2013, 6 in 2014, 10 in 2015, and 5 in 2016 in Thrace Region. The analysis results of soil samples taken from 0-20 cm depth before sowing were given in Table 3.

While the results of all trials were used in determining the relationships between soil parameters and nitrogen fertilizer requirements of sunflower, the results of the trials in which the effect of nitrogen fertilization on crop yield was statistically significant at 5% and 1% levels were taken into account in calibration calculations. Regression was used to investigate the correlation and the results of the experiments with significance levels of 5% and 1% were used.

Mineral nitrogen contents in the trial areas

The $NH_4^+NO_3^-N$ and NO_3^-N contents of soil samples taken from different depths from the experimental areas are given in Table 4. It is preferred to determine sunflower yield based on $NH_4^+NO_3^-N$ rather than solely NO_3-N, as it is expected that NH_4-N determined in samples taken before planting will undergo nitrification shortly and turn into NO_3-N.

Table 3. Results of mineral nitrogen contents of trial areas

Location	Soil depth, cm	2013	2014	2015	2016
		$NH_4^+NO_3^-N$, mg kg^{-1}			
Kırklareli	0-30	10.15	10.5	22.61	33.95
	30-60	12.25	8.7	19.67	20.65
	60-90	14	9.6	14.07	16.45
Edirne	0-30	18.55	14.8	20.37	36.4
	30-60	9.1	15.7	12.95	21
	60-90	9.8	14.8	11.2	15.4
Tekirdağ	0-30	18.2	15.7	18.2	25.2
	30-60	30.8	13.1	19.6	25.55
	60-90	19.6	13.1	18.41	16.45
Keşan	0-30	24.15	35.75	21.35	34.65
	30-60	25.55	20.12	16.45	29.4
	60-90	20.3	19.2	16.1	25.9
Sarımsaklı	0-30	23.45	16.6	24.92	
	30-60	13.3	13.1	18.55	
	60-90	10.85	11.3	16.94	
Pınarhisar	0-30	30.45	19.2	20.58	58.1
	30-60	10.5	20.1	16.17	26.95
	60-90	19.25	17.5	14.35	25.9
Kaynarca	0-30			22.61	
	30-60			15.33	
	60-90			12.81	
Velimeşe	0-30			21.21	
	30-60			18.62	
	60-90			15.05	
Boztepe	0-30			19.53	
	30-60			14.07	
	60-90			13.44	
Hayrabolu	0-30			15.89	
	30-60			20.44	
	60-90			12.67	

Table 4. Sunflower crop yield, soil $NH_4^+NO_3^-N$ contents and Y_3 and % yield increase

Trials	$NH_4^+NO_3^-N$ (0-30cm)		Applied nitrogen, kg da^{-1}					Yield Increase (%) with Y_3*
			0	3	6	9	12	
			Yield, kg da^{-1}					
	mg kg^{-1}	kg da^{-1}	Y_0	Y_1	Y_2	Y_3	Y_4	
Ed-13	18.56	6.96	216	228	252	266	252	23.15
Tek-13	18.20	6.83	302	337	355	355	352	17.55
Kırk-14	10.52	3.95	155	176	205	240	208	54.84
Ed-14	14.80	5.55	242	261	283	299	289	23.55
Tek-14	15.72	5.90	147	155	190	184	174	25.17
Kırk-15	21.36	8.01	185	215	240	251	258	35.68
Ed-15	20.36	7.64	141	155	161	166	167	17.73
Tek-15	18.20	6.83	221	232	326	371	384	67.87
Keş-15	21.36	8.01	265	299	330	325	321	22.64
Sar-15	24.92	9.35	221	231	255	255	251	15.38
Pın-15	20.60	7.73	208	239	245	243	242	16.83
Kay-15	22.60	8.48	108	130	152	137	133	26.85
Vel-15	21.20	7.95	173	187	196	202	197	16.76
Boz-15	19.52	7.32	173	193	206	225	253	30.06
Tek-16	25.20	9.45	246	283	289	302	271	22.76
Kırk-16	33.96	12.74	190	265	244	213	201	12.11
Edir-16	36.40	13.65	241	280	270	265	262	9.96
Pın-16	58.12	21.80	239	284	286	265	256	10.88
Keş-16	34.64	12.99	185	262	238	242	226	30.81
			203	232	249	253	247	

*: Calibration calculations were made assuming 375 tons of soil in a decare of 0-30 cm depth.

Sunflower-Nitrogen Calibration Based on the Amount of Mineral Nitrogen in Soil

Sunflower-Nitrogen Calibration by Ammonium+Nitrate Content (0-30 cm depth)

In this study, calibration calculations were made based on the total amount of ammonium and nitrate in the soil at 0-30 cm depth before sunflower planting (Table 3). In Table 4, $NH_4^+NO_3^-N$ at 0-30 cm depth was converted from mg kg^{-1} to kg da^{-1}. In this conversion, 1 da soil was accepted as 375 tons. According to the results of variance analysis, the average yield values of the trials in which the effect of nitrogen was significant were taken and Y_3 and % yield increase were calculated and given in Table 4. The reason for taking Y_3 here is that maximum yield was reached at the N_3 fertilizer level in most of the trials and yield decreased at the N_4 level. In the calculation of % yield from Y_0 to Y_3; % yield increase = $100*(Y_3-Y_0) / Y_0$ equation was used.

The data obtained as a result of the calculation of percent (%) crop values and Mitscherlich constants are given in Table 6. The relationship between the increases in yield with nitrogen fertilization relative to Y_3 and soil analysis values (kg da^{-1}) at 0-30 cm is shown in Figure 2.

Table 6. Baule units of $NH_4^+NO_3^-N$ amount in soil and fertilizer for sunflower

Baule Units	Sufficiency %	Soil (0-30 cm) $NH_4^+NO_3^-N$, kg da^{-1}	Fertilizer (applied) $NH_4^+NO_3^-N$, kg da^{-1}
1	50.0	3.33	2.58
2	75.0	6.67	5.16
3	87.5	10.00	7.75
4	93.4	13.34	10.33
5	96.9	16.67	12.91
6	98.4	20.01	15.49
7	99.2	23.34	18.08
8	99.6	26.68	20.66
9	99.8	30.01	23.24
10	99.9	33.35	25.82

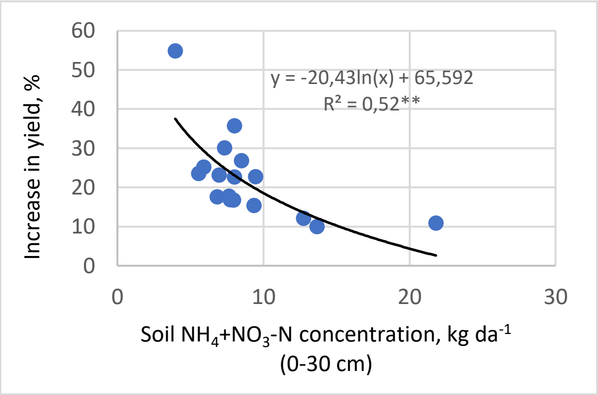

Figure 2. Relationship between increases in sunflower yield and the content of $NH_4^+NO_3^-N$ in the soil (0-30 cm)

Baule units (x) for ammonium+nitrate nitrogen in soil and fertilizer were calculated and given in Table 6. The calibration curve of ammonium+nitrate content at 0-30 cm soil depth for sunflower is given in Figure 3.

Based on the $NH_4^+NO_3$ nitrogen content in the soil at 0-30 cm, the nitrogen fertilizer demand of sunflower was determined by the formula log(A-y)= log A-c1b1-cx. The data obtained for sunflower with this formula are shown in Table 7 and the calibration curve is shown in Figure 4.

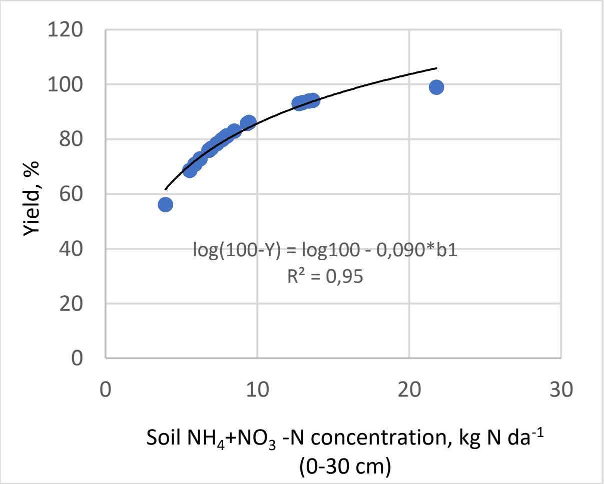

Figure 3. Calibration curve of $NH_4^+NO_3^-N$ content at 0-30 cm depth for sunflower

Economic Fertilizer Levels

The amount of nitrogen fertilizer to be applied to sunflower under rainfed conditions in the Thrace Region will depend on the amount of $NH_4^+NO_3^-N$ in the soil, the targeted yield percentage and the economic feasibility of the fertilizer to be applied. As can be seen from Table 8, as the amount of nitrogen in the soil increases, the amount of nitrogen to be applied will decrease depending on the amount of yield % targeted to be obtained. In this study, total and marginal crop yields were obtained at very low, low, medium, adequate, and high (4, 8, 12, 16, and 20) levels for different soil nitrogen contents by using the *log279,9-0,090b1-0,117x* functional equation (Table 8).

After determining the fertilizer-product relationships as above, it is possible to determine the economic fertilizer levels from fertilizer and crop-price relationships. For this purpose, the marginal crop amounts and marginal fertilizer amounts and their TL values are given in Table 9 (the price per kg of 33% ammonium nitrate fertilizer used in the trials for four years in 2016 was 0.85 TL (Anonymous, 2024a) and the price per kg of sunflower containing 40% oil was 1.7 TL (Anonymous, 2024b).

Table 5. Sunflower yield (%) and Mitscherlich constants with different amounts of nitrogen application

Trials	$NH_4^+NO_3$ kg da^{-1} (0-30cm)	Applied nitrogen, kg da^{-1}					Mitscherlich constants			
		X_0 Control	X_1 3	X_2 6	X_3 9	X_4 12				
		Yield, %					c_1 for b_1	c for X_1	c for X_2	Theoretical maximum yield
		Y_0	Y_1	Y_2	Y_3	Y_4				
Ed-13	6.96	81.22	85.81	94.66	100	94.66	0.104	0.040	0.090	293.1
Tek-13	6.83	85.06	94.98	99.94	100	99.21	0.121	0.157	0.354	383.7
Kırk-14	3.95	64.58	73.33	85.42	100	86.67	0.114	0.041	0.064	285.8
Ed-14	5.55	80.94	87.29	94.65	100	96.66	0.130	0.059	0.092	329.7
Tek-14	5.90	79.89	84.24	103.26	100	94.57	0.118	0.035		203.9
Kırk-15	8.01	73.71	85.66	95.62	100	102.79	0.072	0.088	0.130	286.6
Ed-15	7.64	84.94	93.37	96.99	100	100.60	0.108	0.119	0.116	179.5
Tek-15	6.83	59.57	62.53	87.87	100	103.50	0.058	0.011	0.087	451.8
Keş-15	8.01	81.54	92.00	101.54	100	98.77	0.092	0.121		357.3
Sar-15	9.35	86.67	90.59	100.00	100	98.43	0.094	0.050		273.3
Pın-15	7.73	85.60	98.35	100.82	100	99.59	0.109	0.314		261.9
Kay-15	8.48	78.83	94.89	110.95	100	97.08	0.080	0.206		152.6
Vel-15	7.95	85.64	92.57	97.03	100	97.52	0.106	0.095	0.114	217.6
Boz-15	7.32	76.89	85.78	91.56	100	112.44	0.087	0.070	0.073	253.0
Tek-16	9.45	81.46	93.71	95.70	101	89.74	0.077	0.156	0.106	332.2
Kırk-16	12.74	89.20	124.41	114.55	102	94.37	0.076			225.4
Edir-16	13.65	90.94	105.66	101.89	103	98.87	0.076			277.9
Pın-16	21.8	90.19	107.17	107.92	104	96.60	0.046			279.0
Keş-16	12.99	76.45	108.26	98.35	105	93.39	0.048		0.192	272.7
Average (c_1 and yield)							0.090	0.104	0.129	279.9
Average (x)								0.117		

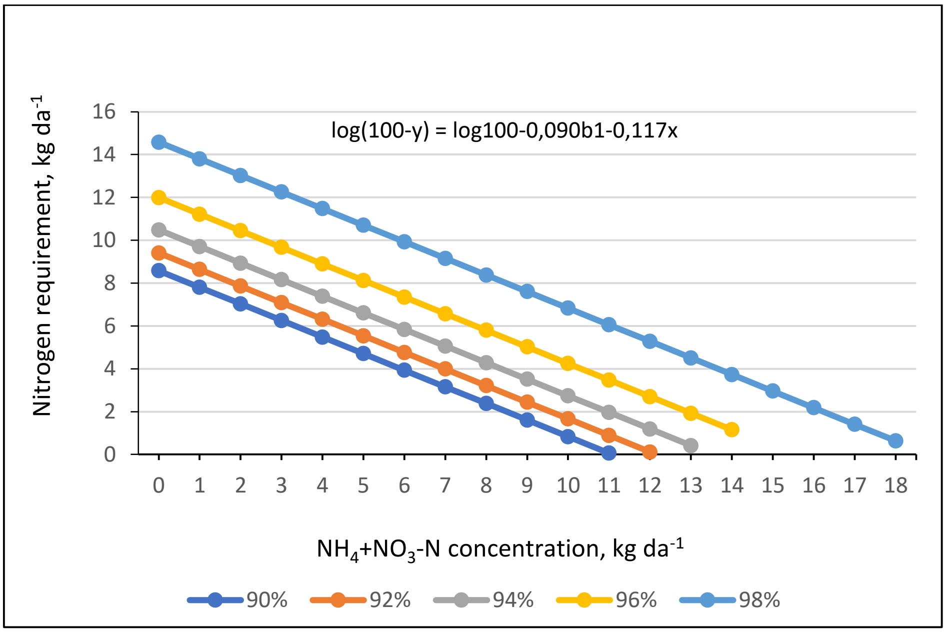

Figure 4. The relationship between the content of $NH_4^+NO_3^-N$ (kg da^{-1}) in the 0-30 cm soil depth and the nitrogen requirement of sunflower grown under rainfed conditions.

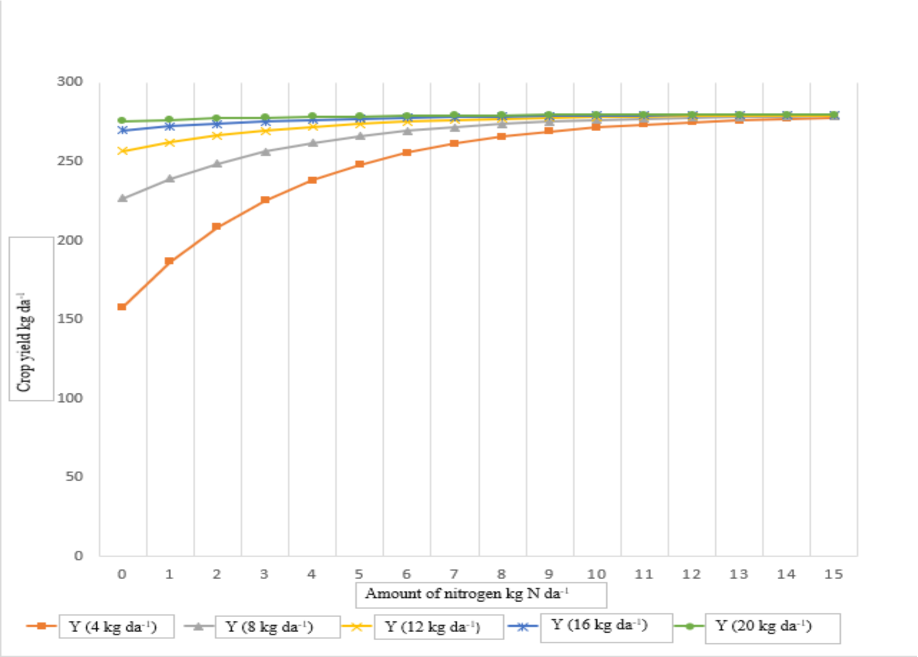

Figure 5. Relationship between nitrogen (NH_4+NO_3-N) content and sunflower yield under rainfed conditions

Table 7. Nitrogen amounts to be given to sunflower grown under rainfed conditions for different yield levels depending on the amount of $NH_4^+NO_3^-$N in the soil (0-30 cm)

$NH_4^+NO_3^-$N kg da^{-1}	Crop, %	Maximum crop percentage				
		90,%	92,%	94,%	96,%	98,%
		Amount of Nitrogen Required, kg da^{-1}				
1	18.77	7.80	8.63	9.71	11.22	13.80
2	34.01	7.03	7.86	8.93	10.44	13.02
3	46.40	6.25	7.09	8.16	9.67	12.25
4	56.46	5.48	6.31	7.38	8.89	11.48
5	64.63	4.71	5.54	6.61	8.12	10.70
6	71.27	3.93	4.76	5.84	7.35	9.93
7	76.66	3.16	3.99	5.06	6.57	9.15
8	81.04	2.38	3.21	4.29	5.80	8.38
9	84.60	1.61	2.44	3.51	5.02	7.60
10	87.49	0.83	1.67	2.74	4.25	6.83
11	89.84	0.06	0.89	1.96	3.47	6.06
12	91.74		0.12	1.19	2.70	5.28
13	93.29			0.41	1.93	4.51
14	94.55				1.15	3.73
15	95.57				0.38	2.96
16	96.40					2.18
17	97.08					1.41
18	97.63					0.64
19	98.07					
20	98.43					

Table 8. Total and marginal yields for sunflower

N kg da^{-1}	NH_4+NO_3- N marginal quantity	N kg da^1 (AN 33%)	b_1=4 kg da^{-1} very low		b_1= 8 kg da^{-1} low		b_1= 12 kg da^{-1} medium		b_1=16 kg da^{-1} adequate		b_1=20 kg da^{-1} high	
			Total crop kg da^{-1}	Marginal crop kg da^{-1}	Total crop kg da^{-1}	Marginal crop kg da^{-1}	Total crop kg da^{-1}	Marginal crop kg da^{-1}	Total crop kg da^{-1}	Marginal crop kg da^{-1}	Total crop kg da^{-1}	Marginal crop kg da^{-1}
0	1	3.33	157.99		226.79		256.75		269.79		275.47	
1	1	3.33	186.68	28.69	239.28	12.49	262.18	5.44	272.16	2.37	276.50	1.03
2	1	3.33	208.61	21.93	248.83	9.55	266.34	4.16	273.97	1.81	277.29	0.79
3	1	3.33	225.39	16.77	256.13	7.30	269.52	3.18	275.35	1.38	277.89	0.60
4	1	3.33	238.21	12.82	261.72	5.58	271.95	2.43	276.41	1.06	278.35	0.46
5	1	3.33	248.01	9.80	265.99	4.27	273.81	1.86	277.22	0.81	278.71	0.35
6	1	3.33	255.51	7.50	269.25	3.26	275.23	1.42	277.84	0.62	278.98	0.27
7	1	3.33	261.24	5.73	271.75	2.50	276.32	1.09	278.31	0.47	279.18	0.21
8	1	3.33	265.62	4.38	273.65	1.91	277.15	0.83	278.68	0.36	279.34	0.16
9	1	3.33	268.97	3.35	275.11	1.46	277.79	0.64	278.95	0.28	279.46	0.12
10	1	3.33	271.53	2.56	276.23	1.12	278.27	0.49	279.16	0.21	279.55	0.09
11	1	3.33	273.49	1.96	277.08	0.85	278.64	0.37	279.33	0.16	279.62	0.07
12	1	3.33	274.99	1.50	277.73	0.65	278.93	0.28	279.45	0.12	279.68	0.05
13	1	3.33	276.13	1.14	278.23	0.50	279.15	0.22	279.54	0.09	279.72	0.04
14	1	3.33	277.01	0.88	278.61	0.38	279.31	0.17	279.62	0.07	279.75	0.03
15	1	3.33	277.68	0.67	278.90	0.29	279.44	0.13	279.67	0.06	279.77	0.02
16	1	3.33	278.19	0.51	279.13	0.22	279.54	0.10	279.71	0.04	279.79	0.02
17	1	3.33	278.58	0.39	279.30	0.17	279.61	0.07	279.75	0.03	279.80	0.01
18	1	3.33	278.88	0.30	279.43	0.13	279.67	0.06	279.77	0.02	279.82	0.01
19	1	3.33	279.11	0.23	279.53	0.10	279.71	0.04	279.79	0.02	279.82	0.01
20	1	3.33	279.28	0.17	279.60	0.08	279.74	0.03	279.80	0.01	279.83	0.01

Table 9. Marginal crop and marginal fertilizer values and their TL values

N kg da^{-1}	Marginal ntirogen amount		Marginal nitrogen value TL	b_1 = 4 kg da^{-1} very low		b_1 = 8 kg da^{-1} low		b_1 = 12 kg da^{-1} medium		b_1 = 16 kg da^{-1} adequate		b_1 = 20 kg da^{-1} high	
	N	AN %33		Marginal crop kg da^{-1}	Marginal crop Value TL	Marginal crop kg da^{-1}	Marginal crop Value TL	Marginal crop kg da^{-1}	Marginal crop Value TL	Marginal crop kg da^{-1}	Marginal crop Value TL	Marginal crop kg da^{-1}	Marginal crop Value TL
1	1	3.33	2.55	28.69	48.77	12.49	21.24	5.44	9.25	2.37	4.03	1.03	1.75
2	1	3.33	2.55	21.93	37.29	9.55	16.24	4.16	7.07	1.81	3.08	0.79	1.34
3	1	3.33	2.55	16.77	28.51	7.30	12.41	3.18	5.41	1.38	2.35	0.60	1.02
4	1	3.33	2.55	12.82	21.80	5.58	9.49	2.43	4.13	1.06	1.80	0.46	0.78
5	1	3.33	2.55	9.80	16.67	4.27	7.26	1.86	3.16	0.81	1.38	0.35	0.60
6	1	3.33	2.55	7.50	12.74	3.26	5.55	1.42	2.42	0.62	1.05	0.27	0.46
7	1	3.33	2.55	5.73	9.74	2.50	4.24	1.09	1.85	0.47	0.80	0.21	0.35
8	1	3.33	2.55	4.38	7.45	1.91	3.24	0.83	1.41	0.36	0.62	0.16	0.27
9	1	3.33	2.55	3.35	5.70	1.46	2.48	0.64	1.08	0.28	0.47	0.12	0.20
10	1	3.33	2.55	2.56	4.35	1.12	1.90	0.49	0.83	0.21	0.36	0.09	0.16
11	1	3.33	2.55	1.96	3.33	0.85	1.45	0.37	0.63	0.16	0.27	0.07	0.12
12	1	3.33	2.55	1.50	2.55	0.65	1.11	0.28	0.48	0.12	0.21	0.05	0.09
13	1	3.33	2.55	1.14	1.95	0.50	0.85	0.22	0.37	0.09	0.16	0.04	0.07
14	1	3.33	2.55	0.88	1.49	0.38	0.65	0.17	0.28	0.07	0.12	0.03	0.05
15	1	3.33	2.55	0.67	1.14	0.29	0.50	0.13	0.22	0.06	0.09	0.02	0.04
16	1	3.33	2.55	0.51	0.87	0.22	0.38	0.10	0.16	0.04	0.07	0.02	0.03
17	1	3.33	2.55	0.39	0.67	0.17	0.29	0.07	0.13	0.03	0.05	0.01	0.02
18	1	3.33	2.55	0.30	0.51	0.13	0.22	0.06	0.10	0.02	0.04	0.01	0.02
19	1	3.33	2.55	0.23	0.39	0.10	0.17	0.04	0.07	0.02	0.03	0.01	0.01
20	1	3.33	2.55	0.17	0.30	0.08	0.13	0.03	0.06	0.01	0.02	0.01	0.01

Conclusion

In this study, sunflower-nitrogen calibration was made based on the mineral nitrogen forms (NH_4^+-NO_3^- N) at 0-30 cm soil depth as an alternative to the amount of soil organic matter used in nitrogen fertilization recommendations of sunflower under rainfed conditions. In order to determine the nitrogen fertilizer requirement of sunflower under rainfed conditions, log (279.9-y) = log279.9-0.090b_1-0.117x Mitscherlich calibration equation was determined. These calibration equations were evaluated with current crop and fertilizer prices to determine the amount of fertilizer that should be applied economically to obtain optimum yield in the presence of a certain amount of $NH_4^+NO_3^-N$ in the soil. The results of this study seem to be compatible with the evaluations stated by Mortvedt et al., (1996) regarding the amount of nitrogen that should be applied to sunflower based on the amount of mineral nitrogen in the soil.

Antoniadis et al., (2013) found no significant relationship between nitrate nitrogen and other soil properties (organic matter, texture, pH) when one-by-one correlations were sought in the model they developed to determine the nitrogen fertilizer requirements of sunflower, wheat, and maize, however, a significant relationship was found when multiple regression was performed when all soil properties were treated as independent variables. According to the results of this study, the level of mineral nitrogen in the soil can be used to determine the amount of nitrogen to be applied to plants such as sunflower, maize, and wheat.

Within the scope of the study, calibration equations could be obtained based on the amount of $NH_4^+NO_3^-N$ at 0-30 cm depth. Therefore, it is recommended to use the log (279.9-y) =log279.9-0.090b_1-0.117x functional equation to determine the nitrogen fertilizer requirement of sunflower under rainfed conditions in the Thrace Region. The use of these equations and their effects on yield can be determined by future studies.

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

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Author Contribution

MAG: Conceptualization, Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Project Administration, Resources, Supervision, Visualization, Writing -original draft. **TAK:** Data Curation, Formal Analysis, Funding Acquisition, Investigation, Methodology, Resources, Visualization, Writing -review and editing.

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REVİEW PAPER

The Use of Hose Reel Irrigation Machines and Energy Efficient Components in Irrigation

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Abstract

The energy consumed for irrigation is one of the most important inputs in crop production. Irrigation water is distributed within the parcel with minimum loss by using winged or gun systems together with a hose reel irrigation machine (HRIM). The increase in the amount of energy consumed for irrigation increases the cost of the unit product. To reduce the unit product cost, irrigation systems must be used with energy-efficiency units. Frequency converters (FC), pressure transmitters (PT), and programmable logic controllers (PLC) are among the components used to provide energy efficiency. A change in the amount of current drawn by the motors according to the changes in the required flow rate in the pumping facilities is possible by using FC, PT, and PLC. In addition, with more than one motor pump pair; it is necessary to use FC and PLC to be used by connecting in parallel, to operate with the principle of co-aging, and to make a soft start. Instantaneous pressure information is transmitted to PLC and FC via a PT to be installed on the collector in the discharge line in systems with parallel-connected pumps. In this way, the motor revolutions used to drive the pumps are changed via FC, in real-time according to the changes in the flow. Thus, pump-motor pairs are operated with the principle of "constant pressure variable flow" and energy savings are achieved.

Introduction

The increase in the world population day by day and the rapid decrease in agricultural areas make it necessary to use innovative technologies in the production of nutrients. For this reason, "food production and digitalization" have become two fields whose importance has increased and interaction has been studied in recent years. Accessible fresh water resources in the world are less than 1% of the total water resources and 77% of this amount is used in agriculture. If necessary, measures are not taken for the protection and efficient use of water resources in Turkey, in 2030, 49% of the total population and 78% of the irrigated agricultural areas will face the risk of water deficit. The averageirrigation efficiency in Turkish agriculture is 50%. It is aimed to increase this rate to 65% by using modern irrigation systems (Anonymous, 2023a). Measures taken due to global climate change are basically divided into two as structural and non-structural (Balta, 2023). These structural and non-structural measures are given below.

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Structural Measures can be listed as,

- Completion of storage facilities to develop economically usable water potential,
- Completion of inter-basin water transfer projects,
- The irrigation systems to be built should be pressurized irrigation systems,
- Transformation of traditional irrigation systems in agricultural enterprises to pressurized irrigation systems within the scope of renewal and modernization works,
- Ensuring that renovation and modernization works are carried out quickly by finding alternative financing methods,
- Increasing the transmission efficiency by meeting the maintenance and repair needs of irrigation facilities without delay within the scope of BAK-ONAR Projects,
- Ensuring fair and reliable transmission and distribution of water,
- Equipping irrigation facilities in enterprises with measuring equipment in order to detect losses and leaks,
- Expanding the use of automation systems in irrigation systems and
- Construction of the necessary facilities within the scope of the studies carried out for the use of used water in irrigation.

Non-structural measures are can be listed as,

- Preparation of operation programs for all dams that have been put into operation,
- Within the scope of Irrigation Management Activities, general irrigation planning according to plant water needs in irrigation facilities,
- In order to prevent the use of water more than needed, with the application of a gradual water usage service fee in pressurized irrigation facilities with suitable infrastructure,
- Information and coordination work on drought and the measures to be taken.

Yükçü and Atağan (2009) define the concept of productivity as the production of an output with the least cost, and the concept of efficiency as the ability to do things right through an input-output mechanism. Inputs such as water and energy are used more efficiently with innovative technologies in agricultural production. For productivity, it is necessary to use high-tech components in modern systems instead of components found in traditional systems. Those who resist the transformation of traditional systems into modern systems will not be successful. However, those who use technologies such as artificial intelligence will be successful (Gül, 2023). Climate changes caused by global warming have made it necessary to use water resources and the energy consumed for irrigation efficiently. For this reason, traditional irrigation systems should be abandoned and should be adopted modern irrigation systems using digital techniques and objects. The effects of climate change, seen in many fields such as engineering, economy, social and cultural, are waiting for cost-effective solutions (Şen, 2009).

Apart from the question of what the pump characteristics should be, the most important question to be asked while designing the pumping facilities of agricultural irrigation systems is whether different amounts of flow will be needed. The answer to this question by many farmers who produce plant varieties in different families, genera and species is “Yes”. Because the total amount of water needed by plants is different of different genera and different species in the same family during the growth and development period. For example, the water consumption of cool climate cereals and warm climate cereals, all of which are in the cereal family (Gramineae), differ from each other. In order to show the relationship between the water consumption of some cereal species and the dry matter production rate, the amount of dry matter they provide with 1 liter of water and the amount of water they consume to produce 1 g of dry matter are given in Table 1. According to the findings obtained from different researchers, it is stated that cool climate cereals consume 500-700 grams of water for the production of 1 gram of dry matter, while hot climate cereals consume 300-400 grams of water (Kün, 1994). However, a significant part of the total amount of water needed in cool climate cereals is met by natural precipitation. In hot climate cereals, a significant part of the total water need is met by irrigation.

Table 1. Ratio of water consumption and dry matter production of some cereal species (Kün, 1994)

Species		Dry matter supplied with 1 liter of water (g)	Water consumed for 1 gram of dry matter (g)
Winter Cereals	Rye	1,46	690
	Oat	1,70	590
	Wheat	1,94	515
	Barley	2,30	495
Summer Cereals	Corn	2,72	370
	Sorghum	3,11	320
	Millet	3,20	315
	Canarygrass	2,86	350

The water needs, irrigation times and methods of different species in different families such as starch and sugar plants, cereals, legumes, meadow-pasture and forage plants, medicinal and aromatic plants, oil plants, vegetables and ornamental plants are quite different from each other. However, plant type is not the only effective factor in determining the required flow rate and head when designing a pumping plant for irrigation of different species. For this reason, when designing a pressurized irrigation system, physical parameters such as hydraulic radius, irrigation line length, and number of branches separated from the main line, number of fixtures installed on the main line and laterals, and suction and discharge heights are used to calculate the pump characteristics. In addition to these, it is necessary to know which plant species will be grown in how much area and the maximum amount of water to be consumed.

One of the ways to save energy in pumping facilities is to use more than one pump in parallel for the flow rate to be provided by the facility. The flow rate of a pump can be changed instantly by changing the number of revolutions. The flow rate to be provided by a pumping facility with more than one pump is also provided by instantaneously changing the number of pumps operated simultaneously to feed the same collector in that pumping facility. The need for automation components both to use more than one pump and to manage these pumps as desired increases the investment cost. However, the supplied automation components will amortize for themselves after a certain period. Atay et al. (2009) stated that as a result of the studies they carried out within the scope of the Photovoltaic (PV) Power Supported Micro Irrigation System Project, the use of solar energy, which is a renewable resource, instead of energy obtained from fossil fuels, should be included in energy policies in order to both reduce imports and obtain cleaner energy.

Hose Reel Irrigation Machine and Energy Efficient Components

Hose Reel Irrigation Machine

Hose reel irrigation machine (HRIM) is a trailed type machine. The machine consists of two parts, the body and the water distributor. The body part is connected to the water source and does not move during irrigation. The water distributor is drawn to the head of the parcel to be irrigated and is linearly moving. The water distributor can be easily used on sloping plots. The machine is extremely easy to use, maintain and transport from one place to another. Hose reel irrigation machines are preferred by businesses or farmers with medium-sized land with a mwater source. Hose reel irrigation machines can be used with both boom and gun water distributor. The boom has a small diameter and many, while the water distributor with a gun has a large diameter and one nozzle. Boom is preferred for irrigation in low water pressure and windy conditions. In addition, the water distribution uniformity of the boom is higher than the uniformity of the gun.

There is a water turbine-gearbox pair that produces the necessary moment for the polyethylene (PE) irrigation pipe on the hose reel irrigation machines to be wound on the drum. Hoses with a length of 500 m can be used in these machines. The water turbine drives the ring gear on the drum with the help of the gearbox with four different speed stages and enables the drum to move. Generally, the water turbine and the gearbox are integrated. The boom or gun water distributor used with the machine can be easily mounted on the carrier arms by using the hydraulic system on the machine and the road condition can be reached. The drum, which is mounted on the tower on the trailer, can rotate to the right and left in the horizontal plane to scan 270° angles. The water usage efficiency of these machines is quite high (~ 99%). For this reason, they ensure efficient use of the energy in the transmission of irrigation water to the plant root zone. An image of a hose reel irrigation machine with a boom is given in Figure 1.

Figure 1. Hose reel irrigation machine with a boom

Energy Efficient Components

Correctly Selected Pump-Motor Couple for HRIM

Hose reel irrigation machines can distribute water at high capacity (30-90 m^3/h). Therefore, they should be supplied with pumps that can press water at high capacity. If the right pump and the right motor are not selected to be able to pump water at high capacity, more energy is consumed than is needed. Vertical pumps are preferred because they lubricate with water and take up less space. In addition, since there is no transmission mechanism between the motor-pump pairs in vertical pumps, the efficiency is higher. Images of vertical shaft pumps used for hose reel irrigation machines are given in Figure 2 (Polat and Bowler, 2010). The characteristics of the pumps are 150 m and 100 m^3/h. The power of the electric motors used to drive the pumps is 90 kW.

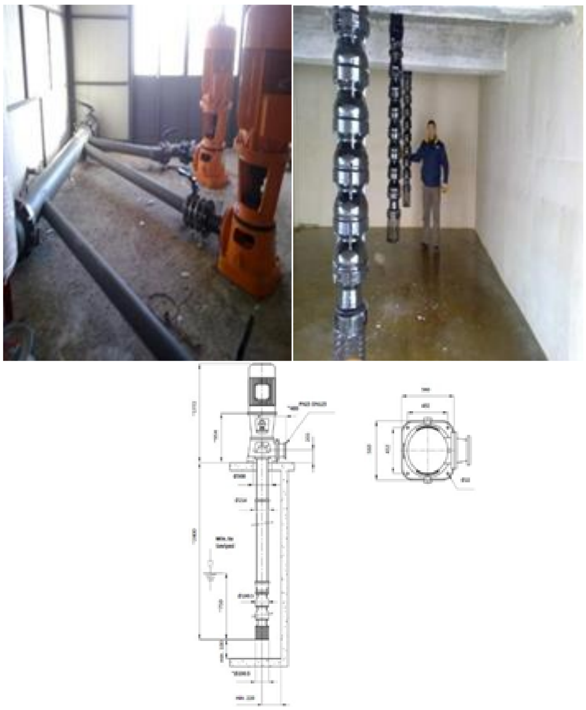

Figure 2. Parallel connected vertical pumps (Polat and Bowler, 2010)

Frequency Converter

Different types of plants can be produced in different sizes parcels. Therefore, different amounts of irrigation water are needed at different times for different plant species produced in these different sized parcels. Pumping plants with large capacities may need to be operated at a value below their capacity. Pumps that provide small flow can be connected in parallel to increase the flow. Similarly, it is possible to reduce the flow rate by sequentially deactivating the pumps connected in parallel or by reducing the number of revolutions. Changing the revolutions of the pumps driven by electric motors is provided by changing the revolutions of the electric motors. Changing the number of revolutions of electric motors is also provided by changing the frequency of the alternating current. Frequency converters (FC) are used to change the frequency of alternating current.

Frequency converters are generally used with high-tech components. By using frequency converters together with automation systems, it is ensured that the electric motors used to drive the pumps connected in parallel are operated at different speeds, they are put into operation in a sequential manner and they start to work by making a soft start. Thus, the electric motors are not suddenly loaded into the grid and mechanical stresses are prevented.

Energy saving is achieved by adjusting the motor speed according to the need. About 20% of the total energy produced in the world is consumed in pumping systems, especially centrifugal pumps (Shankar et al., 2016). Therefore, efforts to save energy in enterprises using centrifugal pumps are very important in terms of both unit product cost and environment. Using a frequency converter with water pumps reduces energy consumption by about 15-20% (Yimchoy and Supatti, 2021). The image of the frequency converter used to feed a submersible pump and an inline pump by operating at different speeds is given in Figure 3.

Figure 3. Frequency converter used in series connected pumps

Pressure Transmitter

One way to save energy in farms where variable amounts of irrigation water are needed is to use more than one pump in parallel. With the activation and deactivation of each pump connected in parallel, the amount of water pumped into the line used in water transmission increases and decreases as the flow rate of each pump. Similarly, an increase or decrease in the number of laterals connected to the irrigation line causes the line pressure to decrease or increase, respectively. For this reason, operating the pumps according to the required flow rate ensures efficient use of energy.

Different types of each water distributors (nozzles, sprinkler heads, etc.) used in irrigation systems have their own operating pressure ranges. These different types of distributors irrigate at the most suitable operating pressures with the most appropriate wetting radius. Thus, the areas wetted by the successive water dispensers are prevented from overlapping excessively or not at all. The important issue for proper water distribution in pressurized irrigation systems is to transmit water to the distributors at a constant pressure throughout the irrigation period. Deactivation or activation of one of the laterals during irrigation in an irrigation line causes the line pressure to change. Therefore, the water distribution uniformity is disturbed. For this reason, the line pressure should be measured instantly and digitally reported to the automation system used to manage the pumps.

Pressure transmitters reliably convert small pressure changes into electrical signals as well as large pressure changes. They usually produce a 4-20 mA output signal. They react to pressure changes in pressurized lines within a few milliseconds (Anonymous, 2023b). An image of a pressure transmitter used in irrigation systems is given in Figure 4.

Figure 4. A pressure transmitter used in irrigation systems (Anonymous, 2023b)

Programmable Logic Controller

Automation systems are used in every field of industry, and their use in agricultural production is increasing day by day. Production is carried out successfully with automation systems used in different disciplines of agricultural production such as seed selection units, milking facilities and irrigation system. Reasons such as the increase in the human population in our country and in the world, the decrease in agricultural production areas, and the low number of qualified producers cause the product costs to increase. Therefore, it is a necessity to use automation systems in order to reduce product costs and obtain quality products.

Today, when automation is mentioned, almost everyone thinks of Programmable Logic Controller (PLC). However, automation does not mean a system consisting only of PLC. PLCs are devices that control the actuators by evaluating the data received from the sensors and other devices in the system within the scope of the preloaded logic program (Karaçor and Keleş, 2007). For example, PLCs provide variable-speed management of pumps by using the data from the sensor that measures the irrigation line pressure. Thus, energy is used efficiently. The images of PLC used in an irrigation pumping plant operating with constant pressure variable flow principle are given in Figure 5.

Figure 5. PLC used in an irrigation pumping plant

Polyethylene Pipes

Polyethylene (PE 100) pipes; It is used in many areas such as agricultural irrigation and drainage systems, sea discharge systems, sewage discharge systems, geothermal systems and underground drinking and utility water lines. The advantages of polyethylene pipes are given below as items (Anonymous, 2009c).

- They are long-lasting and do not rust,
- Due to their flexibility, they are not affected by the topography during their establishment and then by soil movements,
- They are robust due to their high crack and impact resistance,
- Due to their high resistance to corrosion, they do not rot and corrode,
- They do not require cathodic protection measures,
- Due to the smooth inner surfaces, less friction will occur during operation, so less electrical energy is consumed,
- They are not affected by sunlight (Ultraviolet) because they contain catalysts,
- They can be perfectly welded with each other or with armatures by butt welding or electrofusion methods,
- Due to their lightness, they can be laid easily and quickly,
- It can be produced for any pressure class,
- They are frost resistant.

"Internal surface smoothness", which is one of the features listed above, is extremely important in terms of reducing the "system friction losses" seen in pressure pipelines used in water transmission and distribution in irrigation systems. The fact that the system friction losses are low means that the irrigation is done with less energy consumption. In other words, it means increasing energy efficiency.

The images of the PE 100 pipes used to feed the hose reel irrigation machines and the jointing works by the butt-welding method are given in Figure 6.

Figure 6. PE 100 pipes and jointing works by butt welding method

Flowmeter and Water Meter

Flow rate in irrigation systems is defined as the amount of water passing through a line per unit time and is measured with a flow meter. The amount of water pumped by the pumps per unit time is also a flow rate. The flow rate, symbolized by the letter "Q" in the continuity equation, is equal to the product of the area of the cross section (A) through which the fluid passes, and the fluid velocity (V). Therefore, units such as L/s, L/h and m^3/h are used to indicate the amount of flow.

Counters are used to measure the total amount of fluid passing through a line. A water meter is a measuring instrument designed to measure, store and display the volume of water coming from the measuring transducer under measuring conditions (Çiftçi, 2008). Many types of meters have been developed for water measurement. By adding a GSM module to the recently developed meters, remote reading and high accuracy measurement can be made. Energy saving is achieved due to the low shape losses caused by these meters, which have a flat measuring tube that is resistant to wear and has no moving parts. In addition, the meters, which have a dustproof and submersible protection class (IP 68), can be used by mounting underground (Anonymous, 2023d). The image of a high-tech water meter that can be used to measure the amount of instant and total water consumed is given in Figure 7.

Figure 7. A water meter with a high technological level (Anonymous, 2023d)

Turkish farmers use 74% of the water potential in Turkey for agricultural irrigation. Due to such a high water consumption, meter systems should be used in order to save water in agricultural irrigation (Özbek, 2023). Farmers who do not have sufficient awareness may consume more water than necessary despite using pressurized irrigation systems such as drip or sprinkler. Excessive use of water will not increase the yield, but it also causes the emergence or increase of many problems such as salinity, washing of plant nutrients, soil erosion, and the proliferation of diseases and pests. Measuring the amount of irrigation water consumed with a meter is important in terms of efficient use of both the water and the energy consumption in water transmission and distribution.

Photovoltaic Panel

Wind energy is converted into electrical energy by using wind turbine and solar energy using photovoltaic panel (PV). Therefore, the electric motors used in irrigation systems can be fed independently from the electricity grid by systems using wind turbines or PV panels. For this reason, in areas with frequent power cuts, irrigation can be done without any problems by using a wind turbine or PV panel. However, the use of solar panels in electricity generation is more common than wind turbines. This is because there is not always enough wind to produce enough electricity in every area. Therefore, electricity generation from solar panels is also more common in irrigation. Irrigation can be done independently of the electricity grid with systems using thermal motor-pump couple. However, these systems require periodic maintenance and refuelling. On the other hand, the maintenance and operating costs of renewable energy systems, which have relatively high installation costs, are quite low (Atay et al., 2011).

With a general definition, fertilization is the delivery of plant nutrients to the plant and/or plant root zone. Fertilization and irrigation are essential cultural practices in crop production. The images of the works made by using a fertilizer spreader and solid granular fertilizer in wheat production are given in Figure 8. Burt, (1995) stated that systems with high water distribution uniformity, which are more environmentally friendly and can make sensitive applications with low energy consumption, have been developed in the last 20 years in the irrigation industry. Burt explained that in some state's irrigation water is priced according to the efficiency principle. Burt even stated that there are systems that start and stop irrigation according to the weather and soil moisture with the help of computers and sensors. Burt explained that these systems could be used with systems such as drip irrigation, subsurface drip irrigation and micro sprinkler. In addition, referring to the report published by the California Polytechnic University ITRC (Irrigation Training and Research Center) Board and stated that as much as the energy used in the production of chemical fertilizers, energy is consumed in their distribution within the production area. He stated that the systems to be designed in the future would be advanced equipment called "fertigation technique", which mixes plant nutrients into irrigation water according to the need in order to increase crop yield.

Figure 8. Fertilizer application studies in wheat production

In a recently developed fertigation system, a 25 W solenoid-based dosing pump was used to pump liquid fertilizer into the water inlet pipe of hose reel irrigation machines. There is a monocrystalline photovoltaic panel with a maximum output power of 195 WP in the system in order to meet the electricity need of the dosing pump used independently from the grid. Liquid chemical fertilizers could be mixed with the components used in the system with a high homogeneity of 99% into the irrigation water (Polat et al., 2022). Thus, it has been revealed that fertilization can be done by irrigation in enterprises using hose reel irrigation machine, without using solid granular fertilizer with tractor and fertilizer spreader. It has been explained that the fertigation application using a photovoltaic panel with a hose reel irrigation machine is a suitable technique for energy efficiency by eliminating the necessity of energy expenditure for fertilizer distribution (Polat and Çolak, 2022). The images of the fertigation system components developed for hose reel irrigation machines are given in Figure 9.

Figure 9. Images of the fertigation system developed for HRIM

The performance of a "fixed solar cell irrigation system" established in Şanlıurfa to take advantage of the high solar energy potential has been analyzed. In the first year of the study, which was carried out with the drip irrigation method, an accumulator was used with photovoltaic panels. In the second year, irrigation was done without using accumulators. At the end of the operation, irrigation can be done at any time of the day or for 24 hours when the accumulator is used; however, it has been determined that irrigation cannot be done in the early morning and cloudy weather when the accumulator is not used (Atay et al., 2012).

Float valve

Float valves are used to ensure that the water level in the pools used as reservoirs is not higher than the desired maximum level. The valve, which has an object that acts as a floater is installed at the water inlet of the buildings used as reservoirs. The floater ensures that the valve closes when the water level rises. Images of float valves used in a pool built for more than one hose reel irrigation machine are given in Figure 10.

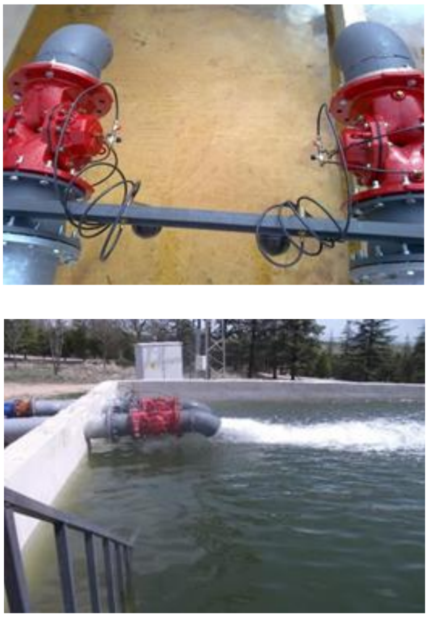

Figure 10. Float valves

Conclusion

The aim of this study is to explain how energy efficiency and water savings are made in irrigation with hose reel irrigation machines. Written to achieve the stated purpose, this article has been prepared by compiling the professional experience and the information obtained from the referenced sources. In this context, it is mentioned that more than one hose reel irrigation machine is operated with the principle of "constant pressure variable flow". In addition, information is given about the components used in the operation of hose reel irrigation machines with the said principle. The block diagram showing the operation of hose reel irrigation machines with the principle of constant pressure variable flow is given in Figure 11.

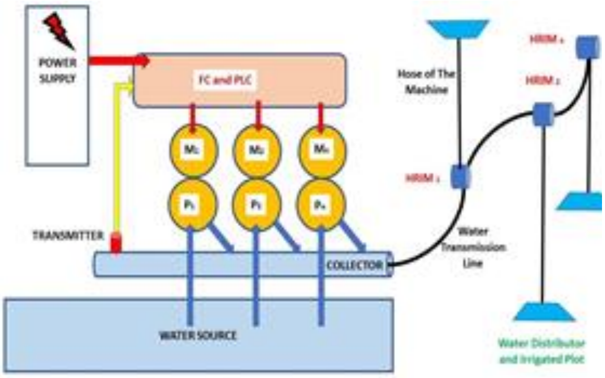

Figure 11. Block diagram of constant pressure variable flow principle

Hydrants are usually installed on the pressure line extending from the collector outlet to the farthest parcel, at intervals equal to the maximum working width of the hose reel irrigation machines. Irrigation can be done by connecting more than one hose reel irrigation machine to these hydrants at the same time. The principle of constant pressure variable flow rate is to keep the collector pressure constant no matter how many hose reel irrigation machines areconnected to the hydrants in the pressurized line. In other words, changes in flow rate do not cause a change in line pressure.

The benefits of feeding hose reel irrigation machines using pumping facilities operating with the principle of constant pressure and variable flow are given below.

- Operating the hose reel irrigation machine under constant pressure ensures that the water distribution uniformity is realized at a high rate and with a constant working width.
- More than one hose reel irrigation machine can be fed from a center.
- Components such as turbine, gearbox, PE pipe that make up the hose reel irrigation machine are not damaged because there are no sudden changes in pressure.
- The required amount of irrigation water is supplied to the pressurized pipeline regardless of the number of hose reel irrigation machines used laterally, thus saving water and energy.
- Energy saving is achieved by keeping the collector pressure at the “operating point” value of the pumps.

In order to provide both energy efficiency and water saving, the purpose of the components used in pumping facilities that feed with the principle of constant pressure and variable flow is given below.

- The purpose of using vertical pumps with high efficiency is to reduce maintenance and repair costs, increase profit and provide energy savings.

- The purpose of using FC is to operate the pumps at variable speeds and to provide a soft start of the electric motors.
- The purpose of using PT is to convert the collector pressure into an electrical signal and transmit it to the PLC unit.
- The purpose of using PLC is to operate the pumping system with constant pressure variable flow principle. In addition, the operation of the motors with the principle of co-aging and soft starting is also carried out using PLC.
- The purpose of using PE 100 pipe is to transmit water without being affected by the topography, to reduce friction losses, to save energy and to prevent water losses.
- The purpose of using flow meters and water meters is to measure instant and total water consumption and to ensure fair use of water.
- The purpose of using PV panels is to feed the electrically powered components independently from the grid.
- The purpose of using float valve is to prevent possible water losses in structures used as reservoirs.

An irrigation system with a high technological level and the components in the system should be introduced to all stakeholders, especially farmers. Policies should be developed by governments to establish and support these systems. In this way, on our planet, which is under the threat of global warming, energy consumption will be reduced by protecting the extremely important water resources.

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