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Effects of Organic Cropping on Phenolic Compounds and Antioxidant Capacity of Globe Artichoke Herbs

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Abstract: Artichoke herb is of great pharmaceutical importance, mainly due to the high content of phenolic compounds. This paper presents the effect of late nitrate (N) fertilization with mineral and organic N on the yield of air-dried herb, the total content of polyphenolic acids (TCQA), the polyphenolic profile as well as on the antioxidant activity (AA). These parameters were measured in organic (ORG) and conventional (CON) cropping systems. The principal outcomes revealed that the highest TCQA content was determined in the herbal extracts of ORG management treatments with late N fertilization of 20 kg ha^{-1}. This result explained the highest AA content of the extract in the ABTS+ (2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid)), FRAP (ferric-reducing antioxidant power), and DPPH (2,2-diphenyl-1-picrylhydrazyl) assays. Late N fertilization increased the content of cynarin and ferulic acid in both systems. In addition, chlorogenic acid increased between 37% and 45% in the CON cropping systems depending on the fertilizer dose. In the same treatment, luteolin increased 39% compared to the control. Lastly, in the ORG management system, caffeic acid and apigenin content increased 10% and 30%, respectively. Both treatments showed high collinearity values, where ORG systems were related to ferulic acid and cynarin, and CON systems were associated with chlorogenic acid and AA potential (ABTS, DPPH, FRAP). To sum up, ORG cropping systems can obtain an acceptable yield size with a high-quality content of bioactive compounds, allowing a better understanding of the effect of N fertilization in ORG and CON cropping systems.

Keywords: artichoke herb; cropping system; nitrogen fertilization; polyphenols; antioxidant activity

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1. Introduction

The common artichoke (*Cynara scolymus* L.) from the *Asteraceae* family has long been cultivated in warm climate countries as a vegetable. Artichoke leaves (*Cynarae folium*) or artichoke herb (*Cynarae scolymi herba*) are of great pharmaceutical importance, mainly due to the high content of phenolic compounds [1,2]. The high content of caffeic acid derivatives in artichoke has been confirmed by several authors [3–6]. The biologically active compounds found in the raw material include polyphenolic acids (0.02–2% dry matter), e.g., caffeic, chlorogenic, coumaric, ferulic acids and derivatives of di-caffeoylquinic acids (including cynarin, 1,5-di-caffeoylquinic acid; 3,4-di-caffeoylquinic acid; 3,5-di-caffeoylquinic acid), and flavonoids (0.1–2% dry matter) such as luteolin and apigenin [1,4]. A total of 61 bioactive compounds have been identified: hydroxybenzoic acids and flavonols, flavanones, lignans, and other polar compounds [7]. The AA of phenolic compounds extracted from artichoke has been confirmed by ABTS, FRAP, and DPPH tests [8].

Polyphenolic compounds have aroused great interest in the last few years due to their pro-health effects. They show cholagogic, anticancer, anti-inflammatory, antiallergic, and antiviral properties [2]. Artichoke bioactive compounds reduce high blood pressure, prevent atherosclerosis, and lower triglycerides and cholesterol [9].

The effect of N fertilization on the content of phenolic compounds in artichoke heads has been investigated by scientific teams under Mediterranean climate conditions [10–16]. Few studies have analyzed the effect of N fertilization in artichoke cultivation for the pharmaceutical industry [2,17]. Researchers have shown a positive and negative impact of N fertilization on the content of phenolic compounds in artichoke plants [10,12,16,18–22], and therefore, the published outcomes are inconclusive. Agricultural cropping systems, organic (ORG) and conventional (CON), can differ significantly in the amount and type of fertilizers used, plant protection, and crop rotation strategies [2,23]. Little is known about the response of artichoke to the use of organic fertilizers as part of an organic farming system. The ingredients in an organic form, not yet available for plants, can be activated by stimulating plant growth with late N fertilization. Spanu et al. [24] found a beneficial effect of organic matter on the soil's biological and chemical properties and, consequently, plants' rapid growth and vegetative development.

For artichoke, the up-to-date literature appears to be contradictory regarding the effects of the cropping system on the quality and quantity of the yield. For example, Al Mohandes Dridi et al. [25] did not observe yield differences between ORG and CON cropping systems, while others found significant differences [25,26]. Therefore, considering the poor availability of data on the response of artichoke plants grown for the needs of the pharmaceutical industry, this research aims to investigate the effects of N fertilization and the cropping systems (ORG/CON) on the yield and level of polyphenolic compounds (decisive for the biological value and AA of the raw material). This study assumed that organic fertilization would not reduce the yield and quality of the globe artichoke herb compared to the CON cropping system.

2. Materials and Methods

2.1. Characteristics of the Area, Climate, and Soil

Agronomic experiments were carried out at the Felin research station of the University of Life Sciences in Lublin, Poland (51.23° N, 22.56° E), during three growing seasons (2016, 2017, and 2018, respectively S_1, S_2, and S_3). The average temperature of the growing season (May–August) in 2018 was 19.2 °C and was higher than the long-term average by 3.2 °C, and in 2016 and 2017, was higher than the long-term average by 2.2 °C (Table 1). The amount of precipitation was variable during the three years, the highest value being registered in 2018 when it was >317 mm. The previous year (2017), 62.3 mm less than the average value of the three years was recorded. The individual growing seasons were characterized by a diversified sum of hours of sunshine (Table 2). The artichoke cultivation period in 2018 had the highest sum of sunshine hours (834), whereas in 2016 there were fewer hours of sunshine during the cultivation period (799).

Table 1. Meteorological conditions during the artichoke growing season in the three years of the experiment (data from the meteorological station in Felin, Poland 51.13° N; 22.37° E).

Year	May	June	July	August	Average
	Temperature (°C)				
S_1 [a]	15.0	19.2	19.9	18.7	18.2
S_2	14.1	19.6	18.9	20.2	18.2
S_3	16.7	18.8	20.6	20.8	19.2
Average 1951–2012	13.0	16.2	17.8	17.1	16.0
	Rainfall (mm)				Total
S_1	37.9	43.4	129.7	71.4	282.4
S_2	29.1	28.2	107.9	48.0	213.2
S_3	56.1	64.9	124.6	71.8	317.4
Average 1951–2012	57.7	65.7	83.5	68.6	275.5

[a] S_1: 2016; S_2: 2017; and S_3: 2018 and the period 1955–2012.

Table 2. Monthly average temperatures (°C) during the three seasons of the experiment 2016–2018.

Year	Month	Temperature (°C)			Insolation (Sum of Hours)
		Average Maximum	Average Minimum	Average Daily	
S_1 [a]	May	19.2	8.2	14.3	222
	June	22.4	13.0	18.6	205
	July	22.0	14.7	18.4	170
	August	24.5	13.4	18.8	202
	Average/Total	22.0	12.3	17.5	200/799
S_2	May	20.6	8.5	14.2	198
	June	24.1	13.3	18.6	222
	July	23.9	14.5	19.0	185
	August	24.5	13.6	20.0	201
	Average/Total	23.3	12.5	18.0	202/806
S_3	May	18.8	14.4	17.1	245
	June	20.4	16.5	18.8	206
	July	22.6	19.4	20.7	169
	August	23.2	18.1	20.7	214
	Average/Total	21.3	17.1	19.3	209/834

[a] S_1: 2016; S_2: 2017; and S_3: 2018 and the period 1955–2012.

The soil at Felin station is classified as Luvisols (IUSS Working Group WRB, [27]), with a silty clay loam texture in the topsoil layer (0–20 cm). In textural fractions, it should be noted that clay (39%) and sand (35.2%) showed similar values, compared to 25.8% for silt. According to the pH classification, the topsoil can be classified as slightly acid (6.7 in KCl) with these element concentrations (mg DM^{-3}): N-NO_3 27.7; Ca 684; K 159; P-PO_4 90; and Mg 90.

2.2. Plant Material, Experimental Design, and Management Practices

The research was conducted using globe artichoke cv. Green Globe. The seeds were received from Rijnsburg (the Netherlands) and were sown in the field on 29 April 2016, 5 May 2017, and 26 April 2018. This cultivar is characterized by a fast growth rate and abundant foliage; it is a valuable plant due to the high content of bioactive compounds [28]. The experiment was set up in a completely randomized block design with three replications in each growing season. The plot area was 10 m^2 with a plant spacing of 0.4 × 0.4 m and 62 plants. The cultivation procedures included: (i) two cultivation systems: an organic cropping system (ORG) and conventional cropping system (CON); (ii) two levels of late N fertilization (10:10 N and 20:20 N-N, fertilization rate expressed in kg ha^{-1}) and a control (without N fertilization, 0:0 N). The assays were conducted in two separate fields for each cropping system (ORG and CON) in the same area to guarantee identical climatic and soil conditions. The artichoke cultivation under conventional management conditions (CON) was carried out following local horticultural practices, while under organic management (ORG), the EU regulation guidelines were followed [29].

In each growing season, plants were fertilized once with late N fertilization at a dose of 10 and 20 kg ha^{-1} in the phase of 18–20 leaves per plant (3 June 2016; 20 June 2017; 9 June 2018). On the one hand, the CON cropping system used a combination of Polifoska 6-20-30-7 (NPK-S), urea (46% N), and in late N fertilization, Norwegian saltpeter (34% N). On the other hand, the ORG cropping system used granulated manure (7.5% N, 20% C organic). In the pre-sowing stage, the plots were fertilized (kg ha^{-1}) with mineral fertilizer in the conventional system (7 P and 52 K) and with granulated manure for the organic system (9 P and 45 K). Each field was plowed (30 cm deep) and harrowed before sowing. In each experiment, plowing (30 cm deep) and harrowing were performed before sowing. No phytosanitary products were used during the campaigns, and the crops were not irrigated.

2.3. Harvesting the Raw Material and Postharvest Treatments

From each plot, biomass was harvested from 120-day-old plants with similar developmental traits (plant height 40.0–45.0 cm; plants formed a leaf rosette) from an area of 1 m^2. Biomass from each cropping system was dehydrated from each treatment with repetition in a thermal dryer (Ventech, Świebodzin, Poland) at 40 °C. After drying, five consecutive measurements determined the water content.

3. Chemical Analyses

3.1. Reagents

The pure caffeoylquinic acids and flavonoids used for determination or calibration were purchased as certified materials from Merck (Darmstadt, Germany). All solvents and reagents used to prepare standard solutions and extract polyphenols (methanol, ethyl acetate, toluene, acetic acid, and formic acid) were of analytical grade and obtained from Sigma-Aldrich (St. Louis, MO, USA). Methanol, acetonitrile, and other chemicals were purchased from Avantor Performance Materials (Gliwice, Poland).

3.2. Sample Preparation

The dehydrated material was ground and passed through a 1 mm sieve. The resulting powder was divided into three replicates and stored at 15 °C until analyses. All analyses were carried out over 30 days. The methanol extract was prepared with the artichoke leaves' powder. Three grams of the powder were extracted by HPLC grade methanol (80:20, *v*/*v*, methanol/water). In each case, the dried samples of the plant material were pulled out in an RVO 400SD rotary vacuum evaporator (Ingots, Prague, Czech Republic) at a temperature of 100 ± 8 °C for 3 hours. After percolation through Whatman filter paper, gradation 42 (Merck, Warsaw, Poland), the material was re-treated with 80% methanol and extracted twice for 2 hours at room temperature. The filtrate was degreased by stirring three times with petroleum ether (30 mL each), and then the purified water solutions were extracted ten times with diethyl ether (20 mL each). The extracts with diethyl ether were again shaken with this solvent ten times (10 mL each). Ether extracts were joined and dried with anhydrous Na_2SO_4. All samples were stored at T = −22 °C until further analysis. All extractions were performed in duplicate.

3.3. HPLC Analysis

Phenolic compounds in extracts from air-dried artichoke leaves were separated by high-performance liquid chromatography (HPLC) on a Shimadzu series UFLC (Shimadzu Corp., Tokyo, Japan) system coupled to a diode array detector (DAD). Separation was performed on a Phenomenex Synergi Fusion-RP column (4 µm, 250 × 4.6 mm i.d., Phenomenex, Santa Clara, CA, USA) with a sample injection volume of 20 µL. The mobile phase consisted of acetonitrile (eluent A) and water/formic acid (99.9/0.1, *v*/*v*) (eluent B). A gradient program was adopted: 20% A (0 min), 25% A (10 min), 25% A (20 min), 50% A (40 min), 100% A (42–47 min), and 20% A (49–55 min). The flow rate was 1 mL min^{-1}, and the temperature was 30 °C. Detection was performed by scanning within the wavelength range from 190 to 400 nm. The contents of individual phenolic compounds were expressed from the calibration curves of the appropriate standards according to the recommended IUPAC numbering system (IUPAC, 1976). Pandino et al. [30] described the extraction procedure and chromatographic conditions for polyphenols' qualitative and quantitative characterization. Values were expressed in mg per 100 g dry weight (DW).

3.4. ABTS, FRAP and DPPH Methods

The ABTS test was performed according to the method of Prior et al. [31], by measuring the free radical scavenging ability, i.e., ABTS. The results were expressed as µM of Trolox equivalents (TE) per 100 g DW.

The FRAP reagent was prepared according to the procedure described by Gouveia and Castilho [32] with modifications. Methanol solutions with known Fe (II) concentrations were used to prepare the calibration curve. FRAP results were expressed as μM Fe^{2+} per 100 g DW.

The DPPH scavenging capacity of artichoke extracts was assessed according to the previously described method of Choi et al. [33] with modifications. The ethanol extracts (0.2 mL) were mixed with 0.8 mL of 0.2 mM DPPH solution and kept in the dark for 15 min. After this time, the absorbance at λ = 515 nm was measured. The results were reported as μM of Trolox (TE) per 100 g DW.

3.5. Statistical Analysis

Levene's test was used to determine homogeneity, and the data were subjected to a variance analysis (ANOVA) based on a two-way combination of the cropping system (2) × nitrogen dose (3). Means were separated by Tukey's test when the F-test was significant. The Pearson correlation was used to determine the relationship between N fertilization and the total content of polyphenolic acids (TCQA), polyphenolic fractions, and the antioxidant activity (AA) value. Results were shown as mean ± standard deviation (SD). All calculations were carried out with Statistica 13.0 PL software (StatSof Inc., Tulsa, OK, USA).

4. Results

4.1. Artichoke Herb Yield

The yield of air-dried artichoke herb was lower by 0.85 t ha^{-1} in the ORG system than in conventional management (CON) (Table 3). The late N fertilization increased the yield by 20% (10 kg ha^{-1}) and 43% (20 kg ha^{-1}). Moreover, weather conditions did not impact the yield.

In the CON management system, at a nitrogen dose (N) of 10 and 20 kg ha^{-1}, the yield was higher by 0.53 t ha^{-1} and 1.03 t ha^{-1}, respectively, compared to control (0 kg ha^{-1} N) (Figure 1). In the ORG case without N, the yield was 1.75 t ha^{-1}, and after applying a 20 kg N ha^{-1} dose, there was an increase of 0.76 t ha^{-1} compared to the control treatment.

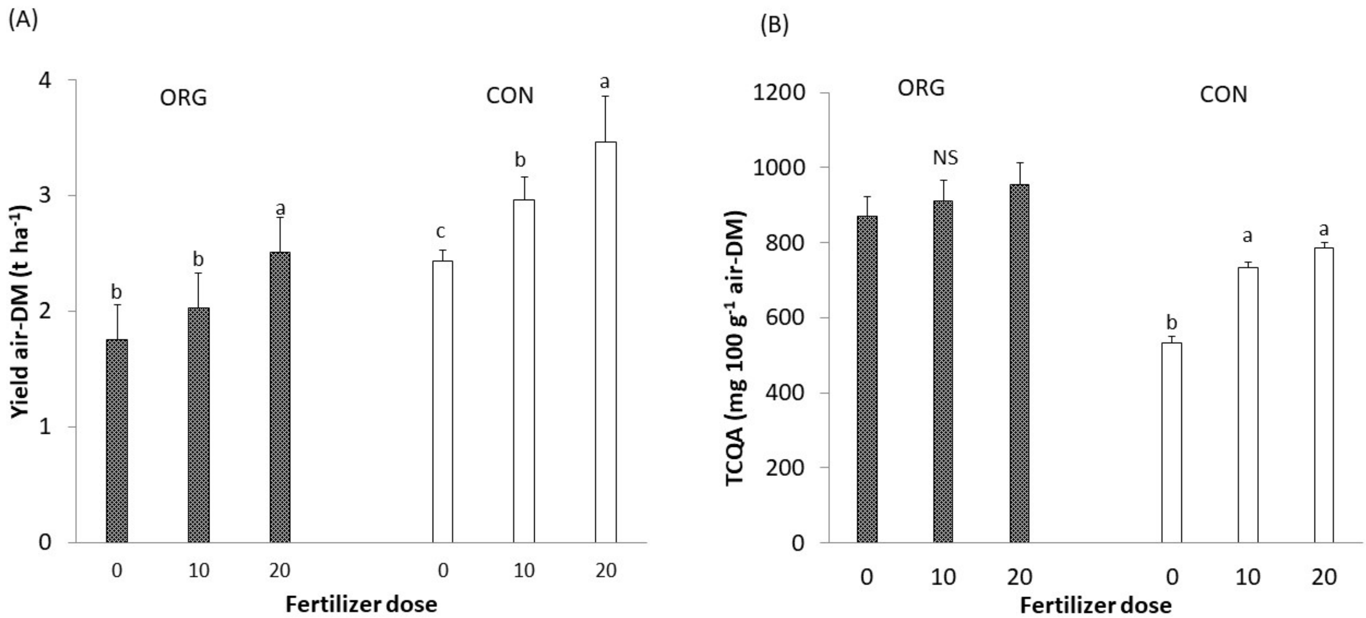

Figure 1. (**A**) Yield of air-dry biomass and (**B**) Content of total caffeoylquinic acids based (TCQA) based on the combination of organic (ORG)/conventional (CON) cropping system × fertilizer dose interaction.10 N; 20:20 N nitrogen dose expressed in kg ha^{-1}. Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three fertilizer doses ($p \leq 0.05$). NS means not significant. Bars indicate ± standard deviation.

Table 3. Yield of dry biomass (t ha^{-1}) and content of total caffeoylquinic acid (TCQA expressed mg 100 g^{-1} of DW) and the antioxidant activity (AA expressed by ABTS, DPPH and FRAP assays) of globe artichoke dry biomass as affected by the main factors.

Factor	Source of Variation	Yield of Air DW	TCQA (mg 100 g^{-1} DW)	ABTS [d] (μM Trolox 100 g^{-1} DW)	DPPH (μM Trolox 100 g^{-1} DW)	FRAP (μM Fe^{2+} 100 g^{-1} DW)
Cropping system (CS)	ORG [a]	2.10 ± 0.04 b	912 ± 11.4 a	280 ± 5.93 a	39.42 ± 1.35 a	60.21 ± 1.94
	CON	2.95 ± 0.05 a	690 ± 18.6 b	156 ± 5.21 b	26.39 ± 1.19 b	57.49 ± 2.60
	p-value	<0.001	<0.001	<0.001	<0.001	NS
Fertilization (F)	0 [b]	2.09 ± 0.04 c	712 ± 12.3 c	175 ± 6.82 b	26.16 ± 1.51 c	44.63 ± 1.53 c
	10	2.50 ± 0.05 b	822 ± 12.2 b	207 ± 7.07 b	34.65 ± 1.20 b	57.50 ± 1.69 b
	20	2.99 ± 0.06 a	869 ± 12.6 a	272 ± 8.58 a	42.42 ± 0.82 a	74.43 ± 2.51 a
	p-value	<0.001	<0.001	<0.001	<0.001	<0.001
Year (Y)	S_1 [c]	2.53 ± 0.05	709 ± 12.5 c	216 ± 9.91	29.12 ± 1.19 b	46.68 ± 1.19 b
	S_2	2.50 ± 0.08	788 ± 12.6 b	217 ± 7.69	28.00 ± 0.96 b	47.35 ± 1.17 b
	S_3	2.54 ± 0.06	906 ± 14.0 a	221 ± 8.09	46.10 ± 1.12 a	82.53 ± 2.10 a
	p-value	NS	<0.001	NS	<0.001	<0.001
CS × F	*p*-value	NS	NS	NS	NS	NS
CS × Y	*p*-value	0.006	<0.001	0.022	0.008	0.018
F × Y	*p*-value	NS	NS	NS	NS	NS
CS × F × Y	*p*-value	NS	NS	NS	NS	NS

Different letters within each column and main factor indicate significant differences at $p \leq 0.05$; NS not significant. [a] ORG: organic cropping system; CON: conventional cropping system; [b] 0:0 N; 10:10 N; 20:20 N nitrogen rate expressed in kg ha^{-1}; [c] S_1: 2016; S_2: 2017; and S_3: 2018; [d] antioxidant activity by ABTS, DPPH, and FRAP assays.

4.2. Polyphenolic Acid Content and Antioxidant Value

In the ORG cropping system, the TCQA content was 32% higher than in the CON, resulting in a higher AA against the ABTS radical and DPPH (not relevant for FRAP) (Table 3). Late N fertilization with 10 kg ha^{-1} significantly ($p < 0.001$) increased TCQA by 15%, while for 20 kg ha^{-1} the increase was 22%. The TCQA content was higher in 2018 than in 2017 and 2016. In 2018, the highest AA values of artichoke leaf extract were recorded, but only for data shown for DPPH and FRAP.

In the ORG cropping system, plants accumulated more TCQA in 2018 (934 mg 100 g^{-1}) and 2017 (906 mg 100 g^{-1}) (Table 4). High TCQA values corresponded to the high AA values shown by the DPPH and FRAP tests in 2018 but not to the AA demonstrated by the ABTS test. The CON management system in 2018 registered a higher TCQA content (878 mg 100 g^{-1}) and the highest AA value using the DPPH and FRAP tests.

Table 4. Yield of dry biomass (t ha^{-1}) and content of total caffeoylquinic acid (TCQA expressed mg 100 g^{-1} of air-DW) and the antioxidant activity (AA expressed by ABTS, DPPH and FRAP assays) of globe artichoke dry biomass as affected by the 'cropping system × year' interaction.

Factor	Yield of DW	TCQA (mg 100 g^{-1} DW)	ABTS [c] (μM Trolox 100 g^{-1} DW)	DPPH (μM Trolox 100 g^{-1} DW)	FRAP (μM Fe^{2+} 100 g^{-1} DW)
ORG [a]					
S_1 [b]	2.30 ± 0.02 a	896 ± 10.8 b	304 ± 5.2 a	36.91 ± 0.92 b	53.05 ± 1.18 b
S_2	1.85 ± 0.04 b	906 ± 10.8 ab	271 ± 5.2 ab	27.81 ± 1.11 c	48.65 ± 1.18 c
S_3	2.15 ± 0.04 ab	934 ± 12.5 a	265 ± 7.3 b	53.56 ± 0.28 a	78.94 ± 1.90 a
p-value	0.041	0.030	0.026	<0.001	<0.001
CON					
S_1	2.76 ± 0.06	521 ± 11.8 c	130 ± 2.56	21.34 ± 0.91 b	40.31 ± 0.86 c
S_2	3.16 ± 0.04	671 ± 10.6 b	171 ± 6.49	28.20 ± 0.90 ab	46.05 ± 1.27 b
S_3	2.93 ± 0.04	878 ± 10.5 a	167 ± 5.60	38.64 ± 1.16 a	86.12 ± 2.40 a
p-value	NS	<0.001	NS	0.005	<0.001

Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three years ($p \leq 0.05$); NS: not significantly different. [a] ORG: organic cropping system; CON: conventional cropping system. [b] S_1: 2016; S_2: 2017; and S_3: 2018. [c] antioxidant activity by ABTS, DPPH, and FRAP assays.

4.3. Fractions of Polyphenolic Acids and Flavonoids

Compared to the CON cropping system, the content of polyphenolic compounds in the ORG management system was higher. More specifically: caffeic acid increased 10%, apigenin 30%, chlorogenic acid 33%, ferulic acid 39%, and luteolin 51% (Table 5). The herb contained 21% less cynarin in ORG management than in traditional cultivation. Along with the increase in N doses, the content of polyphenol fractions in the herb increased significantly. In general, plants accumulated more polyphenolic compounds during the harvest period in 2018 and less in 2016. Only the content of cynarin was higher in 2018 and 2016 than in 2017.

In the ORG cropping system, the herb obtained from 2017 and 2018 plants contained more caffeic acid, chlorogenic acid, and luteolin than in 2016 (Table 6). In the ORG, the cynarin content was higher in 2016 and 2018 than in 2017. In CON management, plants accumulated more chlorogenic acid and apigenin in 2018 and caffeic acid in 2017.

Table 5. Content of cynarin, caffeic acid, chlorogenic acid, ferulic acid, apigenin and luteolin (mg 100 g^{-1} DW) in globe artichoke leaves affected by the cropping system and fertilization dose.

Factor	Source of Variation	CYN [a]	CAF	CHL	FER	API	LUT
Cropping system (CS)	ORG [b]	0.719 ± 0.03 b	1.76 ± 0.22 a	672 ± 8.8 a	2.98 ± 0.15 a	232 ± 3.96 a	1.866 ± 0.06 a
	CON	0.869 ± 0.04 a	1.60 ± 0.24 b	506 ± 16.5 b	2.14 ± 0.07 b	179 ± 4.71 b	1.238 ± 0.02 b
	p-value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Fertilization (F)	0 [c]	0.379 ± 0.01 c	1.56 ± 0.20 c	531 ± 19.6 b	1.30 ± 0.02 c	177 ± 5.00 b	1.383 ± 0.05 c
	10	0.742 ± 0.01 b	1.66 ± 0.24 b	604 ± 15.2 a	2.60 ± 0.04 b	211 ± 4.42 ab	1.533 ± 0.05 b
	20	1.262 ± 0.02 a	1.81 ± 0.23 a	632 ± 14.3 a	3.79 ± 0.12 a	229 ± 4.72 a	1.741 ± 0.05 a
	p-value	<0.001	<0.001	<0.001	<0.001	0.007	<0.001
Year	2016	0.853 ± 0.05 a	1.43 ± 0.19 b	512 ± 16.7 c	2.25 ± 0.13 b	191 ± 6.21 b	1.083 ± 0.01 b
	2017	0.715 ± 0.05 b	1.80 ± 0.14 a	590 ± 14.4 b	2.68 ± 0.12 a	192 ± 3.19 b	1.766 ± 0.05 a
	2018	0.815 ± 0.02 a	1.80 ± 0.18 a	666 ± 11.8 a	2.75 ± 0.13 a	233 ± 4.57 a	1.808 ± 0.06 a
	p-value	0.006	<0.001	<0.001	0.010	0.015	<0.001
CS × F	*p*-value	0.014	0.018	0.026	<0.001	NS	NS
CS × Y	*p*-value	0.041	0.003	0.023	NS	NS	<0.001
F × Y	*p*-value	<0.001	NS	NS	NS	NS	NS
CS × F × Y	*p*-value	0.015	NS	NS	NS	NS	NS

Different letters (a–c) within each column and main factor indicate significant differences at $p \leq 0.05$; NS not significant. [a] CYN: cynarin; CAF: caffeic acid; CHL: chlorogenic acid; FER: ferulic acid; API: apigenin; LUT: luteolin. [b] ORG: organic cropping system; CON: conventional cropping system. [c] 0:0 N; 10:10 N; 20:20 N nitrogen rate expressed in kg ha^{-1}.

Table 6. Content of cynarin, caffeic acid, chlorogenic acid, ferulic acid, apigenin and luteolin (mg 100 g^{-1} DW) in globe artichoke leaves affected by the 'cropping system × year' interaction.

Factor	CYN [a]	CAF	CHL	FER	API	LUT
ORG						
S_1 [b]	0.803 ± 0.04 a	1.56 ± 0.17 b	655 ± 19.9 b	2.73 ± 0.16	235 ± 6.18	1.03 ± 0.01 b
S_2	0.579 ± 0.03 b	1.80 ± 0.18 a	679 ± 14.8 ab	3.08 ± 0.14	219 ± 1.78	2.23 ± 0.01 a
S_3	0.777 ± 0.02 a	1.92 ± 0.16 a	682 ± 19.0 a	3.15 ± 0.16	243 ± 3.24	2.33 ± 0.01 a
p-value	<0.001	<0.001	0.004	NS	NS	<0.001
CON						
S_1	0.90 ± 0.06	1.30 ± 0.08 c	368 ± 10.9 c	1.80 ± 0.16	148 ± 1.93 b	1.13 ± 0.01
S_2	0.85 ± 0.04	1.80 ± 0.11 a	500 ± 10.9 b	2.28 ± 0.18	165 ± 1.18 b	1.30 ± 0.02
S_3	0.85 ± 0.02	1.69 ± 0.11 b	648 ± 10.9 a	2.35 ± 0.18	223 ± 5.74 a	1.28 ± 0.03
p-value	NS	<0.001	<0.001	NS	0.009	NS

Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three fertilizer doses ($p \leq 0.05$); NS: not significantly different. [a] CYN: cynarin; CAF: caffeic acid; CHL: chlorogenic acid; FER: ferulic acid; API: apigenin; LUT: luteolin. [b] S_1: 2016; S_2: 2017; and S_3: 2018.

4.4. Nitrogen Fertilization in an Organic and Conventional System

Increasing the fertilization dose (10N and 20N) in CON, the level of TCQA increased by 27–32% compared to the control (0N) (Figure 1). On the contrary, the applied N doses in ORG management did not significantly affect the TCQA content, although it seems slightly higher with a 20N dose (954 mg 100 g^{-1}). Even though the ORG system did not affect TCQA, there was an improvement in the cynarin content with both doses 10N (+122%) and 20N (+247%). Conversely, CON treatments only registered an increase with the 20N dose (+226%) compared to control (Figure 2).

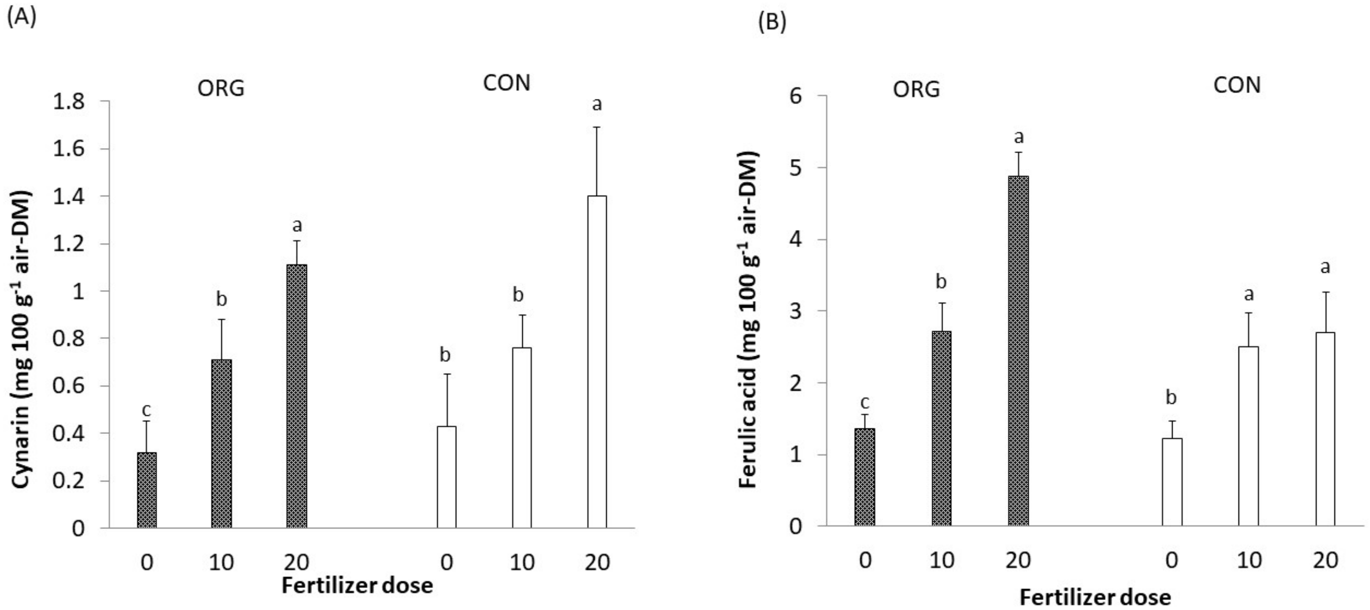

Figure 2. (**A**) Cynarin content and (**B**) Ferulic acid content based on the combination of organic (ORG)/conventional (CON) cropping system × fertilizer dose interaction. 0:0 N; 10:10 N; 20:20 N nitrogen dose expressed in kg ha^{-1}. Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three fertilizer doses ($p \leq 0.05$). Bars indicate ± standard deviation.

The N fertilization raised the content of ferulic acid in both systems (Figure 2). In the ORG management system it increased by 99% (10N) and 259% (20N), whereas in the CON situation, the improvement was 103% and 120%, respectively.

Caffeic acid was also another variable affected by N fertilization because it was significantly boosted by 22% in the ORG cropping system (20 kg ha^{-1} dose). In CON management, the differences between fertilizer treatments were insignificant (Figure 3).

The Chlorogenic acid content in CON increased significantly with the applied dose of 10N and 20N by 37% and 45%, respectively, compared to 0N, but in the ORG system did not show significant effects due to N fertilization (Figure 3).

Similarly to the caffeic acid level, the apigenin content increased by 28% with 20N application in the ORG cropping system, while in the CON management system, the differences were insignificant (Figure 4).

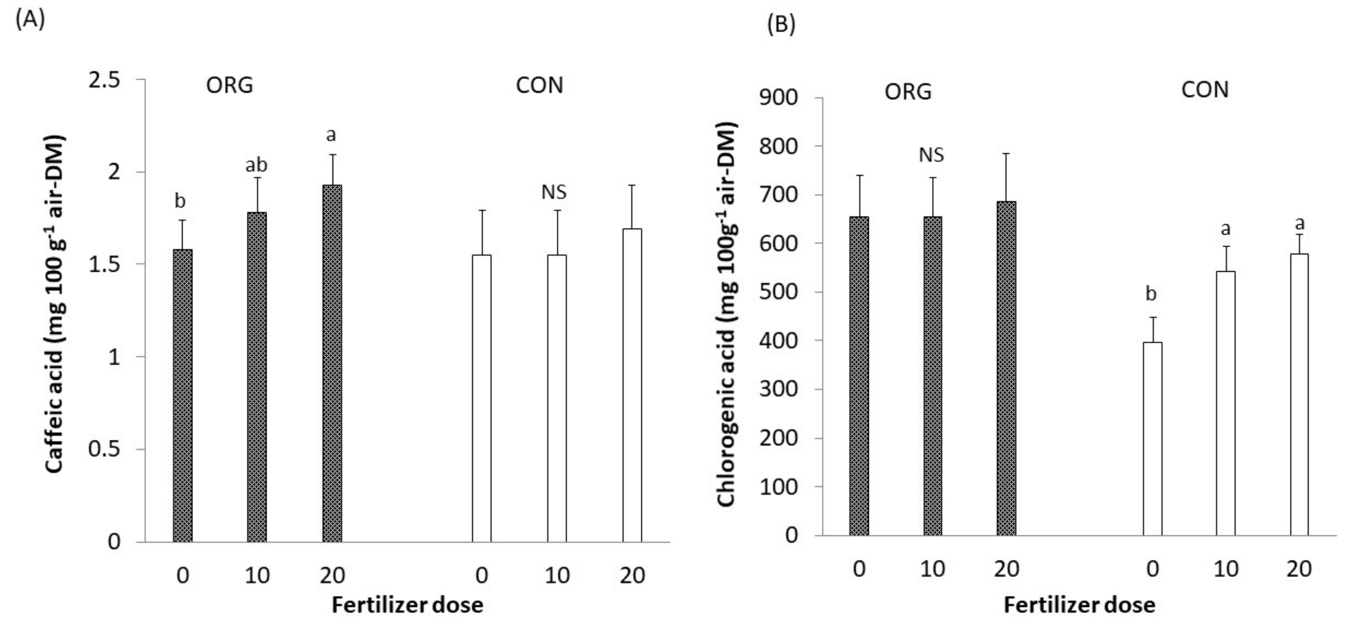

Figure 3. (**A**) Caffeic acid content and (**B**) Chlorogenic acid content based on the combination of organic (ORG)/conventional (CON) cropping system × fertilizer dose interaction. 0:0 N; 10:10 N; 20:20 N nitrogen dose expressed in kg ha^{-1}. Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three fertilizer doses ($p \leq 0.05$). NS means not significant. Bars indicate ± standard deviation.

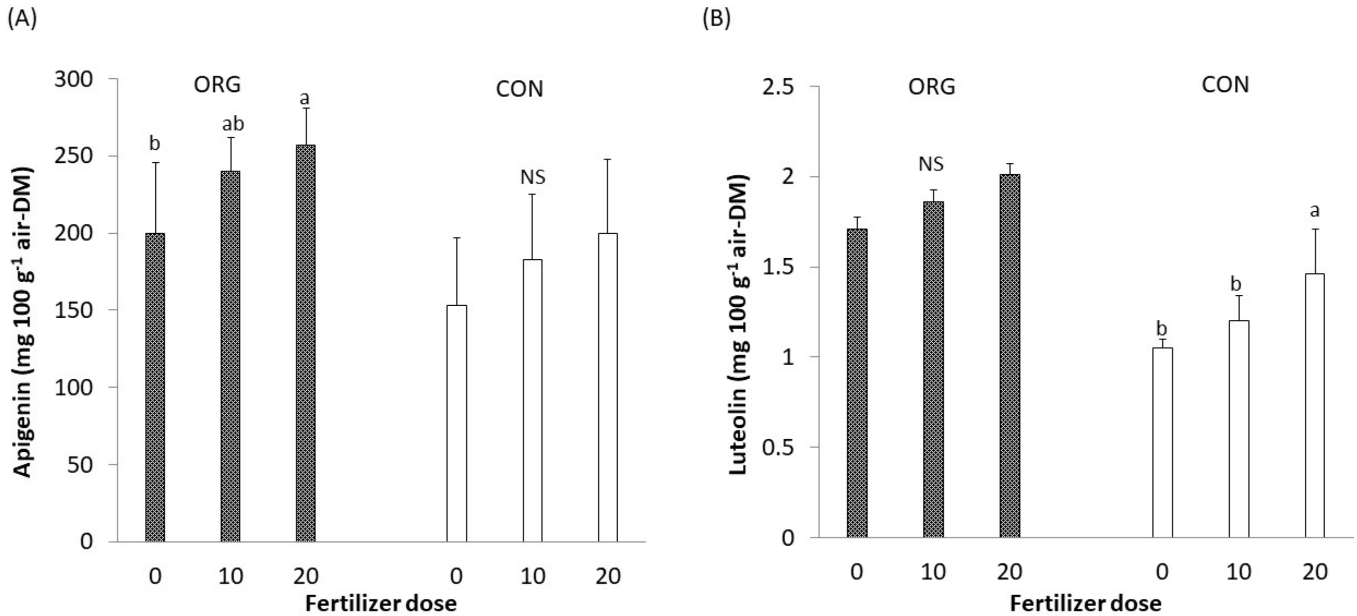

Figure 4. (**A**) Apigenin content and (**B**) Luteolin content based on the combination of organic (ORG)/conventional (CON) cropping system × fertilizer dose interaction. 0:0 N; 10:10 N; 20:20 N nitrogen dose expressed in kg ha^{-1}. Different letters (a–c) are significantly different for each separate cropping system (ORG and CON) between the three fertilizer doses ($p \leq 0.05$). NS means not significant. Bars indicate ± standard deviation.

The luteolin content in the CON cropping system increased by 39% with an applied N dose of 20 kg ha^{-1} compared to 0 kg ha^{-1}. There was no significant effect of N fertilization in the ORG (Figure 4).

4.5. Correlations between Parameters

In both cropping systems, the correlation between fertilization and TCQA content was positive with weak collinearity (r = 0.30 for ORG and r = 0.34 for CON) (Table 7). The value of the correlation coefficient for ferulic acid in both systems (r = 0.80–0.81) proved a strong relationship between fertilization and the content of this acid. The model explains 65–78% of the variability of the ferulic acid content in air-dried herb, based on N fertilization. In ORG, the correlation coefficient for cynarin was very high (r = 0.72), while in the CON cropping system, the mean registered value was 0.48. The correlation coefficient for luteolin in ORG (r = 0.49) and CON (r = 0.42) showed a relevant relationship between N fertilization and the content of this compound.

Table 7. Summary of regression analyses of the fertilization and the significance of correlations among the chemical parameters analyzed in organic and conventional cropping systems.

Parameter	ORG				CON			
	r	r^2	a_0	a_1	r	r^2	a_0	a_1
TCQA [a]	0.30 *	0.11	1.58	0.00	0.34 *	0.22	0.01	0.00
CYN	0.71 **	0.51	7.37	0.03	0.47 **	0.22	9.40	0.01
CAF	0.39 *	0.15	1.48	0.00	0.24 ^{NS}	0.06	1.52	0.00
CHL	0.07 ^{NS}	0.00	548.18	0.38	0.73 **	0.54	391.75	2.16
FER	0.81 **	0.65	1.36	0.02	0.80 **	0.78	1.34	0.01
API	0.03 ^{NS}	0.00	165.68	−0.04	0.08 ^{NS}	0.00	168.61	0.06
LUT	0.49 **	0.24	2.12	0.00	0.42 *	0.17	2.34	0.00
ABTS	0.48 *	0.00	208.43	0.15	0.72 **	0.53	147.80	0.02
DPPH	0.48 *	0.00	49.66	0.03	0.72 **	0.53	35.00	0.19
FRAP	0.48 *	0.00	93.81	0.07	0.72 **	0.53	66.12	0.37

*, and ** indicate significant differences at $p \leq 0.05$ and $p \leq 0.01$, and ^{NS}, not significant. [a] TCQA: total caffeoylquinic acids; CYN: cynarin; CAF: caffeic acid; CHL: chlorogenic acid; FER: ferulic acid; API: apigenin; LUT: luteolin; ABTS, DPPH and FRAP: antioxidant activity determined by ABTS, DPPH and FRAP assays.

For caffeic acid, the correlation coefficient was 0.39 on average, but only in ORG, because the value was irrelevant in CON management.

In ORG management, the correlation coefficient for chlorogenic acid was also insignificant, while in the CON system it was very high (r = 0.74). There was no collinearity between fertilization and apigenin content in both cropping systems.

In CON systems, the value of the correlation coefficient for AA expressed by the ABTS, FRAP and DPPH test is 0.72, which proves a strong linear dependence of AA on nitrogen fertilization. In the ORG system, the correlation coefficient for AA expressed by the ABTS, FRAP and DPPH test was average.

5. Discussion

5.1. Influence of the Cultivation System on the Globe Artichoke Yield and Antioxidant Properties

The average yield of the dried herb was 2.5 t ha^{-1} and was close to the yield (2.5–3.3 t ha^{-1}) of artichoke cultivated in Germany for the pharmaceutical industry [17]. To our knowledge, there have been no previous studies on the cultivation of artichoke for herb harvesting in the ecological system. In the present study, the yield of air-dried artichoke biomass in the organic cropping system (ORG) was significantly lower, but with a higher content of total polyphenolic acids (TCQA) compared to the conventional cropping system (CON). These results indicate a disproportion between the plants' demand for nutrients and their actual availability in sensitive plant development stages. According to Zarabi and Jalai [34], the release rate of minerals in ORG management may not optimally match the requirements of plants. It is worth noting that the temporary unavailability of N in organic farming reduces the yield of other plant species, e.g., cauliflower [35].

The results showed a higher content in all the variables (TCQA, caffeic acid, chlorogenic acid, ferulic acid, luteolin, and apigenin) in the ORG system than CON. Only the cynarin showed a lower content. Fateh et al. [26] also observed a trend of increasing TCQA and chlorogenic acid in the ORG compared to the CON cropping system. The higher polyphenol content in artichoke from the ORG cropping system confirms the CNB (carbon–nutrient balance) hypothesis. It states that the concentration of secondary metabolites in plants depends mainly on the availability of light, carbon, and minerals [36]. In ORG cropping systems, plant metabolism changes, and in the first place, the compounds containing mainly carbon in their chemical structure are carbohydrates, phenolic compounds, and some vitamins, e.g., ascorbic acid. In research conducted by Leskovar and Othman [37], artichoke grown for bud collection in organic systems showed an increase in chlorogenic acid content by 31%, whereas cynarin increased by 12% compared to traditional cultivation. The organic cultivation extract showed a higher AA than the conventional extract in ABTS and DPPH tests. The DPPH test assessment showed relatively small AA potential differences between both cropping systems (39 µg Trolox 100 g^{-1} for ORG and 26 µM Trolox 100 g^{-1} for CON). The outcomes indicate that the higher AA activity of the artichoke extract is associated with the higher TCQA content. An earlier study also showed a higher TCQA content with a simultaneously higher AA of artichoke extract [15]. These results demonstrate the potential for improving the health value of organically grown vegetables and herbs.

5.2. Influence of Nitrogen Fertilization on the Herb Yield

The applied late N fertilization (10 and 20 kg ha^{-1}) increased the raw material yield relating to the cultivation without fertilization. Under the experimental conditions, the total dose of N fertilization was 90–100 kg ha^{-1} and was similar to that used in artichoke cultivation for the pharmaceutical industry in Germany [17]. In German studies, increasing the doses of N (from 40 to 240 kg ha^{-1}) increased the yield; however, it caused a deterioration in quality, an increase in the content of nitrates in leaves, and a decrease in the level of TCQA and flavonoids. Baier et al. [17] determined the optimal N fertilization was in the amount of 120 kg ha^{-1} before the first harvest of leaves and 50 kg ha^{-1} in the period preceding the second harvest. Many studies have shown that N fertilization can significantly increase the yield of artichoke buds in vegetable cultivation [15,19,38,39]. The maximum dose of N in the form of ammonium nitrate (100 kg ha^{-1}) provided the highest yield of artichoke buds with a high content of polyphenolic compounds [19]. In the climatic conditions of Italy, it was established that 200 kg ha^{-1} is the upper limit for increasing the yield of artichoke buds [15]. Large doses (500 kg ha^{-1}) of N did not increase the yield and, at the same time, reduced the quality of buds.

5.3. Influence of Nitrogen Fertilization on the Content of Polyphenolic Compounds

The content of bioactive compounds in this study classified the raw material of globe artichoke as a rich source of phenolic compounds compared to the results described for the cultivars grown in Italy [15] and Germany [17,38]. In general, N fertilization increases the content of polyphenols in artichoke [15,16]. In contrast, Shinihara et al. [12] found that N fertilization had a negligible effect on the content of chlorogenic acid and cynarin in artichoke.

The predominant polyphenol compounds in the leaves are mono- and di-caffeoylquinic acids (e.g., chlorogenic acid and cynarin), and a range of flavonoids derived from apigenin and luteolin [16]. Additional nitrogen fertilization raised the cynarin content by 233% and ferulic acid by 191%. To a lesser extent, an increase of between 16% and 29% was recorded in caffeic acid, luteolin, chlorogenic acid, and apigenin compared to the cultivation without N.

In the studies of Negro et al. [19], N fertilization increased the caffeoylquinic acids and luteolin derivatives and decreased the apigenin content. Lombardo et al. [15] and Baier et al. [17] showed that moderate fertilization promotes the synthesis of carbon-based secondary metabolites, such as TCQA, and under over-fertilization conditions, the accumulation of polyphenolic compounds tends to decrease. According to the same authors, high doses of N increased vegetative growth. This situation may cause the self-shade of plants with a reduction of photosynthesis efficiency and of caffeoylquinic acid and flavonoid content.

In all tests, artichoke leaf extracts fertilized with N were characterized by a higher AA than those from nonfertilized plants. The increase in the AA value of artichoke extracts under the influence of N fertilization was observed by Lombardo et al. (2015) in Jerusalem artichoke [40]. It was assumed that N plays a fundamental role in the antioxidant defense of plants and lipid peroxidation in stressful situations [15,41].

5.4. Influence of the Growing Season on Polyphenols

Little information is available in the literature on the influence of the meteorological pattern on phenol content in a humid temperate climate, where the duration of vegetation and herbal yield can be very variable depending on weather conditions.

The TCQA content was higher in 2018 because the average temperature of the growing season was 3.2 °C higher than the long-term average, with a high sum of sunny hours (834). The high TCQA content in 2018 was accompanied by the high AA value of the extract (DPPH and FRAP).

The raised level of TCQA was due to the high content of caffeic acid, chlorogenic acid, ferulic acid, apigenin, and luteolin. Likely, the greater availability of N and the higher temperatures in July and August in 2018, compared to 2016 and 2017, may have been the reason for the more significant accumulation of TCQA by artichoke plants. In addition, higher minimum temperatures during the period of vigorous plant growth in 2018 in July and August at night increased the transpiration rate of artichoke plants, which may have increased TCQA accumulation due to lower cell sap dilution. The mean maximum temperatures could also influence the accumulation of TCQA. The presence of days with high temperatures in 2016 and 2017 during intensive growth could accelerate plant maturation and, consequently, reduce the content of polyphenolic compounds, and has been observed in previous studies by Mohd at al. [18].

5.5. Interaction of "Crop System × Fertilization"

In the CON cropping system, the content of TCQA increased with increasing the dose in fertilization. In the ORG management system, the applied doses in the late N fertilization did not increase the TCQA content compared to the cultivation without fertilization. On the other hand, the TCQA content was higher in the ORG cropping system than in CON. It may suggest that the cultivation system influences the growth of microorganisms and the level of active enzymes in the soil in different ways. In organic cultivation, microorganisms use the food base more favorably, which is due to the competition between microorganisms and plants being smaller. As a result, the effect of the fertilizers is less progressive in contrast to conventional cultivation. According to Marinari et al. [23], mineral fertilization stimulates the enzymatic activity of the soil to a lesser extent than organic fertilization. Leskovar and Othman [37] concluded that increasing the organic matter in the soil improved the physico-chemical properties of the soil. The main consequence was an improvement in the uptake of micro- and macroelements. In addition, they recorded an increase in plant biomass which contributed to the boosted production of secondary metabolites and antioxidant compounds. According to the same authors, a higher amount of organic matter causes an increase in porosity, which entails a decrease in the specific density of the soil. It makes it easier for microorganisms to penetrate the soil environment and use organic compounds, thereby plants have greater access to the nutrients.

In this study, N fertilization increased the content of cynarin and ferulic acid in both cropping systems; chlorogenic acid and luteolin in CON, and caffeic acid and apigenin content in the ORG management system. The differences could be related to the higher organic carbon content in the ORG cropping system due to the multiplication of the microflora. An increase in the activity of microorganisms significantly favors organic matter mineralization. Negro et al. [19] observed the stimulating effect of organic fertilizers in increasing the CO_2

content in the soil and, as a result, increasing the level of chlorogenic acid by 31% and cynarin by 12% compared to mineral fertilizer.

5.6. Interaction of "Cultivation System × Growing Season"

The most considerable differences in the yield size between the ORG and CON cropping systems were found in 2017. In the three-year study, the air-dried biomass yield was lowest in the ORG and highest in the CON system (the differences between years in the conventional systems were insignificant). This difference could be due to the different availability of N from the soil throughout the growing season. In 2017, the sum of precipitation from May to August was 62 mm lower than the long-term sum, and the average air temperature was higher by 2.2 °C than the long-term average. In the ORG cropping system, water scarcity and the accompanying high air temperatures reduced the availability of nutrients from the soil.

It has been determined that the low availability of minerals under severe drought stress conditions is responsible for the accumulation of phenolic compounds in a warm climate [6]. On the contrary, the experiment was developed in a temperate climate, and the plants accumulated more TCQA in 2018 (in both systems). This increase coincided with the season that showed more precipitation and total duration of insolation, and high temperatures. These situations occurred during the intensive plant growth in May, June, and July. During the growing season in 2016, with a low average daily temperature and a low total number of sunshine hours, low levels of caffeic acid and chlorogenic acid were found in both systems (CON and ORG). Moreover, luteolin was also found low in the ORG cropping system and apigenin in the CON. Only the level of cynarin was the lowest in 2017, with little precipitation. When assessing the impact of drought in artichoke cultivation, it was stated that mild drought stress increases the content of phenolic compounds, while intense water stress reduces AA [15].

In ORG, the ABTS test revealed significant differences in the level of antioxidant potential of artichoke: 304 μM TE 100 g^{-1} DW (2016) and 265 μM TE 100 g^{-1} DW (2018). In the DPPH and FRAP tests, artichoke leaf extracts showed the highest radical scavenging capacity in 2018. These results indicate a higher AA effectiveness of leaf extracts, which were the richest in phenolic compounds. In the CON cropping system in 2018, in which the content of phenolic compounds was the highest, the artichoke leaf extract showed a higher AA as expressed by the DPPH and FRAP test. Pandino et al. [8] reported a positive relationship between secondary metabolites and the AA of artichoke leaf extract.

5.7. Correlations

Although N fertilization increased the content of TCQA in the raw material in ORG and CON cropping systems, the values of the correlation coefficients indicate a weak correlation between late N fertilization and TCQA. However, in the ORG management system, the correlation coefficients for ferulic acid, chlorogenic acid, and cynarin indicated a high relationship between their content and the applied N fertilization. In CON, fertilization with N caused the most significant increase in chlorogenic acid and an average increase in luteolin and cynarin. The interaction between chlorogenic acid content and N fertilization in both cultivation systems was noted.

It has been reported that there is a positive relationship between phenolic compounds and their AA, which was mainly attributed to chlorogenic acid [15]. Nitrogen fertilization (100 kg ha^{-1}) increased the total phenolic compound content and, at the same time, the AA capacity in artichoke buds. A limited or increased N availability was less favorable for accumulating the above compounds [19].

In this paper, the CON cropping system showed a strong positive correlation (0.72) between fertilization and the results of ABTS, DPPH and FRAP tests. It indicates that phenolic compounds were the carriers of the antioxidant activity of artichoke extracts, as the content of TCQA and chlorogenic acid was high. On the other hand, in ORG, no such relationship was found between AA and N fertilization in the case of the nitrogen supply in organic form. Jakovljević et al. [42] report that a higher nutrient availability may improve protection against oxidative stress. It can be hypothesized that the difference in AA is related to the type of N supplied under specific farming conditions.

6. Conclusions

This research confirmed that in the organic farming system (ORG) it is possible to obtain an acceptable yield size with a high-quality content of bioactive compounds in the plants. Polyphenolic compounds have been identified in artichoke extracts, mainly cynarin, ferulic acid, caffeic acid, chlorogenic acid, apigenin, and luteolin. In the ORG cropping system, due to late N fertilization with the dose of 20 kg ha^{-1}, the TCQA content increased, which resulted in high AA values of the extract in the ABTS, FRAP, and DPPH tests. In both ORG and CON management, N fertilization caused an increase in cynarin and ferulic acid content. Specifically, due to N fertilization, plants in the CON cropping system increased chlorogenic acid and luteolin content.

Moreover, there was an increase in caffeic acid and apigenin content in the organic management system. In addition, there were high collinearity values in ORG systems, which confirmed the relationship between fertilization and the content of ferulic acid, chlorogenic acid, and cynarin. For the CON management system, the collinearity was related to the chlorogenic acid content. As the main conclusion, it can be determined that the present research complements the existing knowledge in the area and suggests that optimal N fertilization influences the formation of a favorable composition of biologically active compounds, including artichoke polyphenols, with antioxidant potential. It will be necessary to conduct further research, in the long term, to evaluate an alternative ORG cropping system on the yield and quality of artichoke raw material for the pharmaceutical industry.

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