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Publishers Ethic Rules

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Efficiency of Resource-Use and Marginal Value Productivity Analysis Among Maize Farmers, Abuja, Nigeria

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Abstract
The study examined efficiency of resource-use and marginal value productivity analysis among maize farmers, Abuja, Nigeria. Specifically, the objectives were to: determine the socio-economic characteristics of maize farmers, analyze costs and returns of maize production, determine the marginal value productivity among maize farmers, evaluate resource-use efficiency of maize production, and determine the constraints faced by maize farmers in the study area, multi-stage sampling technique was used to select one hundred (100) maize farmers. Primary data were used. Data were collected through the use of well-designed and well-structured questionnaire. The analytical tools used were descriptive statistics, farm budgeting technique, financial analysis, Cobb-Douglas production function model, marginal value productivity index, resource-use efficiency index, and principal component analysis. The results show that 65% of maize farmers are less than 50 years of age. The mean age of maize farmers was 47 years. The maize farmers are energetic, active, resourceful in their youthful age. Maize farmers are smallholder, peasant, poor farmers with average of 4.75 hectares of farmland. Maize farmers had on the average of 8 people per household. Maize production is a profitable enterprise with gross margin and net farm income of 776,100 Naira and 758,700 Naira per hectare of farmland respectively. The gross margin ratio of 0.64 implies that for every naira invested in maize production by smallholder maize farmers, 64 kobo covered interest, profits, expenses, taxes and depreciation. Age (X_1), and fertilizer input 〖(X〗_4) are statistically significant factors influencing output of maize production at (P<0.01), while farm size 〖(X〗_2), labour input (X_3), seed input 〖(X〗_5) and chemical input 〖(X〗_6) are statistically significant factors influencing output of maize production at (P<0.05).The coefficient of multiple determinations (R^2) was 0.789. This implies that the explanatory variables included in the Cobb-Douglas production regression model explained 78.9% of variations in output of maize produced. The resource-use efficiency index [r], which is a ratio between marginal value productivity of resource input and marginal factor cost, the factor price shows that land input, seed input, fertilizer input, labour input and chemical input were underutilized. The retained constraints in the principal component analysis faced by maize farmers were lack of fertilizers, poor road infrastructures, lack of improved seeds, lack of credit facilities, lack of extension services and poor storage facilities. The study recommends adequate supply of farm inputs like improved seeds, fertilizers, chemicals such as insecticides and pesticides. Bureaucratic processes and cumbersome administrative procedures involved in accessing credit facilities should be removed, government should provide good roads linking maize producing areas and extension services should be employed who will organize workshops, seminars and training of maize farmers on research findings and efficient use of farm resources.

Key words
Efficiency of Resource-Use, Marginal Productivity Index, Maize Production, Nigeria.

Introduction

Maize (*Zea mays*) is the most important cereal crop in Nigeria. Maize ranks third coming after sorghum and rice which ranks second and first respectively (Alabi and Abdulazeez, 2018). Nigeria is African second largest producer of maize after South Africa (FAOSTAT, 2018). Maize serves as good sources of food for human, feed for livestock, also source of income and foreign exchange earnings to Nigeria. Maize is a good source of raw materials to different agro-based industries as it is an essential material for the industrial production of fuel, starch, medicine, and food sweeteners (Egwuma *et al*, 2019; Amanza *et al.*, 2021). In Nigeria, maize is used by brewing industries for producing various types of beer, production of maize flour by milling industries, corn flakes and confectionary for human consumption. Maize can be boiled, roasted or the grain can be dried, and the dried grain can be made into popcorn (Onuk *et al.*, 2010). It is a good source of minerals, protein, carbohydrates, iron, and Vitamin B. Maize can be grown in marginal areas, it has ability to grow in all ecological zones in Nigeria, that is why the production of maize is widespread across different parts of Nigeria (Ado *et al.*,2004; Yahaya, *et al.*, 2020). Maize production is well distributed in low rainfall and high rainfall around the world, it can grow in hot, humid tropical areas and cool temperate region and can thrive in wide ranges of soils (Philip *et al.*, 2006). Nigeria produces 10 million metric tonnes of maize in 2020 and 11.6 million metric tonnes of maize in 2021, this is about 16% increase over the previous year 2020 (USDA, 2021). As a result of low productivity of maize, Nigeria could barely satisfy the huge quantity of maize demanded which is estimated at 12 – 15 million metric tonnes of maize, in line with this, maize demand-supply create gaps of nearly 4 million metric tonnes of maize. The potentials of Nigeria to produce maize is enormous and the economic importance of maize to the rural populace is much, yet the country has not been able to produce maize to meet the food requirements and the needs of the industries. The inability of Nigeria to produce enough quantities of maize for both human and animal consumption and for local industries is due to low productivity of maize by resource poor farmers, in addition, smallholder farmers were not adopting and use improved technologies for maize production. Nigeria as reported on the average produces 1.69 tonnes of maize per hectare of land in 2019 (USDA, 2020). Among the developed countries, United States of America (USA) is the largest producer of maize in the world with about 383.94 million metric tonnes of maize in 2021/2022 and the average yield of 6 tonnes per hectare of land. According to Awotide *et al* (2008) and Ibrahim *et al* (2008) they all reported that inadequate fertilizers input, use of unimproved local seeds input, lack of farmland input and use of manual labour input limit maize output in Nigeria.

Extension services and easy access to research findings by peasant farmers is also capable of increasing maize output in Nigeria (Bamire *et al.*, 2007). The use of improved maize seeds and agricultural technologies can increase productivity. Resources such as pesticides, fertilizers, and herbicides are scarce, and when available the resource poor maize farmers cannot afford to purchase the quantities, he required. Maize farming is mainly dependent on rainfed system in Nigeria, rainfall is both resource and constraint to maize production in the tropics as maize relates to amount of rainfall and its distributions. Maize farming in Nigeria is also faced with lack of access to credit facilities, poor storage facilities, lack of farm inputs, pests and disease infestations, and lack of mechanized farming. The returns to land in terms of maize output is generally poor (Babatunde *et al.*, 2007). Improving productivity of resource poor farmers is crucial for improving the livelihoods, well-being of smallholder farmers and for economic development (Girei *et al.*, 2018, Msuya, 2008). Low productivity is the major cause of unstable and low value added along the maize value chain which leads to stagnation of the rural economy with high poverty level (Msuya, 2018). Smallholder maize productivity is generally low this is due to the fact that peasant farmers are poor, subsistence in nature and do not practice high yielding farming methods (Isinika *et al.*, 2003). According to Alabi *et al* (2021) farm resource productivity can be increased and improved when smallholder farmers properly understand efficient use of farm resources and how to select farm enterprises. Agriculture in Nigeria is faced with low farm productivity due to inefficient use resources available (Alabi, Oladele and Oladele, 2020; Udoh, 2005; Obasi and Agu, 2000). Efficiency with available technology and resource base can increase and sustain farm productivity (Alabi *et al*., 2021).

Objectives of the Study

The broad objective is to evaluate efficiency of resource-use and marginal value productivity analysis among maize farmers in Abuja, Nigeria. Specifically, the objectives were to:

(i) determine the socio-economic characteristics of maize farmers,
(ii) analyze costs and returns of maize production,
(iii) evaluate factors influencing output of maize production,
(iv) determine the marginal value productivity among maize farmers,
(v) evaluate the resource-use efficiency of maize production, and
(vi) determine the constraints faced by maize farmers in the study area.

Methodology

The research was conducted in Abuja, Nigeria. Abuja is located between Latitudes $9^0\,4^{|}20^{||}$ North and Longitudes $7^0\,29^{|}28^{||}$ East. Abuja has three weather conditions annually, they are: rainy season, dry season and the harmattan period. The brief harmattan period comes in between the rainy and dry seasons. Abuja falls within the savannah zone vegetation, the vegetation in the territory is classified into three savannah types: grassy savannah, savannah woodland and the shrub savannah. Abuja has population of about 776,298 people (NPC,2006). The population of Abuja in 2022 is about 3,652,000 people which is 5.43% increase over the population of 3,464,000 people in 2021(Figure 1). The people are engaged in agricultural production activities. They are involved in growing crops and animal production. Crops grown include: maize, millet, soybean, garden egg, beans, rice, yam, groundnut, sorghum. Animal kept include: poultry, goats, sheep, cattle, rabbit and turkey.

Multi-stage sampling technique was adopted. Sample size of 100 maize farmers were selected. Data used were of primary sources. Data were collected through the use of well-designed well-structured questionnaire. The questionnaire was administered to the target respondents through the help of well-trained enumerators. Data were analyzed through the use of the following analytical tools:

Descriptive Statistics: This involves the use of measures of central tendency which include: mean, percentages, and frequency-distributions. They are used to summarize data collected from the field survey from the target maize farmers. Descriptive statistics was used to summarize the socio-economic characteristics of sampled maize farmers as stated in specific objective one (i).

Farm Budgetary Technique: The farm budgetary techniques used was Gross Margin Analysis (GM) and is defined as the difference between gross farm income (GFI) and total variable cost (TVC). This tool of analysis was used to determine the costs and returns of maize production as specified in specific objective two (ii). The Gross Margin Model is stated thus:

$$GM = TR - TVC \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$
$$GM = \sum_{i=1}^{n} P_i Q_i - \sum_{j=1}^{m} P_j X_j \dots\dots\dots\dots\dots\dots (2)$$
$$NFI = TR - TC \dots\dots\dots\dots\dots . (3)$$
$$NFI = \sum_{i=1}^{n} P_i Q_i - \left[\sum_{j=1}^{m} P_j X_j + \sum_{k=1}^{k} GK\right] \dots\dots\dots . (4)$$

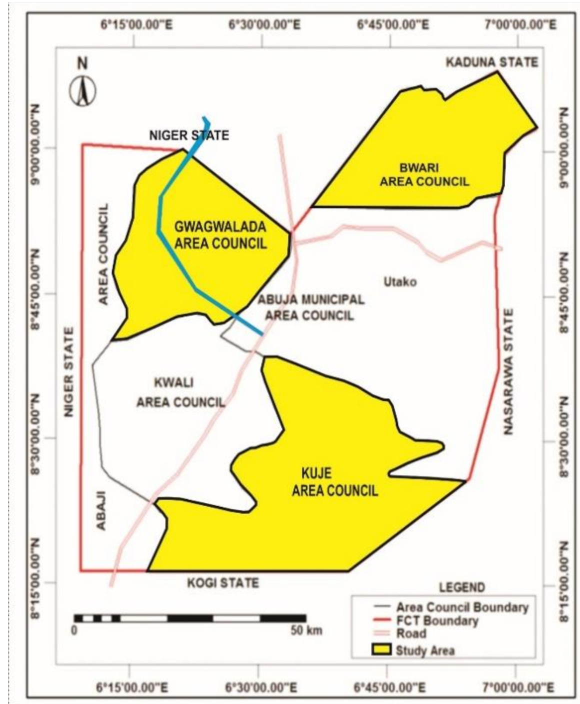

Figure 1: Map of Abuja Showing the Study Areas

Where; P_i = Price of Maize ($\frac{N}{Kg}$),
Q_i = Quantity of Maize (Kg),
P_j = Price of Variable Inputs ($\frac{N}{Unit}$),
X_j = Quantity of Variable Inputs (Units),
$TR =$ Total Revenue obtained from Sales from Maize (N),
TVC = Total Variable Cost (N),
GK = Cost of all Fixed Inputs (Naira)
NFI = Net Farm Income (Naira)

Financial Analysis: This is an analytical tool used to determine the profitability of maize production. The financial analysis was used to achieve part of specific objective two (ii). Gross Margin Ratio according to Alabi, Oladele and Oladele (2020) and Ben-Chendo (2015) is defined as:

$$Gross\ Margin\ Ratio = \frac{Gross\ Margin}{Total\ Tevenue} \dots\dots\dots\dots . (5)$$

The operating ratio (OR) according to Olukosi and Erhabor (2015) is defined as:

$$Operating\ Ratio = \frac{TVC}{GI} \dots\dots\dots\dots\dots\dots\dots\dots (6)$$

Where, TVC = Total Variable Cost (Naira),
GI = Gross Income (Naira),

According to Alabi, Oladele and Oladele (2020) and Olukosi and Erhabo (2015) an operating ratio of less than one (1) implies that the gross income from maize enterprise was able to pay for the cost of the variable inputs used in the enterprise. The rate of return per naira invested (RORI) in maize production according to Alabi, Oladele and Oladele (2020) is defined as:

$$RORI = \frac{NI}{TC} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Where, $RORI$ = Rate of Return per Naira Invested (Unit)
NI = Net Income (Naira)
TC = Total Cost (Naira)

Cobb-Douglas Production Function Model: The model is defined as follows:

$$Log\ Y = \alpha_0 + \alpha_1 Log\ X_1 + \alpha_2 Log\ X_2 + \alpha_3 Log\ X_3 + \alpha_4 Log\ + U_i \dots\dots\dots\dots (8)$$

Y = Output of Maize (Kg),
X_1 = Age of Farmers (Years),
X_2 = Farm Size (Hectares),
X_3 = Labour Input (Mandays),
X_4 = Fertilizer Input (Kg),
X_5 = Seed Input (Kg),
X_6 = Chemical Input (Litres),
U_i = Error Term,
$\alpha_1 - \alpha_6$ = Regression Coefficients,
α_0 = Constant Term,

This was used to achieve specific objective three (iii).

Marginal Value Productivity Index: This is defined as follows:

$$MP_x \times P_Y = MVP_x \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$\alpha_i \left[\frac{\bar{Y}}{\bar{X}_i}\right] \times P_Y = MVP_x \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where, MVP_x = Marginal Value Product of x,
P_Y = Price of Output (Naira),
$\bar{Y}$ = Mean Value of Output Y,
$\bar{X}_i$ = Mean Values of Input x_i,
MP_x = Marginal Physical Product of x,
α_i = Regression Coefficients

This was used to achieve specific objective four (iv).

Resource-Use Efficiency Index: This is stated as follows:

$$r = \frac{MVP}{MFC} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where, MFC = Marginal Factor Cost (Naira),
r = Efficiency Ratio (Unit),
$r = 1$ Resources is Efficiently Utilized,
$r > 1$ Resources is UnderUtilized,
$r < 1$ Resources is OverUtilized,

This was used to achieve specific objective five (v)

Principal Component Analysis: The constraints facing maize farmers was subjected to principal component analysis. This was used to achieve specific objective six (vi).

Results and Discussion

Socio-Economic Profiles of Maize Farmers in the Study Area

Table 1 presented the socio-economic profiles of maize farmers. About 65% of sampled maize farmers were less than 50 years of age. The mean age of maize farmers was 47 years. This implies that maize farmers were young, active, resourceful, and energetic. Young and energetic maize farmers can withstand stress, adopt new research findings and farm technologies on maize production. Also, 97% of maize farmers had formal education. Educated farmers can easily take advantages of new innovations and research findings. These findings are in line with Alabi, Oladele and Oladele (2020); Alabi and Abdulazeez (2018), and Udoh and Nyienekuma (2008). Maize farmers with basic education are better equipped and will be able to make informed farm decisions (Girei *et al*, 2018). Education has the tendency to significantly improve agricultural productivity (Adenuga *et al*, 2013). About 67% of maize farmers had less than 10 years farming experience. Averagely, maize farmers had farming experiences of 9 years. This is an indication that maize farmers had enough farming experience to enhance maize production. Experience of farmers are linked to age, as maize farmers get older, they must have acquired more experiences in maize production (Alabi, Oladele and Oladele, 2020). Furthermore, 65% of maize farmers had less than 10 people as members of household. The mean household size was 8 people. According to Ozor and Cynthia (2010) who reported that fairly large household size means more family labour available for the household farm activities. About 79% of maize farmers had less than 5 hectares of farm size. Averagely, maize farmers had 4.75 hectares of farm land. This implies that they are smallscale, smallholder, peasant, poor farmers. According to Alabi and Abdulazeez (2018), farmers are classified as smallscale if they have 0.1 – 5.0 hectares of farm land; medium scale if they have between 5.1 – 10 hectares of farm land and large scale if they have above 10 hectares of farm land.

Table 1: Socio-Economic Profiles of Maize Farmers

Socio-Economic Profiles	Frequency	Percentage	Mean
Age (Years)			
31 – 40	21	21.00	
41 – 50	44	44.00	**47.0**
51 – 60	35	35.00	
Gender			
Male	85	85.00	
Female	15	15.00	
Educational Status (Years)			
Primary	19	19.00	
Secondary	31	31.00	
Tertiary	47	47.00	
Non-Formal	03	03.00	
Farming Experience (Years)			
1 – 5	28	28.00	
6 – 10	39	39.00	**9.0**
11 – 15	31	31.00	
16 – 20	03	03.00	
Household Size (Units)			
1 – 5	39	39.00	
6 – 10	26	26.00	**8.0**
11 – 15	35	35.00	
Farm Size (Hectares)			
1 – 5	79	79.00	
6 – 10	10	10.00	
11 – 15	08	08.00	**4.75**
16 – 20	03	03.00	
Total	**100.00**	**100.00**	

Source: Field Survey (2021)

Costs and Returns Analysis of Maize Production in the Study Area

The results of profitability and financial analysis of maize production was presented in Table 2. The costs incurred on various activities and the returns of maize production was based on the prevailing market prices of goods and services during the period of field survey. The total variable cost (TVC) accounted for 96.14% of the total cost of production of maize production. The total variable cost consists of: fertilizer input (46.53%); labour input (17.15%); seed input (12.69%); chemical input (08.19%); land preparation (06.16%); transportation cost (03.75%) and loading and offloading cost (01. 68%). The fixed cost accounted for 03.86% of total cost of production. The total revenue was 1, 210,000 Naira per hectare of farmland. The gross margin and net farm income per hectare of farmland were 776,100 Naira and 758,700 Naira respectively. The implies that maize production is profitable in the study area. The results of financial analysis show that the operating ratio, gross margin ratio and rate of return on investment in maize production were 0.56, 0.64 and 1.68 respectively. The gross margin ratio of 0.64 implies that for every naira invested in maize production by smallholder farmer, 64 kobo covered interest, profits, expenses, taxes and depreciation. The remaining 36 kobo covered cost of operations involved in activities of maize production. Operating ratio is used to measure profitability and operating efficiency of maize production. It shows whether or not the cost component in the sales number of maize produce is within the normal range. Operating expenses in the computation of operating ratio exclude interest, taxes, and depreciation. An operating ratio that is decreasing is viewed as a positive sign as it indicates that operating expenses are becoming an increasingly smaller percentage of maize produce sales. Lower operating ratio means a higher operating profit; on the other hand, a high operating ratio indicates less operating profit. Operating ratio of maize production was estimated at 0.56, this implies that 56% of maize produce sales revenue was used to cover cost of maize produce sold and other operating expenses. This result is in line with findings of Alabi, Oladele and Oladele (2020), Yahaya *et al* (2020) and Alabi and Abdulazeez (2018). The rate of return on investment in maize production was estimated to be 1.68. This shows that for every one naira invested on maize production, a higher return of 168 kobo is obtained, this is an indication that the investment is worthwhile. This result is in line with findings of Zalkuwi *et al* (2010), and Adam (2018), in their results, they obtained higher return per capital invested in maize farming.

Table 2: Costs and Returns Analysis of Maize Production per Hectare

Variable	Value (N)	Percentage
(a) Variable Cost		
Land Preparation	27,800	06.16
Fertilizer Input	210,000	46.53
Seed Input	57,300	12.69
Chemical Input	36,900	08.18
Labour Input	77,400	17.15
Transportation Cost	16,900	03.75
Loading/Offloading Cost	7,600	01.68
(b) Total Variable Cost	**433,900**	**96.14**
(c) Fixed Cost		
Depreciation of Assets/Farm Tools	5,700	01.26
Interest	4,800	01.07
Taxes	6,900	01.53
(d) Total Fixed Cost	**17,400**	**03.86**
(e) Total Cost of Production	**451,300**	**100.00**
(f) Total Revenue	**1,210,000**	
(g) Gross Margin	**776,100**	
(h) Net Farm Income (NFI)	**758,700**	
(i) Operating Ratio	**0.56**	
(j) Gross Margin Ratio	**0.64**	
(k) Rate of Return on Investment	**1.68**	

Source: Field Survey (2021)

Factors Influencing Output of Maize Production in the Study Area

The results of multiple regression analysis of Cobb-Douglas production function model are presented in Table 3. Age (X_1), farm size (X_2), labour input (X_3), fertilizer input (X_4), seed input (X_5) and chemical input (X_6) were the explanatory variables considered in the model. All the explanatory variables included in the model had positive coefficients. Age (X_1), and fertilizer input (X_4), are statistically significant at $(P < 0.01)$. Farm size (X_2), labour input (X_3), seed input (X_5) and chemical input (X_6) were statistically significant at $(P < 0.05)$. The F-value of 356.78 was significant at $(P < 0.01)$, this implies that all explanatory variables included in the model jointly were responsible in explaining for the variations in maize output. The coefficient of multiple determinations (R^2) was 0.789, this implies that 78.9% of variations in output of maize produced were explained by explanatory variables included in the model. The regression coefficients in Cobb-Douglas production function model are the elasticities of production. The elasticities of production for farm size, fertilizer input and seed input were 0.2349, 0.4672 and 0.1798 respectively. The sum of elasticities of production gave the return to scale. The return to scale was estimated at 2.380, this means increasing return to scale. These results are in line with findings of Alabi, Oladele, Oladele (2020), Alabi and Abdulazeez (2018), Girie *et al* (2018) and Onuk *et al* (2010).

Table 3: Result of Multiple Regression Analysis of Cobb-Douglas Production Function Model

Variable	Regression Coefficient	Standard Error	t-Statistics
Age (X_1)	0.5642	0.1938	2.91***
Farm Size (X_2)	0.2349	0.1062	2.21**
Labour Input (X_3)	0.5321	0.2236	2.38**
Fertilizer Input (X_4)	0.4672	0.1455	3.21***
Seed Input (X_5)	0.1798	0.0661	2.72**
Chemical Input (X_6)	0.4019	0.1702	2.36**
Constant	1.8921		
RTS	2.380		
R^2	0.789		
Adjusted R^2	0.718		
F-Value	356.78***		

Source: Data Analysis (2021)

**-Significant at 10% probability level*

***-Significant at 5% probability level*

****-Significant at 1% probability level*

Marginal Value Productivity and Resource–Use Efficiency among Maize Farmers in the Study Area

The marginal value productivities of each resource input and the resource-use efficiency among maize farmers are presented in Table 4. The regression coefficients in the multiple regression analysis of Cobb-Douglas production function model $[\alpha_i]$ are used in the computation of marginal value productivities of each resource input and resource-use efficiency ratios $[r]$ among maize farmers. Marginal value productivities for land, and chemicals were estimated at 411,840 and 400,080 respectively. The factor price is the marginal factor cost (MFC) of the factor input used by the maize farmers. Maize farmers with resource-use efficiency ratios $[r]$ close or equal to unity (one) were adjudged to be efficient in the utilization of that resource inputs. The resource-use efficiency index $[r]$ which is the ratio of marginal value productivities to the factor price (marginal factor cost) of various farm resource inputs shows that maize farmers underutilized the following resource: land, seeds, fertilizer, labor and chemical inputs. Similar cases of underutilization of resource inputs were reported by Alabi, Oladele, and Oladele (2020), Onuk *et al* (2010), Nwakpu (2008) and Iheke *et al* (2008).

Table 4: Marginal Value Productivity and Resource-Use Efficiency among Maize Farmers

Variable Input	MP_x	MVP_x	MFC (N)	r	Decision
Land	17.16	411,840	25,700	16.02	Underutilized
Seeds	16.56	397,440	6,500	61.14	Underutilized
Fertilizer	22.39	537,360	31,000	17.33	Underutilized
Labour	12.67	304,080	5,700	53.34	Underutilized
Chemical	16.67	400,080	7,500	53.34	Underutilized

Source: Computed from Data Analysis (2021)

Constraints Faced by Maize Farmers in the Study Area

Constraints faced by maize farmers are subjected to principal component analysis model and presented in Table 5. In the principal component analysis model, constraints with Eigen-values greater than one (1) were retained and used in the model. Constraints with Eigen-values less than one (1) were discarded by principal component analysis model. The retained constrains in the principal component analysis model explained 89.24% of all constraints included in the model. Lack of fertilizer with Eigen-value of 2.8082 was ranked 1st in order of importance based on the perception of smallholder farmers and they explained 13.09 % of the retained constraints in the model. Lack of improved seed input was ranked 3rd and this 14.92% of all retained constraints in the model. The number of retained constraints facing maize farmers in the model were six (6). The Bartlett test of sphericity of 3279.29 was found to be significant at ($P < 0.01$).This result is similar to the findings of Alabi, Oladele and Oladele (2020).

Table 5: Principal Component Analysis of Constraints Faced by Maize Producers

Constraints	Eigen-Value	Difference	Proportion	Cumulative
Lack of Fertilizer	2.8082	0.3679	0.1309	0.1309
Poor Road Infrastructure	2.7065	0.5142	0.1411	0.2720
Lack of Improved Seeds	2.6521	0.2901	0.1492	0.4212
Lack of Credit Facilities	2.2340	0.3172	0.1512	0.5724
Lack of Extension Services	1.9732	0.3501	0.1578	0.7302
Poor Storage Facilities	1.8230	0.4205	0.1622	0.8924
Bartlett Test of Sphericity				
KMO	0.824			
Chi Square	3279.29***			
Rho	1.000000			

Source: Computed from Data Analysis (2021)

****-Significant at 1% probability level*

Conclusion and Recommendations

Maize production is dominated by male farmers who are active, energetic, and resourceful in their youthful age. Maize farmers are smallholder, poor farmer with an average 4.75 hectares of farmland. Maize production in the area is profitable and worthwhile enterprise with gross margin and net farm income of 776, 100 Naira per hectare and 758,700 Naira per hectare of farmland respectively. Age, farm size, labour input, fertilizer input, seed input, and chemical input were statistically significant factors influencing output of maize production in the study area. The resource-use efficiency index $[r]$ which is the ratio between marginal value productivity of resource input to marginal factor cost, the factor price shows that the resources of land input, seed input, fertilizer input, labour input and chemical input were underutilized. Lack of fertilizer, poor road infrastructures, lack of improved seeds, lack of credit facilities, lack of extension services and poor storage facilities were constraints retained in the principal component analysis model facing maize farmers in the study area. The research study recommends the following:

(a) Government should provide adequately farm inputs such as improved seeds, fertilizer inputs, chemical inputs such as insecticides and pesticides, with adequate access to farmland.

(b) Bureaucratic processes and cumbersome administrative procedures involved in accessing credit facilities by maize farmers should be eliminated.

(c) Extension services should be employed, who will teach maize farmers on research findings, organize workshops, seminars and train farmers on efficient use of farm resources

(d) Maize farmers should form cooperative groups, the groups can access farm inputs at subsidized price and the group can market farm produce, they can pool resources together and access adequate funds to finance activities of maize production.

(e) Government should provide good roads linking maize producing areas, this will facilitate easy evacuation of maize produce to nearby marketplaces.

(f) Government should make tractors available for mechanization, this will lead to lower cost of production

Statement of Conflict of Interest

The author(s) declare no conflict of interest for this study.

Author's Contributions

The contribution of the authors is equal

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Effect of Applications of Boron and Gibberellic Acid (GA_3) on Phytochemical Contents in Different Strawberry Varieties

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Abstract

Strawberry is one of the most popular fruits in Turkey, and its production is expanding due to its resilience to a variety of climatic and soil conditions. In terms of both growth circumstances and the applicability of excellent agriculture and organic agriculture, greenhouses and traditional agriculture are favoured in strawberry farming. According to the World Health Organization, good agriculture and organic agriculture have grown in importance in generating reliable and high-quality food (WHO). Organic compound applications are expanding as a result of these factors. As a result, the number and variety of organic compounds has grown. The research was developed in a protected cultivation system in the 2020 year. The purpose of this study was to see how applying boric acid and gibberellic acid (GA_3) affected the phytochemical content (organic sugars and organic acids) in strawberry cultivars. Albion and Sabrina strawberry varieties were used in this study. The organic sugar ratios in the Sabrina cultivar were generally higher than those in the Albion variety. The highest levels of L-ascorbic acid, Malic acid, and Succinic acid were detected in Sabrina varieties when BA 500 ppm was applied. The highest level of citric acid was recorded in the Control group at 822.48. After the applications, it was determined that there was a difference in strawberry varieties among organic sugars and acids.

Key words
Strawberry, DPPH, organic sugars, organic acids, Boron, Gibberallic acids (GA_3).

Introduction

The strawberry plant (*Fragaria ananassa*) is a member of the Rosaceae family (*Rosoideae* subfamily) and is indigenous to Europe. Because of its ability to adapt to a variety of soil and climate conditions, the strawberry (*Fragaria x ananassa Duch*) is widely grown around the world (Esitken et al., 2010). Strawberries are grown in each of Turkey's nine agro-climatic zones, with Mediterranean and subtropical climate zones being the most prominent producers. Consumers may enjoy this fruit almost all year thanks to the variety of climates around the country, as well as the development of short-day and day-neutral cultivars and the use of various planting strategies (Ozdemir et al., 2013; Torun et al., 2014).

Strawberry fruits appeal to consumers because of their appealing aroma, flavor, color, structure, and nutritional qualities such as hydroxycinnamic acid, flavanols, and anthocyanins (Battino et al., 2019; Giampieri et al., 2017; Gündüz, 2016). Strawberries are high in bioactive chemicals and nutrients, and they've been used for a long time to provide health advantages like detoxification, improved blood circulation, and fatigue recovery (Kim and Shin, 2015; Naemura et al., 2005). With the increased focus on phytochemicals in recent years, many people have increased their vegetable and fruit diet in order to avoid aging and cancer. Strawberries are high in antioxidants and have been shown to reduce the formation of free radicals including superoxide radicals and peroxyl (Wang and Lin, 2000).

Sugars are the major results of photosynthesis, and they were traditionally regarded to be a key component of fruit quality, flavor, and caloric value. Sugars are now known to be essential for the synthesis of plant cell wall components and energy sources, as well as aroma compounds and signaling molecules. Embryogenesis, seed germination and seedling growth, vegetative and reproductive organ development, senescence, responses to biotic and abiotic stresses, coordinating the expression of many genes, and the synthesis of organic and amino acids, sugars, polyphenols, pigments, and aroma compounds are just a few of the processes they are involved in (Wind et al., 2010; Halford et al., 2011; Teker and Altindisli, 2021). Sugar quantification is regulated by ripeness stage, plant age, soil quality, fertilizer, location and weather conditions, agriculture, geographical origin, and genotype (Okan et al., 2018).

The goal of this study is to see how different doses of boric acid and GA_3 alter dpph and total phenolic content in the strawberry cultivars Albion and Sabrina. Five different doses of boric acid (Control, 100, 200, 300, 400, and 500 ppm) and GA3 (Control, 20, 40, 60, 80, and 100 ppm) were used for this experiment.

Material and Methods

Material

The study was conducted in a strawberry greenhouse with a low tunnel. 'Albion' strawberry variety was developed in the USA and recently carried to many regions of the world, including Turkey, where is commercially cultivated under different climatic conditions and cultivation modes (Gunnes et al., 2009). Sabrina Strawberry variety was developed in the province of Huelva by the Planasa company in Spain. Sabrina variety is currently widely used in strawberry fields of Europe (Lozano et al., 2016). Frigo seedlings were sown in a triangular configuration on the bobbins at 30x30 cm intervals. The initial blossoms and stolons of strawberry types cultivated in the strawberry garden were plucked in order to promote vigorous root development in the first year.

Method

Fruit samples were gathered from this strawberry greenhouse, which was in full production in 2020, throughout the harvest period (March to May). When the fruits were fully red, they were collected. The samples were taken to the Vocational School's laboratory in the Sivaslı district of Uşak province, where pomological analyses of the fruit samples were performed immediately and the remaining materials were preserved at -20 ^{o}C for biochemical analyzes.

In the study, several dosages of boric acid and GA_3 were utilized. The applications were created in the Vocational School's laboratory in the Sivasli district of Uşak province. A total of ten fertilizer applications and control groups were used in the study. It consists of 5 boric acid and GA_3 replications, as well as control groups. Boric acid and GA_3 were made by pouring 50 mL of pure alcohol into tiny beakers. Then, using a precision balance, Boric acid and GA_3 were weighed. Following the weighing, 50 mL of pure alcohol was added to each duplicate and stirred until it dissolved. Finally, the samples were poured into bottles containing 950 ml of pure and shaken until fully mixed for all replications. The quantities of boric acid and GA_3 in Table 1 have also been provided. Five replications and control groups of strawberry types were chosen for the experiment. For each replication, twenty plants were used.

Table 1: Boric acid and GA_3 application levels

Amounts of Boric acid application	**Amounts of GA_3 application**
Control	Control
100ppm= 0.1 g per 1 liter of pure water	20ppm= 0.02 g per 1 liter of pure water
200ppm= 0.2 g per 1 liter of pure water	40ppm= 0.04 g per 1 liter of pure water
300ppm= 0.3 g per 1 liter of pure water	60ppm= 0.06 g per 1 liter of pure water
400ppm= 0.4 g per 1 liter of pure water	80ppm= 0.08 g per 1 liter of pure water
500ppm= 0.5 g per 1 liter of pure water	100ppm= 0.1 g per 1 liter of pure water

Organic sugar analysis

Glucose, fructose, and sucrose content in the juice obtained from the harvested strawberries were determined by Kafkas et al. (2007). Before analysis, frozen juice samples were thawed at 25 ˚C 1 mL of juice was added to 4 mL of ultrapure water (Millipore Corp., Bedford, MA, USA). The reaction mixture was placed in an ultrasonic bath and sonicated at 80 ˚C for 15 min and then centrifuged at 5500 rpm for 15 min and it was filtered before HPLC analysis (Whatman nylon syringe filters, 0.45 µm, 13 mm, diameter). The high-performance liquid chromatographic apparatus (Shimadzu LC 20A VP, Kyoto, Japan) consisted of an in-line degasser, pump, and controller coupled to a Refractive index detector (Shimadzu RID 20A VP) equipped with an automatic injector (20 µL injection volume) interfaced to a PC running Class VP chromatography manager software (Shimadzu, Japan). Separations were performed on a 300 mm × 7.8 mm i.d., 5 µm, reverse-phase Ultrasphere Coregel-87C analytical column (Transgenomic) operating at 70 ˚C with a flow rate of 0.6 mL min−1. Elution was isocratic ultrapure water. Individual sugars were calculated based on their standards and expressed in % of FW.

Organic acids analysis

Strawberry juice extract was measured by HPLC analysis developed by Bozan et al. (1997). The changes in l-ascorbic, citric, malic, succinic and fumaric acid contents in strawberry juice samples were measured. 1 ml of the sample and 4 ml of 3 % metaphosphoric acid were mixed for organic acids extraction. The mixture was placed at 80 °C for 15 minutes in ultrasonic water bath and it was sonicated and centrifuged at 5500 rpm for 15 minutes. The HPLC vials were then removed after the mixture was filtered (Whatman nylon syringe filters, 0.45 m, 13 mm diameter). We employed a high-performance liquid chromatographic system HPLC (Shimadzu LC 20A vp, Kyoto, Japan) with a UV detector (Shimadzu SPD 20A vp) and an 87 H column (5 m, 300 7.8 mm, Transgenomic) to examine the extract organic acids. As a solvent, 0.05 mM sulfuric acid was utilized. Column temperature was 40°C; injection volume was 20L; detection wavelength was 210 nm and flow rate was 0.8 mL/min. The retention duration of peaks and the comparison of spectral data to standards are used to identify organic acids and determine peaks. The detected acids were assessed using the appropriate standard calibration curves.

Statistical analysis

Raw data of the experiments were summarized in Microsoft Excel and figures were prepared to better present the results. Then, the data were subjected to the analysis of variance and the mean separation was performed with Tukey's HSD test at $p < 0.05$. The R-free software was then used to perform the principal component analysis and correlations among the study parameters.

Results

The results showed that applying Boric Acid and GA_3 to various concentrations of strawberry extract had a significant effect on organic sugars (mg/100 g) (Table:2).

Table 2. The content of organic sugar (mg/100 g) in fruits of strawberry cultivars

	Sabrina			**Albion**		
Treatment	Fructose	Glucose	Sucrose	Fructose	Glucose	Sucrose
BA (100 ppm)	16.49±1.16	26.85±2.14	0.36±0.08	11.75±0.87	19.22±2.46	0.28±0.06
BA (200 ppm)	13.03±0.79	20.62±1.34	0.16±0.01	11.18±0.66	19.28±0.18	0.12±0.02
BA (300 ppm)	14.53±0.63	22.52±1.25	0.21±0.03	10.71±0.21	15.20±1.19	0.38±0.03
BA (400 ppm)	14.16±0.48	21.11±0.66	0.33±0.01	11.41±0.48	21.01±1.32	0.67±0.07
BA (500 ppm)	13.54±0.26	24.30±0.82	0.33±0.01	11.44±0.03	20.39±0.85	0.33±0.05
GA_3 (20 ppm)	10.00±0.22	17.32±0.16	0.14±0.05	11.37±0.07	17.51±0.99	0.35±0.05
GA_3 (40 ppm)	12.06±0.19	19.21±0.23	0.32±0.02	10.28±0.13	19.00±0.14	0.22±0.03
GA_3 (60 ppm)	12.39±0.06	21.77±0.44	0.30±0.04	11.44±0.66	21.10±0.28	0.31±0.08
GA_3 (80 ppm)	13.47±0.07	21.44±0.06	0.37±0.06	10.76±0.65	18.41±0.35	0.30±0.06
GA_3 (100 ppm)	11.15±0.05	18.39±0.02	0.52±0.07	11.47±0.47	20.27±0.33	0.34±0.01
Control (0 ppm)	11.64±0.29	20.19±0.01	0.29±0.02	10.12±0.80	16.48±0.73	0.23±0.03

The fructose level of the Sabrina variety ranged from 10.00 to 16.49 (mg/100 g). The maximum value was found when Boric Acid 100 ppm was applied, while the lowest value was observed when GA_3 20 ppm was applied. The glucose level of the Sabrina variety ranged from 17.32 to 26.85. The high value was found in Boric Acid 100 and the lowest level was in GA_3 100. The Sucrose levels were found between 0.14-0.52 (mg/100 g). The highest level was found in GA_3 100 ppm application and the minimum value was found in GA_3 20 ppm application. The Boric Acid application (in Sabrina variety), the fructose value ranged from 10.12 to 11.75 (mg/100 g). The maximum value was found when Boric Acid 100 ppm was applied, while the lowest value was observed when Control 0 ppm was applied. The glucose value was found between 15.20 (BA 300 ppm) – 21.10 (GA_3 60 ppm) (mg/100 g). Values of sucrose were found between 0.12 (BA 200 ppm) – 0.35 (GA_3 20 ppm) (mg/100 g).

Strawberry sugar concentration is an important taste element that is strongly linked to customer acceptability (Jouquand et al., 2008). The most abundant soluble components in strawberries are glucose, fructose, and sucrose. Sucrose levels were determined to be extremely low in the study and were not presented. Strawberry fruit has lower sucrose contents than fructose and glucose, according to Wang et al. (2000). The highest amounts of organic sugar content were achieved from both PT and OF in the first year of research, but only from PT in the second year. Organic sugar concentration was observed to be considerably lower in GH in both years. The difference in day and night temperatures in GH can explain this. Fruit matures faster and has lower sugar content when the temperature difference between day and night is small (Shiow & Camp, 2000). The quantities of fructose and glucose in the fruit varied significantly between genotypes. The highest total sugar was found in 'Ebru,"Osmanlı," and 'Kaşka.' Koşar, Paydaş, Kafkas, and Başer all reported similar outcomes (Gunduz and Ozdemir, 2014). Moreover, recent studies determined the effects of foliar-based boron treatments with various doses on fruit quality parameters. It has been concluded that boron applications can increase fruit quality parameters in some strawberry varieties (Urün et al., 2021), olive (Gündeşli and Nikpeyma, 2016), pistachio (Gündeşli et al., 2020).

The results showed that applying Boric Acid and GA_3 to various concentrations of strawberry extract had a significant effect on organic acids (mg/100 g) (Table:3).

Table 3. The content of organic acid (mg/100 g) in fruits of strawberry cultivars

	Sabrina					Albion				
Treatment	L-ascorbic acid	Citric Acid	Malic Acid	Succinic Acid	Fumaric Acid	L-ascorbic acid	Citric Acid	Malic Acid	Succinic Acid	Fumaric Acid
BA (100)	0.53±0.03	758.57±2.41	72.67±0.85	212.18±4.39	1.36±0.16	1.14±0.18	673.03±2.11	69.50±0.61	192.01±1.39	1.17±0.05
BA (200)	1.44±0.04	758.55±2.15	68.84±0.13	188.07±2.51	1.24±0.42	1.34±0.05	686.59±0.24	78.44±0.04	166.52±0.15	0.96±0.05
BA (300)	0.35±0.06	756.25±0.36	69.03±1.22	193.32±3.32	1.15±0.61	1.28±0.07	712.94±0.38	68.44±0.05	178.74±0.13	1.09±0.05
BA (400)	1.12±0.02	643.54±1.48	69.41±0.65	179.12±3.55	1.23±0.13	2.61±0.04	736.02±0.33	81.51±0.06	176.98±0.20	1.05±0.04
BA (500)	1.71±0.01	805.67±0.64	83.43±2.48	220.77±2.16	1.20±0.06	4.07±0.05	736.93±0.48	71.86±0.09	184.03±0.08	0.81±0.08
Control	0.29±0.08	822.48±0.88	75.98±1.18	216.35±1.09	1.22±0.23	2.50±0.02	574.44±0.27	62.05±0.05	156.90±0.44	0.93±0.05
GA_3 (20)	0.60±0.04	625.95±1.27	64.80±1.33	173.86±2.02	0.81±0.05	1.41±0.01	680.72±0.06	66.02±0.01	168.38±0.63	0.91±0.07
GA_3 (40)	2.10±0.09	600.10±3.29	65.72±1.26	179.62±0.86	0.94±0.01	1.24±0.03	736.31±0.04	70.46±0.02	173.46±0.09	1.03±0.04
GA_3 (60)	1.30±0.06	593.78±6.77	58.28±1.48	168.38±1.33	0.87±0.03	1.71±0.02	724.84±0.02	64.77±0.05	168.70±0.11	0.79±0.01
GA_3 (80)	1.13±0.02	567.92±5.15	67.19±0.81	168.75±1.25	1.06±0.02	4.42±0.04	630.08±0.08	61.66±0.06	163.15±0.60	0.84±0.06
GA_3 (100)	1.01±0.07	630.41±2.12	63.90±1.69	162.78±0.73	0.89±0.01	1.86±0.07	678.61±0.03	64.60±0.04	180.76±0.26	1.07±0.08

The highest levels of L-ascorbic acid, Malic acid, and Succinic acid were detected in Sabrina varieties when BA 500 ppm was applied. The highest level of citric acid was recorded in the Control group at 822.48 (mg/100 g). In a BA 100 ppm application, the maximum value of fumaric acid was found to be 1.36 (mg/100 g). In GA_3 80 ppm foliar treatments, the Albion variety had the highest L-ascorbic acid value of 4.42 (mg/100 g). Citric acid has the highest value of 736.93 (mg/100 g) in BA 500 ppm. Malic acid has the highest value of 78.44 (mg/100 g) in BA 200 ppm. BA 100 ppm foliar sprays had the highest levels of Succinic and Fumaric acid.

Organic acids are tiny components of strawberry fruit, but they are key flavor qualities that, when combined with sugars, influence strawberry fruit sensory quality. Organic acid concentration differed significantly between the genotypes studied (Wang et al., 2002). The cultivars tested in this study included two primary organic acids: malic and citric acid. Citric acid was the most abundant acid, accounting for 82.7 (mg/100 g) percent (in the growing year 2008) and 84 percent (in the growth year 2009), respectively, of the total acid content, which is consistent with earlier studies (Crespo et al., 2010). The cultivar "Osmanli" had the highest total acid content, followed by "Cigouletta," and "Sweet Charlie," which had the lowest.

The correlation among the phytochemical contents of Albion cultivars are given in Figure 1. Results suggested that some of the phytochemicals have moderate to high positive correlation, while the others have a negligible correlation. The highest concentration was observed among the citric acid and malic acid with 0.72 and was followed by the correlation between the citric acid and succinic acid with 0.71. As expected, the fructose and glucose concentrations were also noted to have a moderate positive correlation.

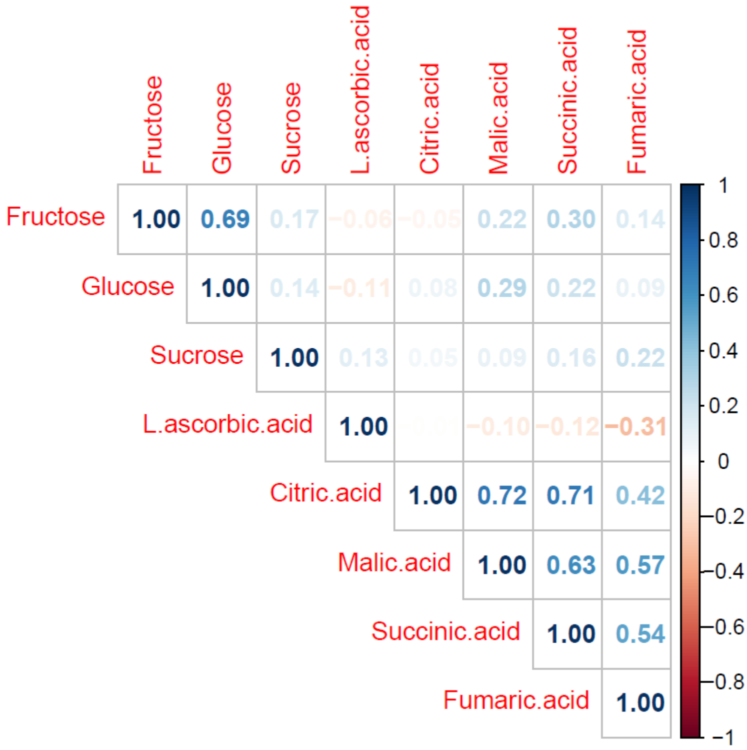

Figure 1: Correlation among the phytochemical contents of Albion cultivar

The correlation results for Sabrina were noted to be similar to the ones for Albion (Figure 2). However, the correlations for Sabrina cultivar were slightly higher than the ones for the Albion cultivar. For example, the correlation between the citric acid and malic acid was noted as 0.84 for Sabrina cultivar. Similarly, the correlation between citric acid and succinic acid was 0.82. The correlation between fructose and glucose was high, with a 0.89 correlation.

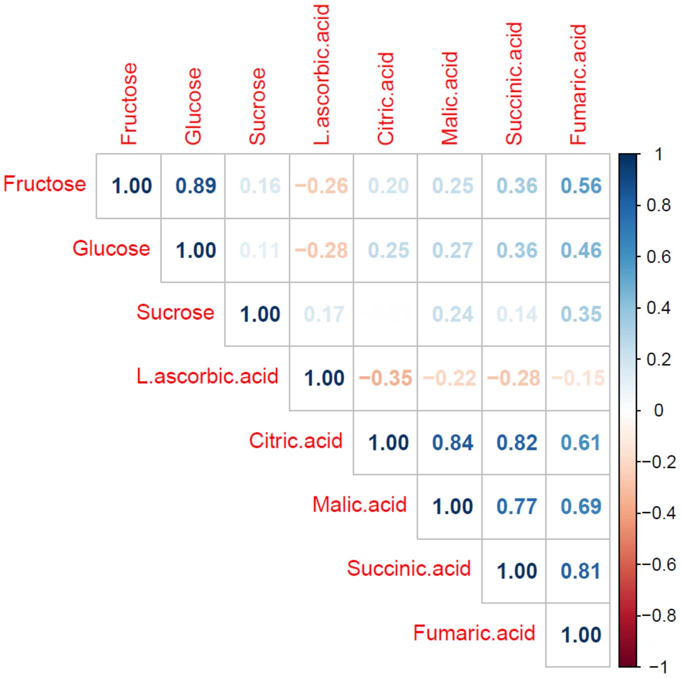

Figure 2: Correlation among the phytochemical contents of Sabrina cultivar

The PCA analysis of the data makes it easy to understand and explain the relationships among the phytochemicals of the strawberries (Figure 3). The loadings which are close to each other, forming a small angle, show that these variables are positively correlated. Results showed that the Fructose and glucose are positive correlation and these two have no correlation with the other test phytochemicals, except the L ascorbic acid, which has a negative correlation.

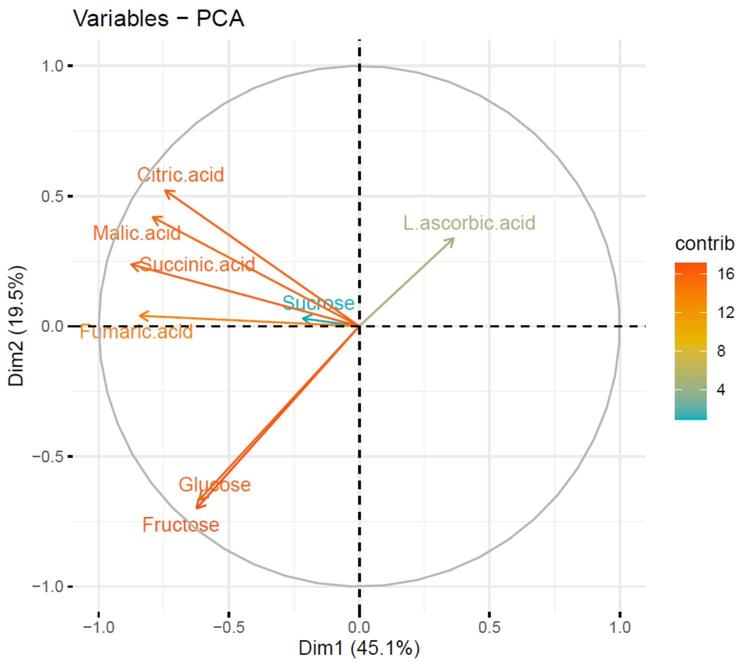

Figure 3: PCA analysis for strawberry cultivars.

N management, farming systems (organic vs. conventional), cultivar selection, planting methods (direct seeding and transplanting), and exogenous administration of plant growth regulators all have a significant impact on root and shoot growth, fruit yield, and quality (Goreta et al., 2004; Leskovar and Othman, 2018, 2021). Many aspects of plant growth and development, including seed germination, stem elongation, leaf expansion, nutrient buildup, pollen formation, and blooming, are regulated by the plant hormones (Achard and Genschik, 2009; Khan et al., 1998).

Conclusion

Field evaluation of Boron and Gibberellic acid (GA_3) applications showed positive effects on values of phytochemical content (organic sugars and organic acids) in strawberry cultivars. In general, Sabrina cultivars had higher organic sugar ratios than Albion varieties. Sabrina varieties tested with BA 500 ppm had the highest levels of L-ascorbic acid, malic acid, and succinic acid. In the Control group, the highest level of citric acid was recorded at 822.48. There was a difference among strawberry varieties among organic sugars and acids after testing. Therefore, it has been determined that Boron and Gibberellic acid applications increase the values in most organic sugars and organic acids.

Statement of Conflict of Interest

The authors are declared that they have no conflict with this research article.

Author Contribution

B.Y.: laboratory work, article writing; V.O.; Field work and article writing; A.M.Ç.: fieldwork; E.K.: laboratory work.

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The Fatty Acid Composition of *Nigella sativa* from Turkey

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Abstract

Nigella sativa, “black seed” or “black cumin” belongs to the Ranunculaceae family. It has been applied in folk medicine since ancient times. The phytochemical contents of black cumin are of interest to researchers in agriculture, pharmacology, and energy. Nowadays, it is so popular to be considered losing weight diets. In this study, the oil content and fatty acid composition of a commercial genotype of Nigella sativa L. from Turkey besides the fixed oil antioxidant activity were evaluated. Omega-6 fatty acid was the major fatty acid in the seed oil of studied black cumin, followed by Omage-9, free acid. However, the major composition of the oil was unsaturated fatty acids and could be considered a healthy fat for daily consumption. Moreover, the seed oil showed relatively high antioxidant activity by DPPH scavenging capacity.

Key words

Black cumin, Fatty acids, Antioxidants, Fat.

Introduction

The presence of medicinal plants in nature is one of the great blessings of God. Since man is a part of nature, nature has certainly provided medicinal plants for every disease. For this reason, the more human beings turn to nature and benefit from its blessings, the faster, better and more assuredly they will be treated for their illness. One of the magic medicinal plants which have been used throughout history is black cumin. Black cumin (Nigella sativa L.) is an important perennial medicinal and aromatic plant from the Ranunculaceae family and is one of the three commonly known species of the Nigella genus.
The plant, also known as “karamuk” and “siyah susam” in Turkish, is an annual and herbaceous plant that grows to about 20-30 cm and has black seeds. Among 12 different species of black cumin grown in the rich flora of Turkey, only Nigella sativa L. is cultivated (Baytop, 1984; Aslan, 2019).
The seeds of black caraway are widely used as spices besides their application in the food, medicine, and cosmetics industries (Baytöre, 2011).

Black cumin is a miraculous medicinal plant with pharmacological, biological, and therapeutic properties due to containing compounds such as fixed oils, essential oils, alkaloids, saponins, and proteins (Moghimi et al., 2018; Mukhtar et al., 2019). Based on previous studies, the seeds of black cumin have been accepted as an important medicine in Asian and Middle Eastern countries for centuries in traditional medicine and are useful for many diseases such as chronic headache, backache, hypertension, diabetes, infection, paralysis, and inflammation (Randhawa and Alghamdi, 2011; Yimer ve ark., 2019). Besides its seed oil which contains high levels of oleic, linoleic, and linolenic fatty acids has antioxidant, anti-inflammatory, anticancer, antidiabetic, antitumoral, antimicrobial, and immune-stimulating activities and gastroprotective properties. (Khan et al., 2011; Ahmad et al., 2013; Adam et al., 2016; Mazaheri et al., 2019). In Turkey, the plant is grown extensively in Mersin, Burdur, Istanbul, Gaziantep, Amasya, and Kahramanmaraş provinces in our country (Baytöre, 2011; Kılıç and Arabacı, 2016).

The antimicrobial property of black cumin is associated with the essential oil containing significant amounts of phenolic compounds (Ahmad et al., 2013). Black cumin contains essential oils such as thymoquinone, thymohydroquinone, carvacrol, dithymoquinone, 4-terpineol, p-cymene, t-anethole, sesquiterpene longifoline, α-pinene and various pharmacological active ingredients such as thymol (Ahmad et al., 2013; Gholamnezhad et al., 2015). Thymoquinone, the most abundant essential oil, is included in pharmacological toxicity studies due to its strong antioxidant, anti-inflammatory, and immune-strengthening capacity. Thymoquinone is also beneficial for liver health. In addition, nigelone present in black cumin prevents the release of histamine leading to reducing the allergic symptoms to a great extent. (Salem, 2005; Darakhshan et al., 2015).

Maideen (2020) reported that the antiviral, anti-inflammatory, antioxidant, immunomodulatory, bronchodilatory, antihistaminic, and antitussive activities of black cumin may make the plant a candidate for herbal treatment of COVID-19, the pandemic disease which caused the death of millions of people all over the World and affected the economy of World in the 21st century. The author also reported that nigellidine and α-hederin as the active compounds of N. Sativa showed an inhibitory effect on SARS CoV-2. N and anti-hypertensive, anti-diabetic, anti-obesity, anti-ulcer, anti-hyperlipidemic, and antineoplastic activities of N.sativa also would help the COVID-19 patients to relieve side effects of the disease in patients. Moreover, Sativa could be used as a side therapy along with offered conventional drugs to relieve the symptoms of COVID-19 in patients besides reducing the adverse effects of conventional medicines.

The fatty acid composition of the seed oil (32-40%) has been reported to consist of approximately 50% linoleic acid, 20% oleic acid, and 10% palmitic acid. Along with these, arachidonic, eicosadienoic, stearic, myristic, linolenic, and palmitoleic acids are some other fatty acids (Gharby et al., 2015; Aziz et al., 2017; Hosseini et al., 2019). The most popular monounsaturated fatty acid is oleic acid with unique characteristics in lowering blood cholesterol. Omega 6 and omega 3 (Linoleic acid and linolenic acid, respectively) are polyunsaturated fatty acids with proven effects on reducing the risks of blood pressure and vascular diseases (Hosseini et al., 2019). Therefore, black seed oil as a rich source of essential fatty acids is considered an extremely valuable and nutritious oil source to be an alternative to traditional oils.

Similarly, in different studies, health benefits have been reported because the fatty acids composition of pomegranate and fig seeds contain oleic acid, α-linolenic acid, linoleic acid, and punicic acid, and it has been emphasized that they should be included more in human diets (Ergun and Bozkurt, 2020; Bozkurt and Ergun, 2021).

In a study by Piras et al. (2013), linoleic acid was higher than other fatty acids in three Turkish and one Egyptian local breeds of N. Sativa. Based on previous studies, the essential oil composition and fatty acid profiles differ by region (Hosseini et al., 2019). Moreover, studies reported that N. sativa L. seed oil can be a good source of biodiesel replacing fossil fuel which is a big challenge for fighting global warming besides meeting increasing population needs. N. sativa L. seed oil had a conversion of more than 93% for transesterification with methanol (Aghabarari et al 2014; Khan et al 2015).

As black caraway is a precious plant with pharmaceutic properties and is consumed in daily health nutrition in Turkey, this study aimed to investigate the fatty acid composition of commercial genotypes of black caraway from Turkey.

Materials and methods

Plant Material

The seeds of *Nigella sativa* L. used in this study were provided by a commercial company. The analyses were done at 5 replicates and the approximately 450-gram seed was used.

Oil Extraction

An automatic soxhlet device was used to extract the total lipids. One hundred fifty grams of dried seeds were used for oil extraction. Hexane (Merck KGaA, Darmstadt, Germany) was used as a solvent. The oil percent in the samples was determined by weighting the extracted oil and expressed as g100g-1 of dry samples. The esterification of fatty acids was done by solving the 100 mg of oil in 10 mL hexane followed by adding 2 N KOH (David et al., 2003).

Determination of Fatty Acids

The fatty acids were analyzed by a GC ("Perkin Elmer, Shelton, USA"). Chromatographic separation was performed using a ("30 m × 0.25 mm ID, 0.25 μm film thickness DB-Wax") column equipped with a "flame ionization detector" (FID). The initial oven temperature was set at 50°C and after 1 min it was raised to 25°C every minute until 200°C, followed by raising 3°C per min to 230°C and was held for 18 min. The" injector" and the "detector" temperatures were set at 280°C and 250°C, respectively. The results were expressed in "GC area %" as a "mean value and ± standard deviation" (David et al., 2003).

Determination of DPPH radical scavenging capacity

"The free radical scavenging activity" of the seed extracts was analyzed using "2,2-diphenyl-1- picrylhydrazyl" (DPPH) assay (Kostiæ et al., 2013). The color loss of DPPH solution was measured at 517 nm scavenging the reaction of DPPH radical with the sample. One hundred microliters of methanolic extract of seed samples were reacted with fresh methanolic DPPH solution followed by incubating for 30 min at room temperature. Then, the absorbance was read at 517 nm against the blank. The ability of the extracts to inhibit DPPH (% RSC) was computed from the decrease in absorbance. The data were expressed as milligrams of Trolox equivalent (TE) "per 100 g of sample"x.

Results and discussion

The physicochemical and nutritional characteristics of each oilseed are influenced by its fatty acid composition. The total fat, fatty acid composition, and antioxidant activity of the studied black caraway are shown in Table 1. The total fat obtained from the seeds of black caraway was 39.5 g/100g. Hosseini et al. (2019) determined the total fat of 16 black caraway from different countries between 27.57-33.04 g/100g. Gharby et al., (2015) obtained the oil yield of black cumin 37% and 27% from solvent or cold press, respectively. Similarly, Atta (2003) compared "solvent" or "cold press" extraction methods and yielded 24.76% and 34.78% of oil content in black cumin, respectively. However, many studies on the total fat content of black cumin from different regions generally showed that the fat content differs in the range of %20-%30 (Burits and Bucar, 2000; Hamrounı-Sellamı et al., 2008; Cheikh-Rouhou et al., 2007; Sultan et al., 2009; Ali et al., 2012; Hosseini et al., 2019, Kiani et al., 2020). The results obtained in this study are the highest among results from previous studies. As reported solvent extraction method was more successful in the determination of total fat in black cumin as it was the preferred method in this study. The high amount of obtained total fat may be due to the extraction method with equipped soxhlet besides the genotype and location of the material.

Totaly 10 saturated and five unsaturated fatty acids were detected in the studied genotype of *Nigella sativa* L. The major fatty acids in *Nigella sativa* were found as linoleic, oleic, and palmitoleic acids (52.89%, 25.12%, and 13.62%), respectively. Approximately half percent of seed oils were polyunsaturated fatty acids mainly linoleic acid. The results are in agreement with previous studies (Burits and Bucar, 2000; Hamrounı-Sellamı et al., 2008; Cheikh-Rouhou et al., 2007; Sultan et al 2009; Ali et al., 2012; Hosseini et al. 2019; Kiani et al., 2020). A high concentration of linoleic acid is a determining indicator of the nutritional value of plant oils and has healthy effects by reducing serum cholesterol leading to a remedy for cardiovascular disorders (Al-Jassir, 1992; Keles, 2020; Guney, 2020; Ergun 2021). Most percentages of seed oil (80.86%) in studied *Nigella sat*iva L. were comprised of unsaturated fatty acids. Palmitoleic acid was found as the main SFA in the seed oil of black cumin. Likewise, measurable amounts of caproic acid (C6:0) an SFA, eicosenoic acid (C20:1n9c), cis-11,14-eicosadienoic acids (C21:2) MUFAs were detected. Pereira et al., (2014) reported that unsaturated fatty acids eicosenoic and cis-11,14-eicosadienoic acids had inflammatory effects. However, genetic factors (cultivar, variety grown), environmental conditions, seed quality (maturity, harvesting, or storage conditions), oil extraction methods, and esterification methods during the determination of fatty acids may be the cause of possible differentiation among results from different studies on oil content and fatty acid composition of *Nigella sat*iva L. (Ramadan and Mörsel 2002; Kiani et al., (2020).

Free radicals generated through routine metabolism pathways may be the basis of many human diseases (Gundesli 2020; Okatan et al., 2021). Antioxidants have the ability to scavenge free radicals by exchanging electrons (Gundesli et al., 2020; 2021). 4-terpineol,t-anethole, and thymoquinone carvacrol isolated from the essential oil of *N. sativa* have considerable free radical scavenging properties (Ali and Blunden, 2003). There are several studies on the antioxidant capacity of black cumin oil. Among various antioxidant capacity measuring assays, DPPH has been widely used in the scavenging assessment of free radicals due to being an easy method (Erkan et al., 2008; Scherer and Godoy, 2009). Erkan et al., (2008) reported that black cumin seeds inhibited DPPH radical formation as 515 of IC50 (μM) mean. Sultan et al (2009) also studied the antioxidant capacity of fixed and essential oils of black cumin via DPPH assay and reported their inhabitation strength of DPPH as 32.32% and 80.25%, respectively. In, this study, the DPPH antioxidant activity of black cumin was determined as 284.70 mg TE/100g. Al Turkmani et al (2015) reported that scavenging DPPH radicals of *N. sativa* essential oil showed a significant difference in samples from two different regions in Syria as 0.607 mg^{-1}ml and 0.240 mg^{-1}ml. Although there are differences in the DPPH antioxidant activity among previous studies, the results are in agreement with each other based on affecting factors such as region, genotype, and extraction solvents.

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Table 1. Fatty acid composition, total fat, and antioxidant activity of *Nigella sativa* L.

Fatty Acids	**%**	
Caproic acid (C6:0)	0.10±0.01	
Caprylic acid (C8:0)	0.04±0.01	
Myristic Acid (C14:0)	0.36±0.01	
Pentadecanoic acid (C15:0)	0.03±0.00	
Palmitic acid (C16:0)	13.62±0.36	
Palmitoleic acid (C16.1)ω−7	0.17±0.00	
Margaric Acid (C17:0)	0.07±0.00	
Stearic acid (C18:0)	3.55±0.01	
Arachidic acid (C20:0)	0.21±0.00	
Behenic acid (C22:0)	0.05±0.01	
ΣSFA	**18.2**	
Oleic acid (C18:1n9c)ω−9	25.12±0.06	
Eicosenoic acid (C20:1n9c)ω−9	0.32±0.01	
cis-11,14-Eicosadienoic acid (C21:2)	2.33±0.04	
ΣMUFA	**27.77**	
Linoleic acid (Cl8:2n6c) ω−6	52.89±0.01	
a-Linolenic acid (C18:3n3) ω−3	0.20±0.01	
ΣPUFA	**53.09**	
Total Fat	**39.50**	g/100g
DPPH Antioxidant Activity	**284.70±8.90**	mg TE/100g

Conclusion

The present study revealed that the commercial genotype from Turkey has a high content of fat besides a good source of linoleic–oleic type fatty acids which are so important for a healthy diet in the cosmetic industry. The study supported the findings of previous studies on the rich phytochemical content of *N.sativa* showing that commercial genotypes also can be used in breeding programs. However, studies on trueness to the name of these genotypes besides the breeding of genotypes with higher content of bioactive compounds should be carried out

Statement of Conflict of Interest

The author(s) declare no conflict of interest for this study.

Author's Contributions

Z.E. and M.Z. contributed equally in fatty acid analyses and the writing of the manuscript. M.T.E helped in writing the manuscript. The authors contributed to the discussion of the results and all of them read and approved the final manuscript.

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The Effect of Different Drying Processes on the Quality of Pepper Seeds Harvested in Uşak Conditions

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Abstract

It stated that drying can delay post-harvest metabolic and physiological processes that contribute to the deterioration of seed quality with storage processes. Generally, as a dryer; silica gel, activated charcoal, bentonite, calcium sulfate, calcium chloride, and zeolite are used. The aim of our study was to determine that different drying methods (FD (frist drying)-SD (second drying)) and post-harvest ripening processes were harvested in Uşak conditions in 3 different maturation periods in the first year after flowering and in 4 different maturation periods in the second year and the change in the viability of pepper seeds. At the end of the applications, parameters such as germination and seedling emergence rate test, and seedling fresh and dry weight and enzyme activity were examined. While pepper seed germination values were tested, the drying and drying+ripening treatments applied to the seed lots that were immature had a positive effect on the results. CAT activity in pepper results, C (control), and PHR (post-harvest ripening) in 60th-day seeds; SOD activity is SD in the first year, C in the second year; APX was found to be high in C and PHR applications. In general, drying and drying+ripening processes according to the harvest periods were found to be advantageous in pepper species.

Key words

Pepper, drying, postharvest ripening, enzyme activity, seed viability.

Introduction

The production of seedlings and seeds should be given priority when thinking about vegetable production. The adequacy of environmental elements must be considered when selecting a seed-producing place. Seed development in production is affected by genetic, physiological, and environmental conditions. For this reason, seed development periods can be different even in plants grown under the same environmental conditions. Conditions of the seed before and after harvest affect the viability and quality of the seed (Demir and Balkaya, 2005). It is important to know the appropriate time for a quality seed harvest (Toole et al., 1956). Two important maturity concepts emerge with seed maturity; physiological and harvest maturity. Determination of the most appropriate harvest time is of great importance since physiological maturity is associated with the maximum accumulation of dry matter transported to the seed. Harvest maturity is the developmental period when the seed becomes suitable for storage. Seed drying processes can be performed in different ways. These drying methods can be listed as a dry room or drying room, desiccants (Silica gel/charcoal), saturated salts/lithium chloride solutions, air-conditioned rooms/vehicles, and incubator dryers. A desiccant is a hygroscopic substance that causes or maintains a desiccant state in its environment. The most common desiccant is silica, and other common desiccants are activated charcoal, bentonite, calcium sulfate, calcium chloride, and zeolites (Ashok et al., 2017). Post-harvest seed drying can be done in different ways. In some crops, the seeds dry out heavily on the mother plant. The seeds can be dried with non-pressurized air, compressed air, or heated (25 °C) compressed air. Products, particularly agricultural ones, are typically dried with warm air. According to studies, immature or even less mature seeds should not be dried quickly in order to produce seeds that will survive for a long time. In addition, it can be determined by tests that drying immature seeds with heated air, as is done in some agricultural products, causes a further decrease in seed life and seed viability (Groot and Groot, 2008). Fruit harvesting stages and the time after they completed ripening had a big impact on how seeds developed and what kinds of yields they produced. The post-harvest ripening stage of seeds offers the possibility of an early harvest of fruits with improved quality and quantity. Additionally, it extends the maturation time of the seeds, improving vigor and germination. Combining these changes showed that seeds were healthy in terms of their physical and physiological conditions during PHR. Additionally, PHR promotes the development of the immature seed inside the fruit and prevents drying-related damage to the cell membrane integrity, which reduces the production of ROS and, as a result, the antioxidant activity (Gill and Tuteja, 2010). One of the key antioxidant enzymes is SOD, which breaks down the superoxide anion (O_2) into H_2O_2 and oxygen before being detoxified by CAT and POX.

In our study, the effects of post-harvest ripening and drying at different speeds on the physiological quality of seeds of pepper species harvested at different maturity periods were investigated.

Materials and Method

The study was carried out in the application field and research laboratory of the Faculty of Agriculture of Uşak University. Pepper (*Capsicum annuum* L.) seed lots of Burdem cultivar, belonging to 3 (40, 50, 60) maturation periods in the first year and 4 (40, 50,60,70) maturation periods in the second year, were used (Fig. 1). It was tried to determine the effect of storage after two different drying applications on seed viability, vigor, and enzyme activation in seeds obtained from fruits harvested at different periods after flowering. The parameters determined as a result of these tests; were moisture content, germination rate (%), seedling emergence rate (%), seedling fresh-dry weight (gr), SOD, APX, and CAT enzyme activities at 25 °C.

Fig 1. Images of peppers harvested at different times (left to the right: 40-50-60-70. DAA)

Table 1. 2018 meteorological data of the location of the application land

Meteorological data (month)	January	February	March	April	May	June	July	August	September	October	November	December
Total precipitation (mm= kg/m^2)	62.1	59.0	56.6	7.9	76.7	48.1	21.0	43.3	0.1	53.8	63.4	92.9
Mean temperature °C	3.6	6.7	9.3	15.3	17.2	20.2	23.7	24.3	20.7	4.9	9.6	3.7
Mean relative humidity %	73.3	73.9	67.9	47.8	61.2	59.3	49.1	48.3	45.6	59.0	67.3	80.3

Table 2. 2019 meteorological data of the location of the application land

Meteorological data (month)	January	February	March	April	May	June	July	August	September	October	November	December
Total precipitation (mm= kg/m^2)	78.8	13.7	14.8	28.8	32.5	36.6	9.3	3.9	29.1	-	-	-
Mean temperature °C	2.8	5.4	7.8	10.4	16.7	20.9	22.8	24.4	19.8	19.0	-	-
Mean relative humidity %	80.5	65.9	58,5	60,6	55,5	58,6	47.1	42.7	51.6	48.2	-	-

Table 3. Application field soil analysis result

	pH	Salt (2micros/cm)	Lime (%)	Organic matter (%)	Saturation (ml)	Total N (%)	Useable P (ppm)	Useable K (ppm)
0-30 cm	7.70	1059	9.1	0.84	65	0.042	0.56	250
Evaluation	Slightly Alkaline	Lightly salted	Medium chalky	Slightly	Clay loam	Poor	Very poor	Sufficiently
Activated lime	0-30	-	-	-	-	-	-	-

Determination of initial moisture content of seed lots

Seed moisture content (%) was determined using the high-temperature oven method (ISTA, 2003) on two replicates of 1 g seeds held at 130 °C for 1 hour. The samples were then allowed to cool for half an hour in a desiccator. Moisture content is expressed on a fresh weight basis.

Seed drying processes

Two different drying processes were carried out in the study. In the first drying (FD), which was continued for five days, the seeds were dried in a saturated solution of CaCl2 in a 35℃ incubator for the first three days, and in the air (at ambient conditions) without any saturated salt solution in a 35℃ incubator on the fourth and fifth days. In the second drying application (SD), KNO_3 (90.79±0.83% RH) on the first day, NaCl (74.87±0.12% RH) on the second day, CaCl (≌45% RH on the third day) in 35℃ incubators) on the saturated solutions, on the fourth and fifth days, it was air-dried in a 35℃ incubator without any saturated salt solution.

Post-harvest ripening application

In the study, the control group (C), first drying (FD) and second drying (SD) processes of the pepper seeds harvested at different harvest periods were applied, as well as the control group, at 35 °C and in hermetic packages (PHR, FD+PHR, SD+PHR) post-harvest ripening process was applied. As a result of this process, seed viability, germination, seedling emergence, and enzyme activity test.

Determination of seed viability

a. Germination test (%)

The paper-to-paper method was used to test the germination of 50 seeds in 4 replications for each lot at a temperature of 25 ºC (ISTA, 2005). At the end of the germination test, normal and abnormal seedlings (%) were determined. The emergence time was calculated using the formula using daily counts during germination (Demir and Güney, 1994).

b.Seedling emergence test (%)

4x50 seeds were sown in peat medium for 21 days at 25°C in 16 hours of light and 8 hours of darkness. A daily emergence count was performed and mean emergence time was calculated (Demir and Güney, 1994). At the end of the emergence experiment, the seedlings were distinguished as normal/abnormal (ISTA, 2003), and the number of normal ones was given as %.

c. Determination of Seedling Fresh and Dry Weight

As a result of the seedling emergence tests, 5 seedlings were randomly selected from each replication and their wet weight was determined and their dry weight (g/plant) was determined by drying at 80°C for 1 day.

d. Enzyme Activation in Seed

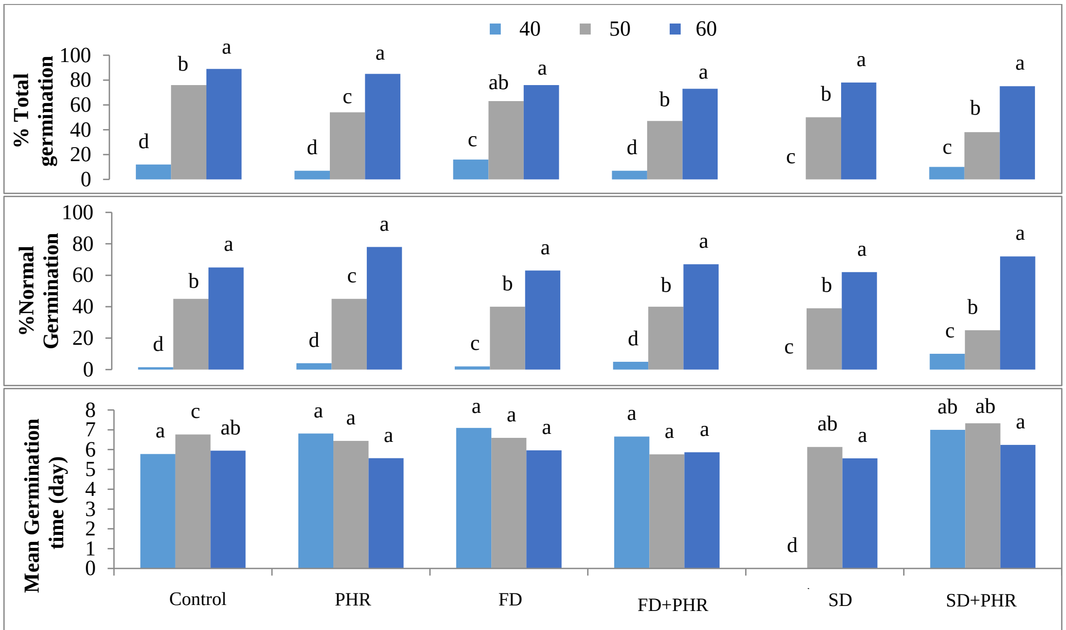
In order to determine the change in the SOD, CAT, and APX enzyme activities of the pepper (50-60) seed harvested at different harvest periods and all the applications applied to these seeds, 0.5 g of seed sample was crushed in liquid nitrogen in porcelain mortars in each replication. It was homogenized with 5 ml of cold (0.1 M Na-phosphate pH 7.5), 0.5 mMNa-EDTA, and 1 mM Ascorbic acid. After the homogenized samples were centrifuged at 18000 rpm for 30 minutes at 4 °C, the obtained samples were kept at room temperature for 1 hour (Jebara et al.,2005; Sairam and Saxena 2000).

Statistical analysis (Duncan) was performed using SPSS 23 to perform ANOVA analyses. The comparison of the averages was made at the 5% level.

Results and Discussion

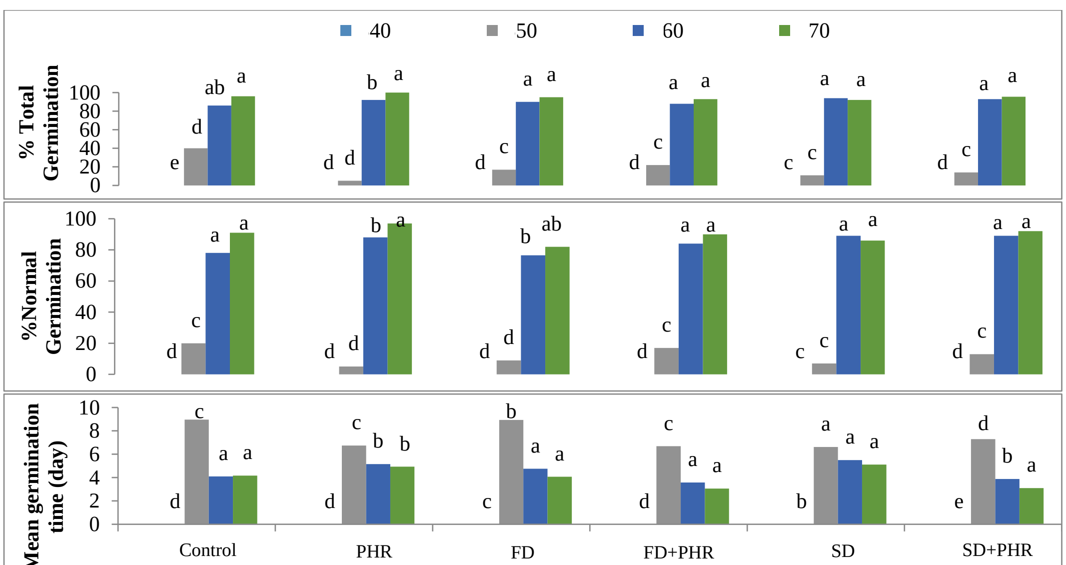
Germination Test Results of Pepper Seeds Harvested at Different Maturity Periods as a Result of Drying and Post-Harvest Ripening Applications (%)

25℃ germination test of seeds belonging to control (C), post-harvest ripening (PHR), first and second drying method (FD, SD) and combination applications of seed lots of Burdem variety harvested at different maturity (40, 50, 60 and 70th days) periods and results (TG, NG, MGT) are given in figure 2. In the results of the germination test performed at 25℃ in the 1st year results, the highest germination values were determined in the 40th day seeds with 16% in the FD group, in the 50th day harvest with 76%, and in the 60th day with 89% in the C group. Normal germination values were determined in the 40th day seeds with the highest 10% in SD+PHR, in the 50th day harvest with 45% K and PHR, and in the 60th day harvest with 78% in PHR applications. When the harvest days are considered on the basis of statistically obtained parameters, TG and NG values were found to be significant at the 1% level, while the MGT value was not significant (p>0,05). However, the parameters were not found significant in terms of drying applications (p<0,01)(Fig 2). Alan and Eser (2007), in their study in which they examined the relationship between fruit location on the mother plant and seed quality; mean germination time (at 15 and 25°C) was significantly affected by fruit position with harvest in 2004, while differences were not statistically significant in 2005. In our study, statistically similar results were obtained in terms of MGT, although seed harvests were carried out regardless of the stage. In our first production year, drying applications in pepper seed lots (40th and 50th days) showed lower germination performance than the control group. According to Herter and Burris (1989), some studies have been conducted on the effect of drying damage on seed germination. For example, Navratil and Burris (1984) reported that drying damage affects root growth more than shoot growth. There have been numerous studies on how changes in the seed during drying might impair germination and reduce quality, including enzyme and protein denaturation, reduced starch grain size, membrane degradation, seed coat cracking, and other issues.



Harvestday*PHR*drying p>0.05, harvestday*drying: p>0.05, P values show the significance of the interaction between Harvestday and applications. The means shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 2 Germination test results of pepper seeds of different maturity at 25 °C between paper (%)(1st year)



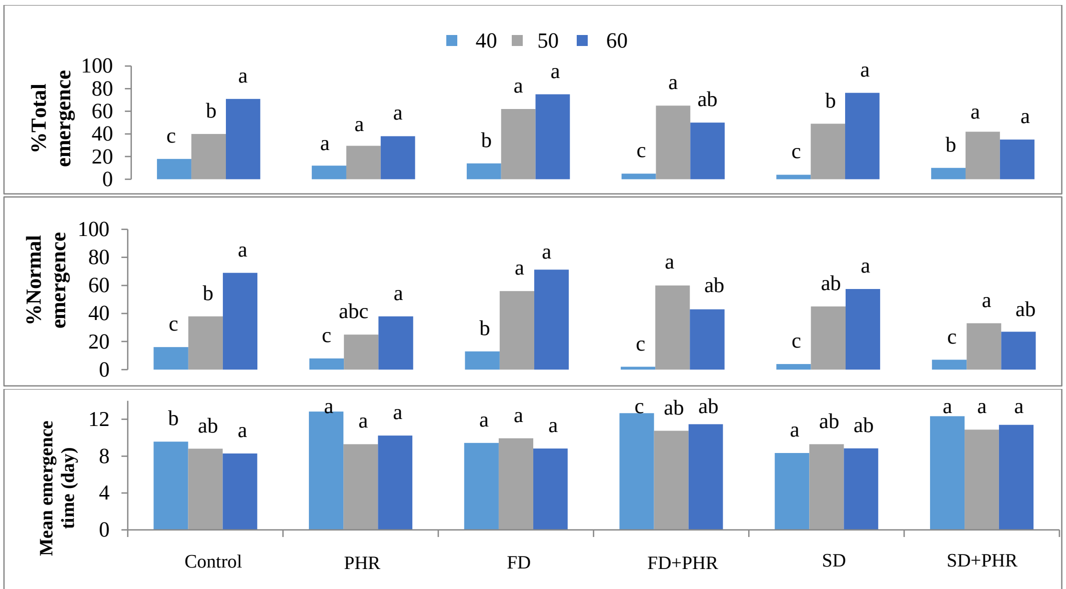
Harvestday*PHR*drying, harvestday*drying: p>0.05, P values show the significance of the interaction between harvest day and applications. The averages shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 3. Germination test results of pepper seeds of different maturity at 25 °C between papers (%) (2nd year)

While there was no germination in the seeds of the 40th day in the germination test performed at 25 °C in the 2nd year, the total germination values of the seeds of the other harvest days were 40% C, in the 50th day seeds, 94% SD in the 60th day seeds, and 100% in the 70th day seeds. The PHR group gave the highest total germination percentage. The highest normal germination percentages were determined in the 50th day seeds with 20% C, 89% SD and SD+PHR in the 60th day seeds, and 97% PHR in the 70th day seeds. The earliest germination in the MGT data was determined in the groups (3.1 days) of the 70th day harvested seeds that were subjected to FD+PHR and SD+PHR treatments. When the harvest days are considered on the basis of the statistically obtained parameters, TG, NG and MGT values were found to be significant at the 1% level, while the parameters were not significant in terms of drying applications ($p<0,01$)(Fig 3.). Vigidal et al.(2011), in a similar study on pepper seeds, stated that seed viability increased during the ripening process, although there were small differences between the strength tests regarding the harvest time when the seed vigor was maximum. Overall, maximum seed viability was recorded after about 60 anthesis when the fruits were red. Maximum seed quality can be determined by a combination of characteristics such as germination percentage and vigor. In general, the greatest dry matter content reached at day 75 after anthesis, and this was attained at about day 75 after anthesis, when the fruit has a red color on the outside, similar to mass maturity, is connected with the maximum germination and viability of sweet pepper seeds. Similar to our seed maturity processes (especially with SD and FD treatments), a high seed germination percentage was obtained, which slowly increased from day 50 to day 70 after anthesis.

Seedling Emergence Test Results with Drying and Post-Harvest Ripening Applications of Pepper Seeds Harvested at Different Maturity Periods (%)

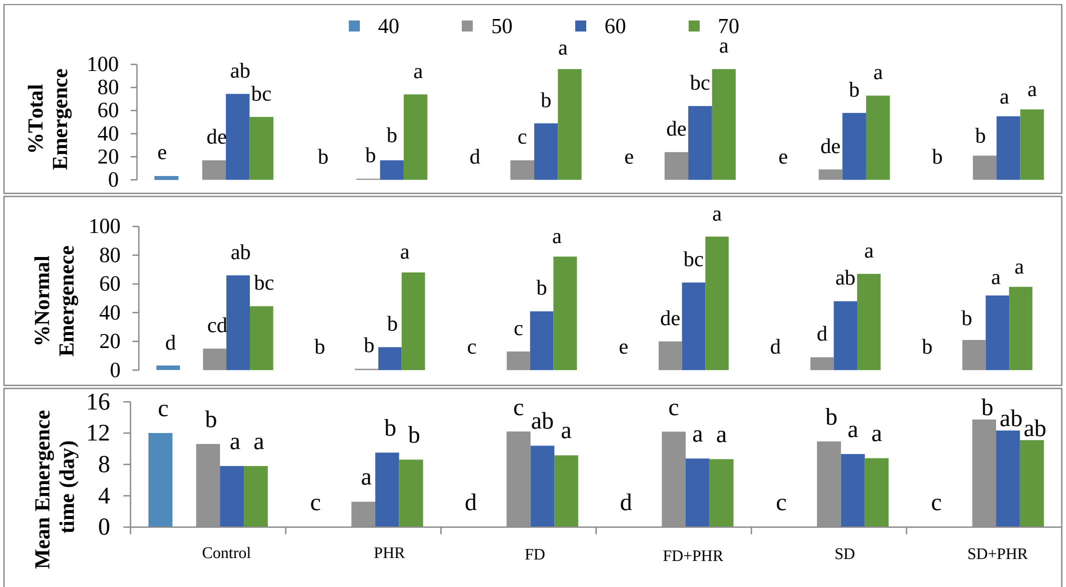
25°C emergence test results (TE, NE, MET) of control (C), frist and second drying method (FD, SD) and combination applications of seed lots of Burdem variety harvested at different maturity (40, 50, 60 and 70th days periods) are given in figure 3. In the results of the first year at 25°C, the total emergence values were determined as 18% in the 40th day seeds, 65% in the 50th day harvest with FD+PHR, and 76.3% in the 60th day harvest. Normal emergence values were determined in the 40th day seeds with 16%, the highest in the 50th day harvest with 60% FD+PHR, and in the 60th day harvest with 71,3% in the FD applications. In terms of MET data, no significant difference was observed in all maturity and applications, and the earliest germination was determined in the C treated group (8.3 days) of the 60th day harvest. The statistically determined parameters were not found to be significant when the harvest dates and drying procedures were considered ($p>0,05$) (Fig 4.). Oliveira et al. (1999), in a study they conducted with pepper seeds (*Capsicum annuum* L.), found high values for germination and viability of seeds extracted from old fruits harvested starting from the 55th day after anthesis, and the highest values were found in fruits harvested between 60 and 70 days after anthesis. quality was found. In pepper seed lots with different maturity, 60th day harvests gave the best results with FD and SD applications.



Harvestday*PHR*drying: $p>0.05$, harvestday*drying: $p>0.05$, P values show the significance of the interaction between Harvestday and applications. Averages shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 4. Evaluation of pepper seeds of different maturity by 25°C seedling emergence test(%)(2018)

In the results of the emergence test carried out at 25°C in the 2nd year, while it was between 0-3% for the seeds on the 40th day, the highest values for the total emergence were FD+PHR for the 50th (24%) day seeds, and C for the 60th (74.5%) day seeds, FD and FD+PHR groups showed 96% on the 70th day seeds. While normal emergence values are between 0-3% in 40th day seeds, the highest values are SD+PHR with 21% in 50th day harvest, 70th day(93%) seeds and 60th (%) seeds. 66) day (87.5) showed group C in seeds. There was no significant difference in all maturity and applications in terms of MET data, and the earliest germination was determined in the C group (3.3 days) of the 50th day harvest. Considering the harvest days on the basis of statistically obtained parameters; In terms of TE, NE values and drying applications, only MET was found to be significant at the 1% level ($p<0,01$)(Fig 5.). Bektaş (2003) investigated the effects of different drying temperatures and harvesting periods on seed quality in seeds taken from the fruits of Sera-Demre 8 pepper variety harvested in different periods. The fruits were harvested 55 (early), 65, 75 (mature) and 85 (over-ripe) days after flowering and the seeds obtained from each harvest period were dried in three groups over $CaCl_2$ solution (%35 RH) at 25 (control), 35 and 45 ºC for 24 hours. Seed quality was determined by germination test, tetrazolium test, cold test and seedling root length. In all quality tests, there was no interaction between temperature and harvest periods, and it was determined that the best harvest period was 65 and 75 days harvest periods. Low values were determined in the 55th day (early) and 85th day (late) harvest periods. He reported that the most suitable harvest time in terms of resistance to drying is the period when the fruit is bright red, which corresponds to the 65th and 75th days after flowering. In our study, especially the 70th day was determined as the suitable seed harvest time for pepper.

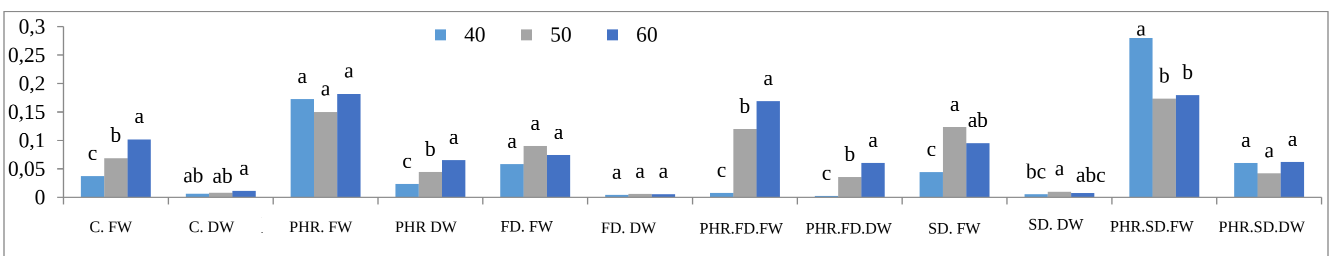


Harvestday*PHR*drying: p>0.05 (excluding MET), harvestday*drying: p>0.05 (excluding MET), P values indicate the significance of interaction between Harvestday and applications. The mean shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 5. Evaluation of pepper seeds of different maturity by 25°C seedling emergence test(%)(2019)

Evaluation of Fresh (FW) and Dry (DW) Weight (g) of Seedlings Obtained After Drying and Post-Harvest Ripening Applications of Pepper Seeds Harvested at Different Maturity Periods

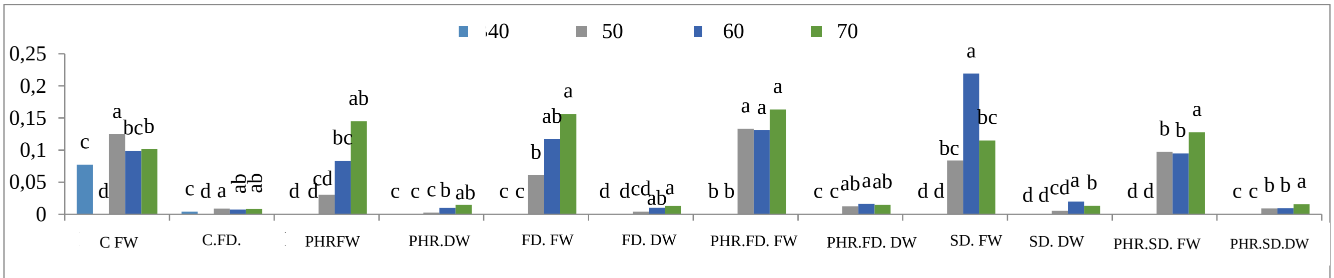
Seedling fresh and dry weight measurements of control (C), first and second drying method (FD, SD) and combinations (CFW, CDW, PHRFW, PHRDW, FDFW, FDDW, PHRFDFW, PHRFDDW, SDFW, PHRSDFW, PHRSDDW) of seeds of Burdem variety harvested at different maturity (40, 50, 60, and 70 days) periods are given in Fig. 6. In general, storage application and drying combinations increased the seedling fresh weight at all maturity. In the first year results, the highest seedling fresh-dry values; PHRSDFW-PHRSDDW was defined in the 40th day seeds, PHRSDFW-PHRDW in the 50th day harvest, and PHRFW-PHRDW in the 60th day harvest. FW and DW values were not found to be significant when harvest days and drying practices were considered on the basis of statistically obtained parameters (p>0,05) (Fig 6.). Hot pepper drying methods were evaluated on the basis of quality parameters such as physicochemical properties according to the combination of temperature and time. Higher viability index, germination, root length, shoot length, seedling dry weight and lower electrical conductivity, moisture content were recorded in sun-dried and mechanically dried seeds at 37°C. In addition to these, nutrients such as capsaicin, ash content, protein, ascorbic acid, and carbohydrates reached high values in this group. In general, the best results were obtained in sun and oven drying, while the worst results were obtained in drying in the shade and room conditions (Christinal and Tholkkappian, 2012). In our study, PHRSD applied to the seeds of the 40th day (immature seed) harvest significantly increased the seedling wet weight.



Harvestday*PHR*drying: p>0.05, harvestday*drying:p>0.05, P values show the significance of the interaction between Harvestday and applications. The mean shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 6 Fresh and dry weight of pepper seedlings of different maturity(2018)(g)

Seedling fresh-dry values were the highest in the 2nd year results; CFW-CDW in 40th day seedlings, PHRFDFW-PHRFDDW in 50th day seedlings, SDFW-SDDW in 60th day seedlings and PHRFDFW in 70th day seedlings were determined. DW values were statistically significant at the 1% level in harvest days and drying applications (p<0,01)(Fig 7.). Goncalves et al. (1998), in their study for the best seed harvest time in All-big pepper cultivar, the germination percentage and seedling growth of seeds taken 60 days after flowering (completely red) gave the best results (Goncalves et al.,1998). In our second year results, SD application, especially on 60th day harvest seeds, gave the highest seedling fresh weight.



Harvestday*PHR*drying: p>0.05, harvestday*drying:p>0.05, P values show the significance of the interaction between Harvestday and applications. The mean shown with different letters within the same application are statistically significant at the level of the specified P value.

Fig 7 Fresh and dry weight of pepper seedlings of different maturity(2019)(g)

Enzyme Activities of Pepper Seeds Harvested at Different Maturity Periods After Drying and Post-Harvest Ripening Applications

When the catalase enzyme activity results of the C, PHR, FD, FD+PHR, SD, SD+PHR groups of the seed lots of Burdem variety harvested at different maturity (50, 60 days) periods are evaluated, the highest values in all ripeness lots are in the C group (0,136-0.173). µmol/min/g) was determined. While APX value increased with PHR and SD (1.896-1.821µmol/min/g) applications, the highest increase was observed in SD (62.55-74.73U/g) application in SOD value according to maturity order. When the harvest days were considered on the basis of the parameters obtained statistically, the CAT value was found to be significant at the 1% level, while the CAT and SOD were significant at the 1% level in terms of drying applications ($p<0.01$). In the 2nd year results, CAT activity was determined in the FD and PHR (0.135;0.284µmol/min/g) groups with the highest values at 50, 60 days of the values obtained in the C group (0.132;0.226µmol/min/g). The highest SOD value was observed in PHR (31.05 U/g) application in 50 days seed lot (Table 4). When the harvest days are considered on the basis of statistically obtained parameters, CAT, SOD, and APX values were found to be significant at the level of 1%, while SOD, APX 1%, and CAT were found to be significant at the 5% level in terms of drying applications ($p<0,01$, $p<0,05$). SOD is an enzyme that acts against reactive oxygen forms and inhibits the action of radical superoxide (O_2) and catalyzes the reactions of electron transfers to produce hydrogen peroxide. In studies with pepper seeds, Vidigal et al. (2009) found a small increase in the intensity of SOD enzyme bands in seeds extracted from fruits harvested starting 50 days after anthesis and then stored for six days. In another study, antioxidant activity was highest in pepper seeds 15 days after flowering. However, it decreased steadily until the 50th day afterward. Seeds collected on the 15th day after flowering had high antioxidant content at the beginning of storage, but relatively decreased under shelf conditions after low-temperature storage (Park et al., 2020). Several studies have shown that ultra-dry treatment significantly affects the activities of antioxidant enzymes in seeds, thereby slowing the decline in the viability of seeds (Cui et al., 2014; Ali et al., 2017). According to our results, CAT activity in the seeds of 60-day harvests in C and PHR groups; SOD activity in SD the group in the first year and in group C in the second year; APX activity in C and PHR group seeds gave high values. The changes in fruit size could have been caused by the minimal moisture loss that occurred during the post-harvest ripening (PHR) period. For bottle gourd, pepper, chili, similar effects of seed moisture loss with delayed PHR harvesting were observed (Alan and Eser, 2008). In accordance with Vidigal et al. (2009), the release of moisture from immature capsicum seeds during PHR stresses the seeds, causing ROS generation to increase and antioxidant enzyme activity to scavenge ROS to increase.

Table 4. Enzyme activity of pepper seeds harvested at different maturity times after drying and post-harvest ripening applications

		2018			2019		
		CAT (µmol/min/g FW)	**APX (µmol/min/g FW)**	**SOD (U/gFW)**	**CAT (µmol/min/g FW)**	**APX (µmol/min/g FW)**	**SOD (U/gFW)**
P50	**C**	**0,136 b**	1,411 a	12,04 b	0,132 b	**1,579** b	18,73 b
P60		**0,173 a**	1,543 a	30,99 a	0,226 a	**3,068** a	**63,02** a
P50	**PHR**	0,136 a	**1,896** a	17,26 b	0,060 b	0,761 b	**31,05** a
P60		0,145 a	1,304 b	26,33 a	**0,284** a	2,600 a	28,98 a
P50	**FD**	0,100 a	1,086 a	5,66 a	**0,135** b	0,782 b	7,24 a
P60		0,107 a	1,304 a	9,77 a	0,218 a	1,839 a	12,01 a
P50	**FD+PHR**	0,074 b	1,154 b	14,35 b	0,055 a	1,389 a	17,06 a
P60		0,115 a	1,746 a	22,66 a	0,072 a	1,193 b	17,47 a
P50	**SD**	0,083 a	1,482 a	**62,55** a	0,068 b	1,154 b	11,06a
P60		0,036 b	**1,821** a	**74,73** a	0,187 a	2,957 a	10,95a
P50	**SD+PHR**	0,090 b	0,882 a	36,00 a	0,043 b	1,071 a	16,39 b
P60		0,162 a	1,107 a	12,17 b	0,205 a	1,357 a	51,99 a

Harvestday*PHR*drying: $p<0.01$ (CAT), harvestday*drying: $p>0.05$, P values show the significance of the interaction between Harvest day and applications. The mean shown with different letters within the same application is statistically significant at the level of the specified P value.	Harvestday*PHR*drying:$p<0.01$, $p<0.05$ (excluding CAT), harvest day*drying: $p<0.01$(excluding CAT), P values indicate the significance of the interaction between Harvestday and applications. The mean shown with different letters within the same application is statistically significant at the level of the specified P value.

Conclusion

During the drying process of seeds, drying temperature and seed moisture content gain importance. If the critical temperature is exceeded, high temperatures carry a risk due to possible damage to the embryo. The general rule in the drying process is to increase the drying temperature after drying with a low temperature at the beginning for seeds containing high humidity. In the germination test of pepper seeds of different maturity, when the advantage/disadvantage situation was evaluated for the total germination parameter compared to the control seeds of the applications, no significant advantages were obtained in general. However, FD (1st year) application for 40-day-old seeds had an advantage compared to control groups (2nd year) in SD applications at 60-day harvest. In the seedling emergence test of pepper seeds of different maturity, when the advantages/disadvantages of the applications are evaluated for the total emergence parameter according to the control seeds, the advantages of the applications vary according to the seed maturity periods. In the first year, the highest advantages were obtained from FD+PHR for 50-day seeds and SD for 60-day harvests, while in the second year, FD and FD+PHR on the 70th day and FD+PHR on the 50th day were determined. Dry weight (DW) values were statistically significant at the level of 1% in pepper seed lots in the second year, on harvest days and drying applications ($p<0.01$). CAT activity in pepper results in 60 days of harvested seeds in C and PHR groups; SOD activity was SD in the first year and in group C in the second year; APX was found to be high in C and PHR applications. Harvestday*drying interaction was not found significant in the first year ($p>0.05$, 0.01), whereas Harvest day*PHR*drying interaction is significant for APX and SOD in the second year. Considering the field conditions in which we conducted our study, the 60th day of the first year and the 70th day of the second year after anthesis were found suitable for seed harvesting.

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Conflict of Interest
This research is a part of Yasemin Çelik’s master thesis. Burcu Begüm Kenanoğlu is the supervisor and corresponding author.

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The Variation of Fatty Acid Composition between Fresh and Stored Avocado (*Persea Americana*)

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Abstract
Avocado is one of the most popular subtropical/tropical fruits and its consumption has increased noticeably during the last century. However, the seeds of avocado are usually discarded after consumption. In order to evaluate new sources of oil for the growing population, avocado agricultural waste including seeds can be considered. Therefore, this study aimed to determine the fatty acid profile of fresh avocado seeds along with the seeds which have been stored at -20 C for two years. The oil was extracted by soxhlet and the percent of fatty acid methyl esters was identified through gas chromatography. The results indicated that total fat (2.88% fresh and 0.86% stored) decreased dramatically during storage and the composition of fatty acids was significantly changed. The major fatty acids in fresh seeds were monounsaturated, while saturated fatty acids were dominant in stored avocado seeds. The results demonstrated fresh seeds of avocado should be evaluated for their application in the energy, cosmetics, and pharmaceutical industry.

Key words
Avocado, Fatty acids, Storage, Oil quality.

Introduction
Avocado (Persea Americana) known also as alligator pear is one of the evergreen subtropical and tropical fruits that are grown in nearly 50 countries from all continents (Bayram et al., 2006). Due to its excellent nutritional and medicinal properties, its cultivation and consumption have dramatically increased in recent years. Avocado is a climacteric fruit and ripens after harvest, not on the tree (Orhevba and Jinadu, 2011). Persea Americana belongs to the Lauraceae family which includes approximately 150 species, the majority of which are the habitat of tropical America and are native to Central and South America. Mexico ranks first in the production of avocados (Villamil et al., 2018). Avocado contains a high amount of fats, fiber, and protein. Due to having low sugar content and digestible oil, avocado fruit is a rich source of energy and can be placed in diabetics' diets as an essential component. The nutritional value of avocado is due to containing high levels of vitamins such as C, E, K, and B groups and minerals such as magnesium, iron, phosphorus, sodium, zinc, and potassium (Orhevba and Jinadu, 2011; Oluwole et al., 2013 and Maitera et al., 2014). Moreover, the whole fruit including pulp, peel, and seed possesses many essential nutrients and phytochemicals with the potential to treat many diseases (Elsayed and Lobna, 2013; Asif, 2015; Adaramola et al., 2016; Yilmaz et al 2020). However, cultivar, storage conditions, ripeness, edaphoclimatic conditions, and geographical growth location affect the quantity and composition of the phytochemicals of avocados (Bora et al., 2001, Setyawan et al., 2021). Increasing the consumption of this preferred fruit brings the challenge of agricultural waste which is needed to be evaluated. Although seeds comprised most of the fruit they are non-edible parts of the fruit and are usually discarded as residues (Adaramola et al., 2016). The exploitation of agricultural waste of avocado fruit is a promising trend that may be profitable in both environmental and industrial aspects by reducing the production of waste and evaluating seeds in the pharmaceutical and energy industry due to containing high levels of valuable bioactive compounds such as antioxidants, antibacterial and fatty acids (Mensah and Golomeke, 2015; AlMatar et al., 2019).
On the other hand, technological advances in energy in the way of world development have increased energetic consumption obtained from fossils. There are serious concerns about the limitation of fossil fuels needed for the increasing population along with environmental issues such as global warming. Therefore, managing agricultural waste can be an alternative solution to these problems. One of the prominent characteristics of avocado seed that makes it a good candidate for pharmaceutical and bio-fuel applications is the oil quality (Reyes-Cueva et al., 2020, Bora et al., 2001). Many studies have proved that avocado seeds have analgesic, vasorelaxant, anti-inflammatory, hypotensive, anticonvulsant, antiviral, wound healing, antiulcer, antihepatotoxic, antioxidant, hypoglycemic, anti-cancer activity (Yasir et al., 2010; Dabas et al., 2013, Setyawan et al., 2021; Soledad, 2021). Some studies also reported that avocado seed oil is suitable for the production of biodiesel due to its characteristics (Hiwot, 2017; Sathishet al., 2021).
However, the oil content and the fatty acid composition of the seed oil are important criteria that specify the quality of seed oil to be evaluated as biodiesel and raw material for the pharmaceutical industry (Zarifikhosroshahi and Ergun, 2022). However, more studies are needed on the identification of fatty acids composition in seed oil because these parameters are so variable due to affecting factors. Therefore, this study aimed to compare the oil content and the fatty acids composition of seed oil of fresh and stored avocado seeds from the Mersin region in Turkey, considering the geographic location of cultivation and storage factors.

Materials and Methods
Plant Material
Avocado fruits for two applications with three replicates were collected from a farm located in Mersin, Turkey in 2019. Mersin is located in the Mediterranean region of Turkey with a subtropical climate and has hot, humid summers and mild, wet winters. The seeds were removed manually from the fruits in the same maturation status. The fresh seeds were cut into small pieces and ground in a grinder. The other samples were kept at -20 for two years. Thereafter, they were also grounded for further analysis.

Oil Extraction
The extraction of oil was carried out using 100 grams of dried seed via an automatic soxhlet device "Gerhardt GmbH & Co. KG" using. The solvent was GC-grade Hexane (Merck, Germany). The yield of oil was calculated by weighting the extracted oil and expressed as g100g-1 of dry samples.

Determination of Fatty Acids

Potassium hydroxide was used for the esterification of fatty acids (David et al., 2003). The methylated fatty acids were analyzed by gas chromatography equipped with a flame ionization detector (FID). DB-Wax column (30 m × 0.25 mm ID, 0.25 μm) was used for the separation of fatty acids. The oven temperature was 50°C for 1 min, raised to 25°C min-1 to 200°C, then 3°C min-1 to 230°C which was held for 18 min, while the injector and the detector temperatures were set at 280°C and 250°C, respectively. The results were expressed in GC area % as a mean value and ± standard deviation (David et al., 2003).

Results and Discussion

The oil content and fatty acid composition of oil from fresh and stored avocado seeds are given in Table 1. The total fat significantly decreased during storage at -20ºC (2.89% and 0.86% in fresh and stored samples, respectively). The oil yield obtained in this study is lower than the results reported by Oluwole et al., (2013) in unripe and ripe seeds of avocado (9.27% and 9.47%, respectively) and also reported (%8.10) by Adaramola et al., (2019). However, Bora et al (2002) obtained a lower oil yield (1.87%) from avocado seeds compared to the results of this study in fresh seeds despite a higher amount than stored seeds. However, so many factors such as plant species and cultivars, environmental conditions, the climate of cultivation location, ripening stage, harvesting time, the oil extraction methods, and solvent used for extraction (Zarifikhosroshahi and Ergun, 2021; Keles, 2020; Guney 2020; Koc et al 2019, Marfo et al., 1986). Although Akinoso and Raji (2010) reported that seeds with oil yield higher than 17% are considered oil seeds, Bwade et al. (2013) reported that the quality of agricultural products is determining criterion for whether or not oil can be industrially processed from them. One of the oil quality parameters which is used for the evaluation of oil in industry and medicine is the composition of fatty acids. The results showed that oleic acid, linoleic acid, palmitoleic acid, palmitic acid, and stearic acid are the main fatty acids in fresh seed oil; respectively while linoleic, oleic, palmitic acid and stearic acid are the main ones in stored seeds, respectively. Saturated fatty acids constituted about 17.65% of the total fatty acids of the fresh seed oil while was the most part of stored avocado seed oil (46.32%). However, PUFA (Poly Unsaturated Fatty Acid) consisted of the same ratio of seed oil in both fresh and stored seeds. However, linoleic acid was detected in different isomeric forms in fresh and stored seeds (gamma in fresh and alpha in stored seeds oil). The amount of total SFA (Saturated Fatty Acid) was high following the total PUFA. In contrast to total PUFA, fresh seeds had lower (17.65%) saturated fatty acids. The stored seeds had high levels of palmitic acid (24.25%) and stearic acid (8.04%) (Fig. 1). Although unsaturated fatty acids consisted the main part of avocado seed oil (80.36% and 51.67% in fresh and stored seed oil, respectively) total MUFA (Mono Unsaturated Fatty Acid)was twice (46.86%) higher in fresh seeds oil. Hiwot (2017) reported that oleic acid was the main fatty acid of avocado seed oil (71.65%) leading to high SFA along with high palmitic acid (13.58%). However, the researcher found a lower amount of linoleic acid (12.48%) than the amount obtained for linoleic acid (27.69%) in this study. These results are compatible with obtained results in this study from avocado fresh seed oil. Contrary, Bora et al (2001) reported that linoleic acid (38.89%) was the major fatty acid of avocado seed following palmitic acid (20.84%) and oleic acid (17.41%) which are different from the results of this study and study by Hiwot (2017). However, all studies proved that saturated fatty acids were dominant in avocado seed oil. The ratio of Oleic/Linoleic acid is a parameter responsible for the oil shelf life. Based on the results, fresh seed oil of avocado has higher shelf life than stored one. The oil obtained from both fresh and stored seeds had favorable C18:2/C18:3 (approximately 5.5). This ratio of oil could be an assessment criterion for reducing the triglycerides and HDL (high-density lipoprotein) in blood plasma (Werman et al., 1991). seed and However, the results of the study showed that long storage of avocado seed caused severe changes both in oil quantity and the composition of fatty acids. During storage, the main change is in the ratio of MUFAs to SFAs. This may be due to an interruption in the conversion of palmitic acid to palmitoleic acid and oleic acid in biosynthetic pathways of plant C18 unsaturated fatty acids (Karki et al., 2019) However, the composition of fatty acids in seed oil is influenced.

Table 1. The fatty acid composition of seed oils of fresh and stored avocado [%]

Fatty acid methyl esters	Fresh Seed	Stored Seed	Mean difference (fresh-stored)
Total oil (g/100g)	2.89±0.21	0.86±0.04	-2.03
Caproic acid (C6:0)	0±0	0.7±0.04	0.70
Caprylic acid (C8:0)	0±0	0.81±0	0.81
Capric acid (C10:0)	0±0	1.08±0.02	1.08
Lauric acid (C12:0)	0.12±0.01	2.32±0.05	2.20
Myristic Acid (C14:0)	1.68±0.01	7.39±0.16	5.71
Pentadecanoic acid (C15:0)	0.26±0.01	0.56±0.02	0.30
Palmitic acid (C16:0)	11.42±0.04	24.25±0.06	12.83
Margaric Acid (C17:0)	0.09±0	0.3±0.01	0.21
Stearic acid (C18:0)	3.75±0.01	8.04±0.11	4.29
Arachidic acid (C20:0)	0.15±0.01	0.32±0.04	0.17
Behenic acid (C22:0)	0.08±0	0.36±0.03	0.28
Lignoseric acid (C24:0)	0.1±0.01	0.23±0.01	0.13
Σ SFA*	**17.65±0.02**	**46.32±0.05**	**28.67**
Palmitoleic acid (C16.1)ω−7	12.85±0	0.94±0.01	-11.92
Oleic acid (C18:1n9c)ω−9	33.89±0.04	19.28±0.11	-14.61
Eicosenoic acid (C20:1n9c)ω−9	0.13±0.01	0±0	-0.13
Erucic acid (C22:1n9)	0±0	0.03±0.01	0.03
Σ MUFA*	**46.86±0.04**	**20.24±0.11**	**-26.62**
Linoleic acid (Cl 8:2n6c) ω−6	27.69±0.01	26.95±0.2	-0.74
g-Linolenic acid (C18:3n6) ω−6	0.05±0.01	3.91±0.21	3.86
a-Linolenic acid (C18:3n3) ω−3	4.97±0.03	0±0	-4.97
cis-11.14-Eicosatrienoic acid (C20:2)	0.06±0	0±0	-0.06
cis-8.11.14-Eicosatrienoic acid (C20:3n6) ω−6	0.41±0.01	0±0	-0.41
cis-11,14,17-Eicosatrienoic acid (C20:3n3) ω−3	0.22±0	0.58±0.06	0.36
cis-13.16-docosadienoic acid (C22:2)	0.11±0.01	0±0	-0.11
Σ PUFA*	**33.5±0.01**	**31.43±0.07**	**-2.07**
Unsaturated/Saturated fatty acid ratio	**4.55**	**1.15**	
Polyunsaturated/Saturated fatty acid ratio	**1.90**	**0.68**	
Oleic/Linoleic acid ratio	**1.22**	**0.72**	

*SFA: Saturated Fatty Acid; MUFA: Mono Unsaturated Fatty acid; PUFA: Poly Unsaturated Fatty acid

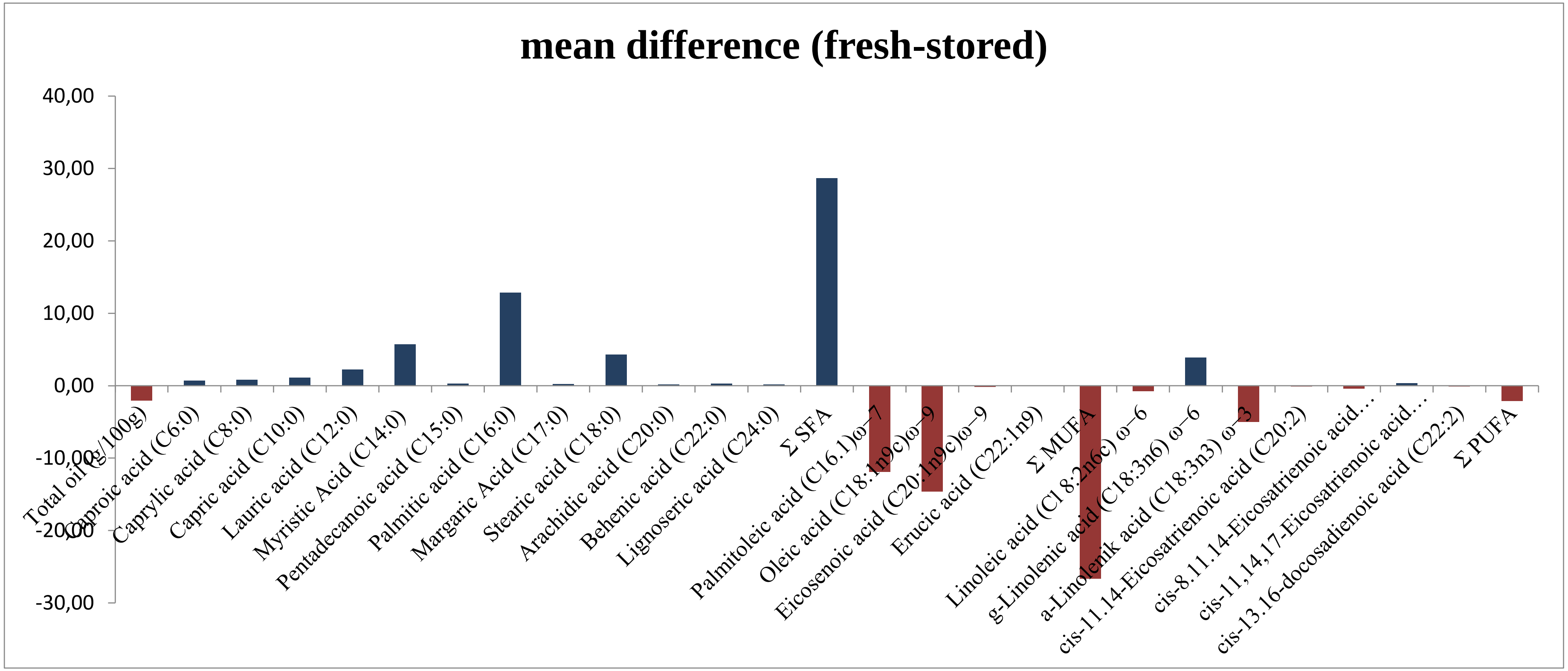

Figure 1. The distribution of fatty acid in fresh and stored seeds of avocado (The increase in SFA and decrease in MUFA during storage are remarkable)

Conclusion

The avocado fruit is very preferred in modern society due to its nutritional characteristics and its outstanding position in a healthy diet. On the other hand, its application in cosmetics, medicine, and energy makes it a precious product for the industry. However, the seeds are considered food waste and most of the time are discarded despite many remarkable properties which can also be evaluated in pharmacology and production of biofuel. This study compared the oil content and fatty acid composition of seed oil in fresh and stored seeds. The results indicated significant changes in oil yield and the composition of fatty acids and offered that long storage of seed in lower temperatures was not suitable. Consequently, avocado seeds can be a good source of oil for industrial applications in pharmacology and energy fields.

Conflict of Interest

The authors declare that they have no conflict of interest.

Author's Contributions

The authors contributed equally to this manuscript.

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Boron Adsorption and Desorption in Soils with High Boron Content

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Abstract

Boron is one of the microelements that should be carefully monitored in boron-rich soils. Boron is not engaged in leaching, volatilization, or oxidation-reduction reactions, controlling adsorption-desorption mechanisms. These soils are prone to extra B loading from soil-forming processes and agriculture. This work aims to explain adsorption/desorption in B-rich soils in connection to soil characteristics. The sorption parameters were determined by batch sorption study by subjecting a series of B solutions (0-40 mg L^{-1}) prepared in 0.01 M $CaCl_2$ background solution. The desorption properties were determined by extracting the adsorbed B with 0.01 M $CaCl_2$ solution. Statistical tests compared sorption data to Langmuir and Freundlich models. Spearmen correlation reveals model parameters and soil coherence. Both models characterized soil sorption with high determination coefficients, although Langmuir isotherm was superior. There was a significant correlation between maximum adsorption capacity and sand content (R^2 = -0.882, p<0.05). Up to 10 mg kg^{-1}, the experimental sorption capacities of soils are unaffected; there was even a decline in adsorption capacity at this concentration, indicating desorption controlled section. When boron sorption reaches a concentration above 8 mg kg^{-1}, boron mobility increases, and plants can be adversely affected by such concentrations.

Key words

Boron Adsorption, Langmuir isotherm, Freundlich isotherm.

Introduction

Plants need 2-4 mg kg-1 of B. This means plants might develop deficiency and toxicity signs in one season. Boron toxicity is higher in dry, semiarid, and heavy soils (Goldberg, 2004). The high B concentration in some areas of Turkey's soils is attributed to the boron deposits (Kar et al. 2006). This raises B levels in river water, which is utilized for irrigation, and B enrichment in the soil is more dangerous.

Adsorption-desorption processes in soils govern plant B uptake (Goldberg, 1997). It is known that B adsorption rises as a function of pH from 3 to 9 (Van Eynde et al. 2020) and declines at pH 10 and above (Goldberg and Glaubig, 1986). It has been shown that the B adsorption maximum values are highly linked with soil pH (Evans, 1987). Researchers reveal that Fe-Al oxides exhibit strong B sorption (Anuo et al. 2021). Boron adsorption happens through ligand exchange with surface hydroxyl groups (Su and Saurez, 1995). Organic matter is also a significant soil component for B adsorption. There are two conflicting views on the B adsorption of organic matter: organic matter contributes significantly to B adsorption (Tlili et al. 2019), and organic matter reduces B adsorption ability by masking B adsorption sites of clays and/or oxide minerals (Diana et al. 2010). All of these above-mentioned adsorption investigations were done within a B-deficient environment. Natural soil formation processes, notably in Turkey, or agricultural techniques, especially fertilization and irrigation, may improve B-rich settings. Due to the inclusion of B as a conditioner in fertilizers (%) (Pişkin, 2021) and B's high solubility in soil, it may seep into natural continental and/or aquatic habitats.

Therefore, the goal of this work is to obtain knowledge about B adsorption and desorption qualities of soils with genetically high B content and to find out the coherence of adsorption parameters and soil features.

Materials and Methods

This research region is located near the Quaternary and Plio-Quaternary basalt and andesite-formed Great and Little Ağrı Mountains. Along the Aras River, Quaternary sediments are prevalent, and there is a Quaternary alluvial fan, slop debris, and moraine on the mountain's downslope. It acquired sediments during the floods, from which soils were produced and used extensively for agriculture. Therefore, the parent material of the examined soils consists of alluvial sediments from the Aras River that are calcareous, heavy, and have a low organic carbon content. In the studied region, basaltic, alluvial, colluvial, regosol, and brown great soil types are prevalent. Iğdır Plain has different problems, such as salinity, alkalinity, and soil drainage, and it is Türkiye's second-largest wind erosion area. There are saline, alkaline, B toxic soils and their combination soils throughout the Plain. Approximately 45% consists of salinity-alkalinity and B toxicity problems which have a surface area of 83.000 ha (Temel and Simsek, 2011). Iğdır has a continental semiarid climate (BSk) with hot and dry summers and cold and snowy winters. Iğdır has one of the most arid climates in Türkiye, averaging 225 mm of mean precipitation per year. The daily average temperature is 12.9°C (Karaoğlu, 2011).

Soil samples (0-20 cm) were taken from 5 points, representing common soil great groups in the Iğdır plain. These soil samples were dried and homogenized by passing through a 2 mm sieve. Some physicochemical properties of the experimental soils were determined by using the suggested methods for neutral to alkaline soils (Sparks et al. 1996). Fractions of sand, silt, and clay were determined by the Bouyoucos hydrometer (Bouyoucos, 1951). pH and EC were measured in suspensions of 1:2.5 with a combined electrode and EC meter (Richards, 1954). The dichromate wet-oxidation method of Walkley-Black was used for organic matter determination (Nelson and Sommers, 1983). The soil's calcium carbonate equivalent (CCE) was determined by a manometric method using a Scheibler calcimeter (Richards, 1954). Cation exchange capacity (CEC) was determined according to the sodium acetate method (Polemio and Rhoades, 1977). Specific surface areas were determined with the aid of a polar molecule ethylene glycol mono ethylene ether (Carter et al. 1986). The plant-available boron was extracted with 0.01 M $CaCl_2$ + 0.05 M mannitol by shaking at 20°C for 16 h and determined by ICP-OES (Thermo Scientific 7200 ICP-OES

Analyzer) (Kinrade and Van Loon, 1974). The amount of B passing into the solution from the soil sample, which was wet-ashed with a mixture of concentrated nitric acid and perchloric acid (3:1, v/v) was determined by ICP-OES (Thermo Scientific 7200 ICP-OES Analyzer) (Kinrade and Van Loon, 1974).

Adsorption/Desorption Experiments

Adsorption

Scoops of 5 g soil samples were weighed into 50 mL plastic tubes in triplicates. The soil samples were equilibrated with 20 mL solutions containing 0, 1, 2, 3, 5, 10, 20, and 40 mg L^{-1} B prepared in 0.01 M $CaCl_2$ at a constant 24±1 °C on a reciprocal shaker at 150 rpm for 23 hours. The supernatants were separated by sequential centrifugation at 4000 rpm for 10 minutes and filtering through Whatman No 42 filter paper. The B concentration in the supernatant solution was then measured by the ICP-OES at 249.773 nm wavelength.

With the following equation, we were able to determine the quantity of B absorbed by comparing the difference between the initial and equilibrium concentrations. The sorption results were checked against the Langmuir and Freundlich adsorption models described below. The confirmation of the sorption data to the Langmuir and Freundlich adsorption models given below were tested.

Ce/Si =Ce/b+1/kb (Langmuir, 1918)

Where k and b are the binding energy and the sorption maximum, respectively.

Si= Kf Cn

The Freundlich isotherm above can be linearized as follows:

Log (Si) = Log Kf + n log Ce

Where Kf and n are coefficients related with distribution coefficient and correction factor respectively.

Desorption

After the adsorption process, 20 mL 0.01 M $CaCl_2$ solution were added, and the indigenous and/or adsorbed boron were extracted by shaking at a constant 24 °C for 23 hours as in the evaluation of B availability in the soil. At the end of the equilibrium period, the solid and liquid phases were separated and analyzed as in the adsorption processes. The desorption ratio was calculated by the following equation:

% desorption=100- (Si-Sides)/Si*100

Where Sides is the quantity of B extracted by the 0.01 M $CaCl_2$ solution (mg kg^{-1}).

Results and Discussion

The physico-chemical properties of the soils used in the study show that the texture classes of the soils are clay (Table 1.). The natural pH of the soils of the region is strongly alkaline, and their EC is in the slightly saline class. They have a high cation exchange capacity above 29.2 cmol kg^{-1} and a very high specific surface area indicating very high clay content. The experimental soils have a lime (CCE) content below 5% with changing organic matter content due to depth of water table and topography. The occurrence of very high phyto-available B in the range of 7.61-15.4 mg kg^{-1} has been limiting economically feasible cultivation of many crops.

Table 1. Some physical and chemical properties of soil

Soil	N	W	pH	EC (µS cm^{-1})	Sand (%)	Clay (%)	Silt (%)	Texture class
A	39° 52' 23"	44° 31' 54"	8.58	1398	20.8	53.3	25.9	Clay
B	39° 55' 14"	44° 25' 56"	8.58	1398	20.8	53.3	25.9	Clay
C	39° 54' 56"	44° 26' 24"	9.15	1259	12.2	54.0	33.8	Clay
D	39° 58' 17"	44° 21' 15"	9.30	1468	1.8	70.2	28.0	Clay
E	39° 58' 40"	44° 18' 20"	9.52	1045	11.8	40.2	48.0	Silty-Clay

Soil	OM (%)	CCE (%)	SSA (m^2 g^{-1})	CEC (cmol kg^{-1})	Available-B (mg kg^{-1})	Total B (mg kg^{-1})	Availability index (%)
A	3.28	4.20	2682	34.7	13.8	213	15.4
B	3.28	4.20	2822	34.6	16.4	231	14.1
C	2.51	4.90	3052	43.1	31.0	262	8.47
D	1.12	3.01	2956	41.0	26.5	202	7.61
E	0.95	4.97	2958	29.2	13.3	170	12.8

CCE calcium carbonate equivalent, SSA specific surface area, CEC cation exchange capacity

Adsorption Isotherm Parameters

Langmuir and Freundlich adsorption models were applied to the boron adsorption data. From these models, qmax (adsorption maximum), KL (Binding Energy), n (adsorption power), and Kf (Binding Energy) values were calculated as adsorption parameters. The isotherm coefficients obtained from the treatment of solutions containing B with different concentrations with five different soils were formed. Adsorption isotherm parameters are as in Table 2.

It was observed that adsorption increased with increasing concentrations in the investigated soils but deviated at higher concentrations (Figure 1). At high pHs, B tends to form in the $[B(OH)_4]^-$ form (Keren and Bingham 1958). The high pH of the investigated soils probably supports the replacement of clay minerals in the form of borate anion with hydroxyl groups (Keren and Bingham, 1958).

Table 2. Adsorption parameters of soils Langmuir and Freundlich isotherm models

0	**Langmuir**				**Freundlich**		
	q_{max}	K_L	R_L	R^2	**n**	**K_f**	**R^2**
A	90.1	1.7	0.1	0.93	3.6	28.3	0.91
B	90.9	0.3	0.2	0.98	4.6	38.7	0.97
C	166.6	0.2	0.1	0.99	4.9	73.9	0.97
D	185.2	0.5	0.1	0.99	6.3	101.6	0.97
E	109.9	0.8	0.1	0.98	8.5	67.8	0.91

Boron adsorption data were calculated according to Langmuir and Freundlich Adsorption models (Figure 1). It was found that the data were at acceptable levels in both models. The high determination coefficient of regression shows that Langmuir isotherm defines adsorption data better than Freundlich isotherm for all soils. Researchers such as Arora and Chahal (2010), Elrashidi and O'Connor (1982) also found similar results to the data we found. It is assumed that single-layer adsorption takes place on the Langmuir isotherm. At increasing doses, B adsorption could occur as a multilayer and/or precipitation reaction. It is also due to the heterogeneity of the Langmuir isotherm monolayer reaction and homogeneity versus high B concentrations (Arora and Chahal, 2010; Hingston, 1964).

In order to determine the suitability of adsorption isotherms, a statistical comparison was made between the adsorption maximum values obtained from the Langmuir isotherm equation and the adsorption maximum values obtained experimentally (Figure 2).

For comparison, correlation analysis was made between the adsorption maximum values obtained from the Langmuir isotherm equation for B and the adsorption maximum values obtained experimentally. In the correlation, a statistically significant relationship ($p < 0.01$) was found between the adsorption maximum values obtained from the Langmuir isotherm equation and the experimental adsorption maximum. This situation implies that the soils are similar in terms of general characteristics and differ from each other in terms of B content.

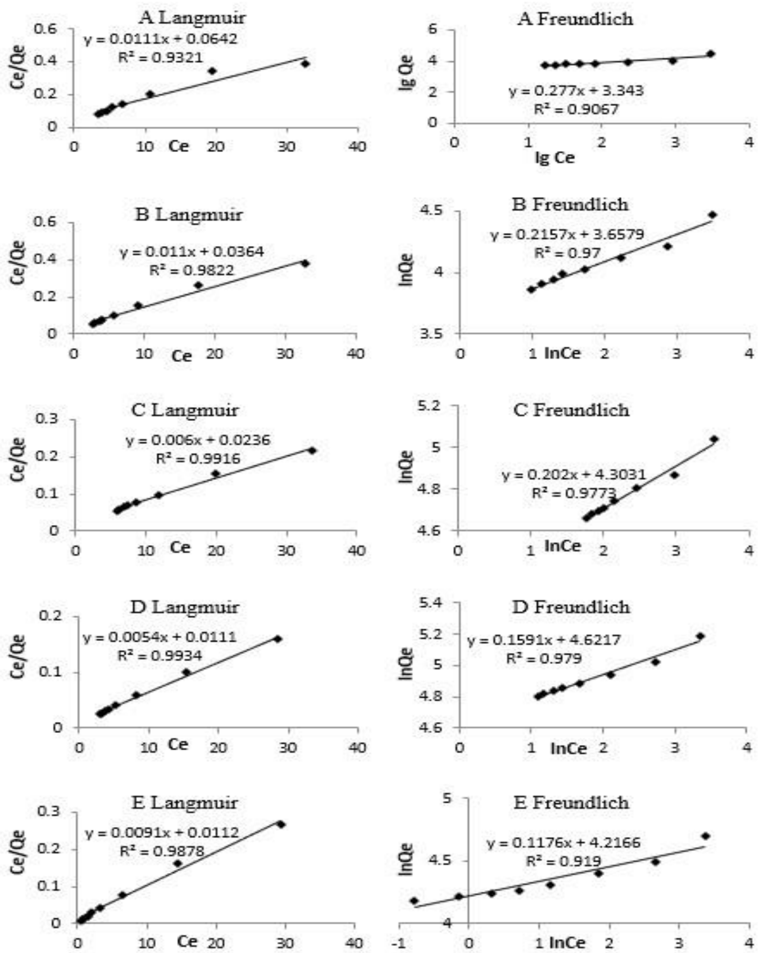

Figure 1. Langmuir and Freundlich isotherms of soils.

There are frequently reported deviations between the experimental data and the ones predicted from the Langmuir model depending on the sorption site heterogeneity, multiple sorption mechanisms, changes in ionic speciation and complexion reactions over a large concentration range, chelate formation, the amount of previously adsorbed sorbate, and desorption. These circumstances in fact result in deviation in the lower and/or upper end of the isotherms leading to the misapplication of the Langmuir equation (Harter and Baker, 1977). Precipitation-derived scavenging mechanism of the sorbate or chelation reactions produces systematically larger sorption maxima with deviation at the upper and lower-end due to apparent decrease and increase in the Ce/Q term, respectively. Since the precipitation reactions were likely to be the main mechanisms in high-loading cases, like the abovementioned case, the calculated sorption maxima were larger than the experimentally observed ones.

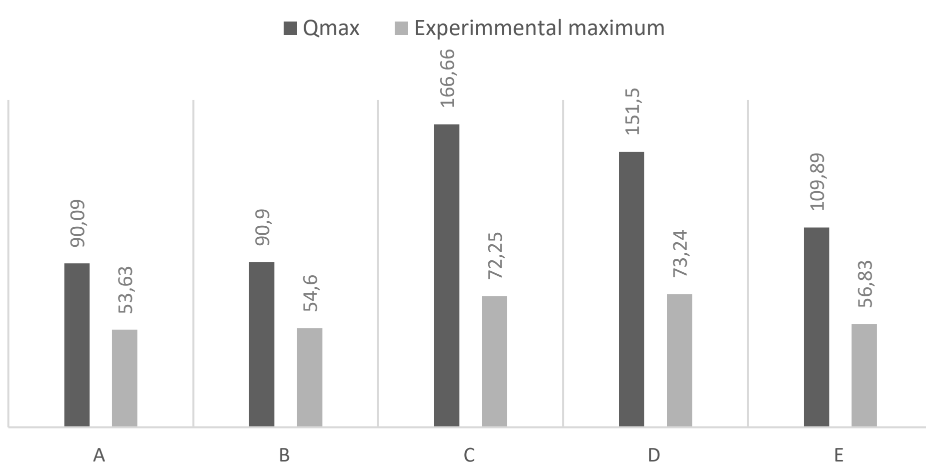

Figure 2. The predicted and experimental B sorption maxima for the soils

Relationships Between the Sorption Parameters and Soil Properties

The correlation analysis between soil properties and coefficients obtained from Langmuir and Freundlich isotherms is given in Table 3. According to these results, the EC value from soil properties is negatively correlated with the RL value obtained from Langmuir isotherms at the level of 0.05. The sand content of soils is negatively correlated with the Kf value obtained from Freundlich isotherms at the level of 0.01.

Table 3. Correlation between soil properties and coefficients obtained from Langmuir and Freundlich isotherms

	K_L	R_L	Qmax	n	K_f
pH	-0.709	0.260	0.342	0.856	0.634
EC	0.408	**-0.879***	0.567	-0.030	0.437
OM	0.552	-0.162	-0.264	-0.834	-0.604
$CaCO_3$	-0.240	0.733	-0.617	-0.059	-0.583
Sand	0.347	0.448	**-0.882***	-0.565	**-0.975****
Clay	-0.156	-0.222	0.703	-0.291	0.536
Silt	-0.128	-0.141	-0.04	0.861	0.244
B	-0.567	-0.120	**0.974****	0.098	0.827
SSA	-0.761	0.097	0.75	0.568	0.802
CEC	-0.431	0.040	0.79	-0.407	0.488
TB	-0.386	0.494	0.23	-0.701	-0.125

* Significant a p≤ 0.05 and ** at p≤ 0.01.

B adsorption is significantly dependent on soil texture. The findings of this study are in line with the results obtained by other studies (Elrashidi and O'Connor, 1982; Mezuman and Keren, 1981; Hatcher et al. 1967; Wild and Mazaheri, 1979) and as clay percentage rises, so does B adsorption maximum (Communar and Keren, 2006). Although there was no statistically significant value, CEC and SSA values were found to be high. As a result, we can say that the soil's clay content and type, pH, specific surface area, and cation exchange capacity are the primary factors influencing boron adsorption. It was found by Keren and Talpaz (1984) that the increased cation exchange capacity of clay was related to the increased B adsorption in smaller clay particles. Contrary to the general knowledge we know about B adsorption, no relationship was found between Qmax and pH, EC, OM, and TB due probably to the similarity of soil properties in many terms.

Boron (B) Desorption

The boron desorption process is related to the amount of B adsorbed. The mechanism of B binding in soils, as well as the type and contact duration of the extraction solution, affect the degree of adsorption and B desorption. It shows that at high saturation of the solid phase matrix, the desorption rate of B is fast, and at high saturation, which indicates that in soils with a capacity of saturated B content, B is rapidly released. In Table 4, the amount of desorbed B was constant at the initial concentrations but decreased after the administration of 10 mg kg^{-1} B. In soils with high B content, it is seen that a low concentration of B desorption is constant, B is adsorbed with high energy, and high concentrations have high B desorption due to physical adsorption.

Table 4. Boron desorption rates of soils

B loading (mg kg^{-1})	Desorbed %				
	A	**B**	**C**	**D**	**E**
0	96.5	96.3	96.9	95.5	67.6
1	94.7	91.3	94.0	94.7	67.1
2	89.0	87.7	92.2	91.8	66.5
3	89.9	85.7	91.6	88.9	66.8
5	87.0	81.9	87.8	83.5	66.1
10	83.7	78.9	84.0	76.1	68.3
20	80.6	77.9	79.8	71.5	71.8
40	80.0	78.1	77.5	71.1	74.8

Desorption as a Function of Soil Properties

The percentage of desorbed B was found to be lower with a higher amount of B added. Elrashidi and O'Connor also found comparable outcomes (1982). Soils with a greater affinity for boron adsorption are said to desorb less B than those with a lower affinity. In this case, adsorption and desorption of B seemed to be virtually antipodal processes. Consistent with the findings of (Elrashidi and O'Connor 1982).

The contact duration of solution B and the intensity of the B binding in soils determine the amount of the differential between the adsorption and desorption of B. From our data analysis, we learn that when the solid phase matrix is just slightly saturated, B desorbs at a moderate pace, but when it is very saturated, it desorbs quickly. Soil with a greater B adsorption capacity would seem to have a slower B release.

Correlation analysis between soil properties and data obtained from desorption data is given in Table 5. According to these results, sand content and desorption data at high concentrations are positively correlated at p≤0.05. The total B content of soils and desorption data at low initial loadings are positively correlated. A significant correlation was also found in other soil properties. When examining the status of the coefficient in varying concentrations, besides the importance of the relations, there is a constantly increasing positive coefficient in the amounts of lime, sand, and the initial B concentrations. There is a decreasing positive correlation coefficient with an increasing initial concentration of TB content. An increasing positive correlation indicates that these components are not effective in B adsorption. The gradually decreasing negative correlation indicates that the components have a strong B retention, but the decrease indicates that this component moves towards the B sorption saturation; therefore, the energy of the retained B decreases as it approaches saturation (Tlili et al. 2019; Arora and Chahal, 2010; Suganya et al. 2019).

Table 5. The effect of initial B concentration and soil properties on the desorption ratio

	Initial B concertation (mg/L)							
	0	**1**	**2**	**3**	**5**	**10**	**20**	**40**
pH	-0.533	-0.559	-0.532	-0.587	-0.576	-0.569	-0.502	-0.412
EC	-0.202	-0.219	-0.258	-0.246	-0.341	-0.441	-0.549	-0.628
OM	0.703	0.723	0.702	0.753	0.724	0.702	0.633	0.541
$CaCO_3$	0.401	0.422	0.461	0.475	0.547	0.646	0.765	0.844
Sand	0.541	0.584	0.600	0.653	0.731	0.839	**0.923***	**0.953***
Clay	0.070	0.038	0.003	-0.047	-0.121	-0.266	-0.461	-0.607
Silt	-0.576	-0.576	-0.549	-0.536	-0.519	-0.444	-0.288	-0.139
B	0.117	0.065	0.050	-0.019	-0.126	-0.293	-0.460	-0.571
SSA	-0.134	-0.180	-0.168	-0.233	-0.297	-0.389	-0.433	-0.437
CEC	0.518	0.476	0.453	0.393	0.294	0.117	-0.097	-0.264
TB	**0.947***	**0.928***	**0.925***	**0.892***	0.844	0.739	0.593	0.457

* Significant a p≤ 0.05 and ** at p≤ 0.01

It can be concluded that boron desorption is mainly governed by the sand content, but this was actually covering the true effect of sorption sites. As the coefficients of possible B sorption surfaces (e.i. CaCO3, OM, and clay) are considered, this fact can be clearly understood. The OM is likely to mediate B desorption up to 10 mg L-1 loadings, and then the effect of CCE showed a serious support trend to the desorption. The organic compounds are to dissolve at alkaline pH to form high molecular weight organic anions such as humate and fulvate anions which can compete for the sorption sites.

According to Nazir and Wani (2015), B desorption is favourably and strongly linked with sand concentration and negatively connected with clay content and cation exchange capacity. The difference in surface area of sand compared to clay and silt was the main factor governing B desorption. The smaller amount of sand, which had less adsorption capacity, resulted in smaller amounts of saturation capacity (Tlili et al. 2019; Arora and Chahal, 2010; Suganya et al. 2019) which in turn yielded a limited magnitude of desorption.

Conclusions

The sorption of B in B-rich soils can be satisfactorily described by Langmuir and Freundlich models despite possible solid phase formation. The B adsorption-desorption abilities of soils with high B content were elucidated towards understanding possible roles of routinely analyzed soil properties. While there were effects on soil sand content and available B parameters in B adsorption, sand content of soils and total B parameters played an important role in B desorption. Although a statistically significant relationship was not obtained with the clay content, specific surface area, and cation exchange capacity of the soil, they had considerable significant effects on the adsorption maxima. These results from adsorption-desorption show that at boron concentrations over 8 mg kg^{-1}, boron mobility increases, and this can exacerbate the hazards for crop production.

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Conflict of Interest

The authors declare no conflict of interest for this study.

Author's Contributions

The authors contributed equally to this manuscript.

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