

Article

# Moderation of Inulin and Polyphenolics Contents in Three Cultivars of *Helianthus tuberosus* L. by Potassium Fertilization

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**Abstract:** Jerusalem artichoke, a widely consumed edible, is an excellent source of inulin and selected phytochemicals. However, the improvement of its chemical composition by potassium fertilization has not yet been studied. Thus, the aim of the study was to evaluate the effect of different potassium (K) fertilization levels ( $K_2O$  150 kg ha<sup>-1</sup>, 250 kg ha<sup>-1</sup>, 350 kg ha<sup>-1</sup>) on the content of inulin; profile and changes in polyphenolic compounds; and the antioxidant capacity, including on-line ABTS antioxidant profiles of freeze-dried tubers originated from *Violette de Rennes*, *Topstar*, and *Waldspindel* cultivars. Inulin content was highest in the early maturing *cv.* *Topstar*. The application of 350 kg ha<sup>-1</sup> of K fertilizer rates during the growth of *cv.* *Topstar* increased the inulin content of tubers by 13.2% relative to the lowest K fertilizer rate of 150 kg ha<sup>-1</sup>. In *cv.* *Violette de Rennes*, inulin accumulation increased in response to the fertilizer rate of 250 kg ha<sup>-1</sup>. A further increase in K fertilizer rates had no effect on inulin content. The inulin content of *cv.* *Waldspindel* was not modified by any of the tested K fertilizer rates. Thus, the accumulation of the inulin was cultivar-dependent. In the cultivars analyzed, 11 polyphenolic compounds were identified and polyphenolic compound content was affected by the applied rate of potassium fertilizer, which was dependent on the cultivar. Chlorogenic acid was the predominant phenolic acid in all cultivars, and it accounted for around 66.4% of the identified polyphenolic compounds in *cv.* *Violette de Rennes* and for around 77% of polyphenolic compounds in *cv.* *Waldspindel* and *Topstar*.

**Keywords:** traditional crop varieties; Jerusalem artichoke; inulin; fertilization; polyphenols; antioxidant capacity

## 1. Introduction

Jerusalem artichoke (*Helianthus tuberosus* L.) is a plant with a long history of cultivation that has been making a revival as an edible vegetable in recent years. Jerusalem artichoke is a minor crop, which is why Food and Agriculture Organization (FAO) and EUROSTAT statistics for its cultivated area are not available. Jerusalem artichoke tubers contain inulin, which increases the concentration of cell fluids and confers resistance to very low temperatures (−30 °C). Inulin is a fructan with hypoglycemic properties, and it is used as a dietary supplement in diabetes management on account of its low energy value. According to the literature, Jerusalem artichoke exerts therapeutic effects by stabilizing sugar blood levels; reducing cholesterol levels; regulating blood pressure; protecting the liver and kidneys; enhancing the absorption of calcium, magnesium, and iron; and preventing osteoporosis [1–3].

The discussed plant promotes the elimination of toxic metabolites, boosts immunity, relieves stress, and improves concentration [4].

Roberfroid et al. [5] analyzed chicory inulin and found that all fructans are well fermented by gut bifidobacteria, which contributes to their anticarcinogenic properties. Inulin induces a 10-fold increase in the *Lactobacillus* population, which is why it suppresses appetite, regulates the passage rate of digesta, and stimulates the immune system [3,6]. Inulin consumed in a daily dose of approximately 20 g does not produce adverse side effects (such as bloating). Inulin consumption is estimated at 3–11 g in Europe and 1–4 g in the United States [7]. Jerusalem artichoke contains Si, Zn, Mn, Se, K, and Mg, and when consumed regularly, it stimulates pancreatic cells to produce insulin. The discussed plant is also characterized by unique antiparasitic activity in the treatment of giardiasis.

Jerusalem artichoke tubers are a rich source of phytochemicals. Tubers contain 221 mg of phenolic compounds in 100 g of fresh matter, and the content of phenolic acids with antioxidant properties is estimated at 16.6% on a dry matter basis. According to Petkova et al. [8], Jerusalem artichoke flour delivers health benefits due to its high total polyphenolic content. Tchoné et al. [9] identified 22 phenolic compounds in Jerusalem artichoke tubers, with a predominance of chlorogenic acid. According to Cieślak and Filipiak-Florkiewicz [10] and Florkiewicz et al. [11], the nutritional composition of Jerusalem artichoke renders it highly suitable for the production of functional foods. Similar to potatoes, Jerusalem artichokes are consumed cooked, roasted, or fried. The plant can be processed into flour, chips, salads, and additives for the production of desserts, ice cream, and fruit preserves [10–13]. Jerusalem artichoke has a high yield potential of approximately 90 t ha<sup>-1</sup> tubers [10,14]. Research has demonstrated that the yield and biological value of Jerusalem artichoke tubers are influenced by cultivar, production technology, and harvest date [15,16]. Most studies of Jerusalem artichoke cultivation have focused on the effect of nitrogen fertilization [17–20]. Sawicka [17], who investigated three Jerusalem artichoke cultivars and four nitrogen fertilization levels, observed differences in the chemical composition of tubers depending on cultivar. Fertilizer rates higher than 100 kg N ha<sup>-1</sup> decreased the biological value of tubers. Another study by Sawicka et al. [19] revealed that rational mineral fertilization, in particular with nitrogen, contributes to the high nutritional value of Jerusalem artichoke. The highest content of macronutrients in the aboveground parts of plants was noted in plots fertilized with 50 kg N ha<sup>-1</sup>. Gao et al. [20] also reported that the tuber and biomass yield of *H. tuberosus* was highest at a fertilizer rate of 50 kg N ha<sup>-1</sup>. Praznik et al. [16] and Matias et al. [18] demonstrated that the agronomic performance of Jerusalem artichoke was affected by harvest date rather than by different levels of NPK fertilization. Research shows that the yield and biological value of Jerusalem artichoke tubers are determined by cultivar, cultivation technology, and harvest date [15,18]. However, the influence of potassium (K) fertilization on the inulin content and the composition of polyphenolic compounds in different Jerusalem artichoke cultivars has not been investigated to date. In view of the above, the aim of this study was to determine the effect of different K fertilizer rates (150 kg ha<sup>-1</sup>, 250 kg ha<sup>-1</sup>, and 350 kg ha<sup>-1</sup>; K<sub>2</sub>O) on the content of inulin and polyphenolic compounds, and the antioxidant capacity of Jerusalem artichoke cultivars Topstar, Violette de Rennes, and Waldspindel in order to improve the nutrition value of such widely consumed edibles.

## 2. Materials and Methods

### 2.1. Materials

A field experiment was conducted at the Agricultural Experiment Station in Tomaszkowo (53° 42' N, 20° 26' E, Poland). The experiment had a two-level factorial design with randomized blocks. The first experimental factor was cultivar. The following German cultivars were investigated: Topstar, an early maturing, edible cultivar with yellow-brown tubers and high yields; Violette de Rennes, a medium-late maturing, edible cultivar with red tubers; and Waldspindel, a medium-late maturing cultivar with red tubers, used in the production of herbal supplements and in the distilling industry (all cultivars were obtained from Topinambur Manufaktur, an organic farm in Germany). The second

experimental factor was the rate of mineral K fertilizer applied to soil: (I) K<sub>2</sub>O 150 kg ha<sup>-1</sup>, (II) K<sub>2</sub>O 250 kg ha<sup>-1</sup>, or (III) K<sub>2</sub>O 350 kg ha<sup>-1</sup> (50% potassium sulfate). Nitrogen and phosphorus fertilizers were applied once before planting (80 kg N ha<sup>-1</sup>; urea (46%), 70 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>; triple superphosphate (46%), CaO 90 kg ha<sup>-1</sup>). Organic fertilizers were not applied. Jerusalem artichoke was planted in the last ten days of April 2016 at a depth of 6–8 cm, 30 cm apart, with row spacing of 75 cm. Tubers were harvested in the last ten days of October 2016. Fertilizer rates were determined based on the results of an experiment conducted in Germany during 1994–2001 [21].

The experiment was established on Haplic Luvisol loamy sand [22]. Composite soil samples were obtained from each plot at a depth of 20 cm to determine the chemical properties of soil. The soil pH was 4.12, and soil nutrient levels were determined at 81.5 mg kg<sup>-1</sup> P (Egner–Riehm method), 107 mg kg<sup>-1</sup> K (Egner–Riehm method), and 31 mg kg<sup>-1</sup> Mg (Atomic Absorption Spectrophotometry-ASS) [23,24]. Pesticides were not used during the experiment.

### 2.1.1. Sample Preparation

Jerusalem artichoke (*Helianthus tuberosus* L.) tubers (12 tubers from each fertilization treatment) were washed, peeled, and cut into 0.5 cm cubes. The cubes were freeze-dried in the Alpha 1-2LD Plus freeze-drier (Martin Christ GmbH, Osterode am Harz, Germany) (50 h; -72 °C) [25,26]. After freeze-drying, the samples were pulverized in a laboratory grinder, vacuum-packed, and stored (-20 °C) until analyses. The dry matter of the samples was on average 24.8%.

### 2.1.2. Identification of Inulin

Inulin content was determined by the methods proposed by Megazyme [26] and Topolska et al. [27]. The results were expressed in grams per 100 g of freeze-dried samples ( $n = 2$ ).

### 2.1.3. Identification and Quantification of Polyphenolic Compounds

Polyphenolic compounds were identified in extracts prepared according to the method proposed by Wojdyło et al. [28]. Identification was performed in the Acquity Ultraperformance Liquid Chromatography system [29] equipped with a photodiode sensor (PDA, UPLC) (Waters Corp., Milford, MA, USA) and G2 QToF Micromass spectrometer (Waters, Manchester, UK) with electrospray ionization (ESI). Polyphenols were separated on an UPLC BEH column (1.7 µL, 2.1 × 100 mm; Waters Corp., Milford, MA, USA) at a temperature of 30 °C.

Polyphenols were quantified in the Acquity Ultraperformance LC system [29]. The retention times ( $t_R$ ) of polyphenolic compounds in tubers were compared against commercial standards (Table 1). Standard curves for chlorogenic, neochlorogenic, cryptochlorogenic, and ferulic acids were developed over a concentration range of 0.05 to 5 mg mL<sup>-1</sup> ( $r^2 = 0.9998$ ). Polyphenol concentrations were determined in a series of replicates and expressed in mg kg<sup>-1</sup> on a dry matter (DM) basis.

**Table 1.** Polyphenols identified in Jerusalem artichoke tubers by LC/MS QToF ( $t_R$ : retention time).

Compound	$t_R$	$\lambda_{max}$ (nm)	MS ( $m/z$ )	MS/MS ( $m/z$ )
Unidentified	2.50	246/263	359.05	297.23/281.42
Neochlorogenic acid	2.79	329	353.07	191.02/135.04
Chlorogenic acid	3.75	329	353.07	191.02/135.04
3,4-Dicaffeoylquinic acid	4.05	325	515.03	353.06/191.02/173.05/135.12
3,5-Dicaffeoylquinic acid	4.62	326	515.03	353.06/191.02
Cryptochlorogenic acid	4.72	324	353.07	191.02
<i>p</i> -Coumaroylquinic acid	5.95	311	337.03	191.02/173.05
Caffeic acid	6.19	323	179.04	136.06
Feruloylquinic acid	6.95	325	3670.5	191.02/172.06
Caffeoyl-glucoside acid	7.13	327	341.04	179.04/161.07
1,5-Dicaffeoylquinic acid	7.25	325	515.03	354.03/191.02/179.04
4,5-Dicaffeoylquinic acid	7.46	327	515.03	191.02/179.04/173.03/135.07

### 2.1.4. Antioxidant Capacity

The antioxidant capacity of Jerusalem artichokes was determined in water–methanol extracts of freeze-dried tubers (1:4; v/v) according to the method described by Wojdyło et al. [28]. Antioxidant capacity was measured in the ABTS radical scavenging activity assay (TEAC ABTS) [30] and the Ferric Reducing Antioxidant Potential (FRAP) assay [31]. The results were expressed in Trolox equivalents per 100 g DM ( $n = 3$ ).

### 2.1.5. Antioxidant Profiling by On-Line HPLC-PDA with Post-Column Derivatization with ABTS

The antioxidant activity of polyphenolic compounds in Jerusalem artichokes was determined by on-line HPLC-PDA coupled with post-column derivatization with ABTS according to the method proposed by Kusznierevicz et al. [32] and described by Tkacz et al. [33].

## 2.2. Statistical Analysis

The results were processed statistically by one-way analysis of variance (ANOVA) (Statistical 10.0, StatSoft, Tulsa, OK, USA). Significant differences ( $p \leq 0.05$ ) between samples were determined by Tukey's test.

## 3. Results and Discussion

### 3.1. Inulin

Jerusalem artichoke tubers are most abundant in inulin between mid-October and December. In successive months, polyfructose content decreases and the concentration of simple sugar increases. The accumulation of oligofructans in tubers is influenced by weather conditions [34].

The inulin content of the evaluated cultivars ranged from 45.94 to 60.85 g 100 g<sup>-1</sup> of freeze-dried samples (Table 2). Similar results were noted by Cieřlik et al. [35] and Florkiewicz et al. [11] in Polish cultivars Albik and Rubik (41.4–50.4 g·100 g<sup>-1</sup>). The coefficient of variation did not exceed 20% in the tested cultivars, which indicates that inulin content is a stable trait. Inulin concentration was most stable in *cv.* Waldspindel.

**Table 2.** The effect of cultivar and potassium fertilizer rate on the inulin content of Jerusalem artichoke tubers (g·100g<sup>-1</sup> freeze-dried sample).

Cultivar	Potassium Fertilizer Rate			Mean	Coefficient of Variation
	150 kg ha <sup>-1</sup>	250 kg ha <sup>-1</sup>	350 kg ha <sup>-1</sup>		
<i>Violette de Rennes</i>	45.94 <sup>d</sup>	50.51 <sup>bc</sup>	51.68 <sup>bc</sup>	49.38 ± 3.03 <sup>c</sup>	5.59
<i>Waldspindel</i>	53.18 <sup>b</sup>	51.79 <sup>bc</sup>	52.00 <sup>bc</sup>	52.49 ± 0.75 <sup>b</sup>	2.74
<i>Topstar</i>	52.83 <sup>b</sup>	49.26 <sup>cd</sup>	60.85 <sup>a</sup>	54.31 ± 5.94 <sup>a</sup>	9.76
Average	50.65 <sup>b</sup>	50.52 <sup>b</sup>	55.01 <sup>a</sup>		

Note: a, b, c, d = values in columns marked with the same letters do not differ significantly at  $p \leq 0.05$  (Tukey's test, analysis of variance (ANOVA)).

An analysis of K fertilization levels revealed that inulin content was highest in response to the highest fertilizer rate (350 kg K<sub>2</sub>O ha<sup>-1</sup>). The analyzed cultivars responded differently to higher rates of K fertilizer. According to Sawicka [17,36], Jerusalem artichoke tubers are characterized by cultivar-dependent variations in nutrient levels. Matias et al. [18] found no differences in inulin content in response to higher rates of NPK fertilizers (Level 1: 54, 108, 162; Level 2: 108, 216, 324) and concluded that unlike harvest date, fertilization has a minor effect on tuber yields.

Inulin accumulation was significantly higher in the early-maturing *cv.* Topstar relative to medium-late maturing cultivars. Higher rates of K fertilizer exerted the greatest influence on the inulin content of Jerusalem artichoke *cv.* Topstar. The inulin content of freeze-dried tubers increased by 8.02 g · 100 g<sup>-1</sup> when the fertilizer rate was increased by 200 kg K<sub>2</sub>O ha<sup>-1</sup>.

Violette de Rennes was characterized by the lowest inulin content and the smallest variations in inulin levels. In this cultivar, the inulin content of freeze-dried tubers increased by  $4.57 \text{ g} \cdot 100 \text{ g}^{-1}$  when the fertilizer rate was increased from  $150 \text{ kg K}_2\text{O ha}^{-1}$  to  $250 \text{ kg K}_2\text{O ha}^{-1}$ . The inulin content of the medium-late *cv.* Waldspindel, which is used in the production of herbal supplements and in the distilling industry, did not change in response to higher rates of K fertilizer.

### 3.2. Polyphenols

The polyphenols content of Jerusalem artichoke tubers is influenced by cultivar [37], harvest date, and storage conditions [38]. According to Terzić et al. [39] and Kapusta et al. [37], differences in the concentrations of polyphenolic compounds are also genetically conditioned. The effect of various rates of K fertilizer on the content of polyphenolic compounds in Jerusalem artichoke tubers has not been investigated to date. In the present study, the total content of the polyphenolic compounds identified in the analyzed cultivars of Jerusalem artichoke ranged from 1477 to 1801  $\text{mg kg}^{-1}$  DM. Similar results were reported by Kapusta et al. [37] (Table 3).

In treatments fertilized with  $150 \text{ kg K ha}^{-1}$ , polyphenol levels were lowest in *cv.* Violette de Rennes and highest in *cv.* Topstar. In *cv.* Violette de Rennes, total polyphenolic content increased by 5% and 13% when the rate of K fertilizer was increased from  $150 \text{ kg ha}^{-1}$  to 250 and  $350 \text{ kg ha}^{-1}$ , respectively. Similar observations were made by Kavalcova et al. [40] in onions, where polyphenol levels measured spectrophotometrically increased with a rise in K fertilizer rate. In this regard, it was concluded that the content of polyphenolic compounds could be a varietal trait in Jerusalem artichoke. In *cv.* Waldspindel and Topstar, polyphenol levels decreased by 6.4% and 1.5% on average, respectively, when K fertilizer rate was increased by 100 and  $200 \text{ kg ha}^{-1}$ . These findings suggest that the potassium-stimulated synthesis of polyphenolic compounds is affected by the unique chemical composition of different cultivars of Jerusalem artichoke.

Chlorogenic acid was the predominant polyphenolic compound in Jerusalem artichoke tubers and leaves [41]. The average content of chlorogenic acid was estimated at 66.4% in *cv.* Violette de Rennes and at 77% in *cv.* Waldspindel and Topstar, regardless of K fertilizer rate. The content of chlorogenic acid was lowest in *cv.* Violette de Rennes and highest in *cv.* Topstar, regardless of K fertilizer rate. In *cv.* Violette de Rennes, the content of chlorogenic acid increased by 5% and 15% in response to K fertilizer rates of  $250 \text{ kg ha}^{-1}$  and  $350 \text{ kg ha}^{-1}$ , respectively. In *cv.* Waldspindel and Topstar, the content of chlorogenic acid decreased by 6% and 10% on average when the K fertilizer rate was increased to 250 and  $350 \text{ kg ha}^{-1}$ , respectively. The above findings indicate that cultivar and chemical composition significantly affect the potassium-induced synthesis of chlorogenic acid.

**Table 3.** The effect of potassium fertilizer rates on the polyphenol content of three Jerusalem artichoke cultivars (mg kg<sup>-1</sup> dm).

Cultivar	Rate (kg K ha <sup>-1</sup> )	Chlorogenic acid	1,5-dicaffeoylquinic acid	3,4-dicaffeoylquinic acid	3,5-dicaffeoylquinic acid	Neochlorogenic acid	Crypto-chlorogenic	Caffeoyl-glucoside acid	p-coumaroyl-quinic acid	Feruloylquinic acid	Caffeic acid	4,5-dicaffeoylquinic acid	Total polyphenols
<i>Violette de Rennes</i>	150	1029.2 ± 16.22 <sup>ab</sup>	156.33 ± 0.62 <sup>c</sup>	96.54 ± 1.71 <sup>abc</sup>	73.82 ± 0.25 <sup>cd</sup>	57.47 ± 1.02 <sup>ab</sup>	23.15 ± 0.03 <sup>d</sup>	15.7 ± 0.36 <sup>de</sup>	11.79 ± 0.34 <sup>b</sup>	5.35 ± 0.57 <sup>bc</sup>	4.33 ± 1.1 <sup>a</sup>	3.64 ± 0.15 <sup>bc</sup>	1477
	250	996.89 ± 33.58 <sup>a</sup>	230.51 ± 13.31 <sup>d</sup>	89.39 ± 2.66 <sup>a</sup>	91.69 ± 3.06 <sup>e</sup>	55.07 ± 3.41 <sup>ab</sup>	23.62 ± 1.86 <sup>d</sup>	26.6 ± 1.7 <sup>f</sup>	15.49 ± 0.86 <sup>c</sup>	7.5 ± 3.24 <sup>c</sup>	4.7 ± 1.61 <sup>a</sup>	3.93 ± 0.18 <sup>c</sup>	1545
	350	1132.74 ± 8.43 <sup>bc</sup>	271.97 ± 2.35 <sup>e</sup>	100.79 ± 0.2 <sup>bcd</sup>	82.01 ± 0.14 <sup>de</sup>	57.51 ± 0.58 <sup>ab</sup>	17.74 ± 0.43 <sup>abc</sup>	45.73 ± 0.22 <sup>g</sup>	16.24 ± 0.8 <sup>c</sup>	6.35 ± 0.56 <sup>c</sup>	5.84 ± 0.01 <sup>ab</sup>	6.05 ± 0.63 <sup>d</sup>	1743
<i>Waldspindel</i>	150	1262.59 ± 57.44 <sup>d</sup>	82.95 ± 7.4 <sup>a</sup>	104.26 ± 3.19 <sup>cde</sup>	64.23 ± 6.83 <sup>bc</sup>	54.22 ± 1.56 <sup>ab</sup>	16.19 ± 0.25 <sup>ab</sup>	12.85 ± 1.07 <sup>cd</sup>	1.78 ± 0.16 <sup>a</sup>	0.84 ± 0.37 <sup>ab</sup>	9.94 ± 0.12 <sup>cd</sup>	2.1 ± 0.64 <sup>ab</sup>	1612
	250	1195.68 ± 9.61 <sup>cd</sup>	72.73 ± 0.06 <sup>a</sup>	112.45 ± 1.24 <sup>ef</sup>	58.79 ± 1.39 <sup>b</sup>	58.88 ± 0.49 <sup>ab</sup>	20.19 ± 1.82 <sup>bcd</sup>	12.46 ± 0.11 <sup>c</sup>	2.35 ± 0.28 <sup>a</sup>	0.77 ± 0.54 <sup>ab</sup>	10.44 ± 0.39 <sup>cd</sup>	2.34 ± 0.52 <sup>abc</sup>	1547
	350	1153.11 ± 13.13 <sup>bcd</sup>	82.29 ± 0.97 <sup>a</sup>	108.91 ± 2.12 <sup>de</sup>	61.87 ± 0.83 <sup>bc</sup>	60.17 ± 1.39 <sup>bc</sup>	22.68 ± 2.79 <sup>cd</sup>	17.57 ± 0.62 <sup>e</sup>	2.54 ± 0.12 <sup>a</sup>	0.28 ± 0.09 <sup>a</sup>	11.7 ± 0.43 <sup>d</sup>	2.94 ± 0.52 <sup>bc</sup>	1524
<i>Topstar</i>	150	1394.84 ± 14.5 <sup>e</sup>	120.22 ± 2.86 <sup>b</sup>	117.62 ± 1.72 <sup>f</sup>	62.34 ± 7.66 <sup>bc</sup>	66.13 ± 1.65 <sup>c</sup>	16.1 ± 1.14 <sup>ab</sup>	5.35 ± 0.29 <sup>a</sup>	2.37 ± 0.25 <sup>a</sup>	9.71 ± 1.23 <sup>c</sup>	6.25 ± 0.39 <sup>ab</sup>	0.81 ± 0.04 <sup>a</sup>	1802
	250	1266.77 ± 65.72 <sup>de</sup>	116.08 ± 4.83 <sup>b</sup>	111.32 ± 0.36 <sup>ef</sup>	41.03 ± 0.61 <sup>a</sup>	53.52 ± 0.56 <sup>a</sup>	30.92 ± 0.75 <sup>e</sup>	5.61 ± 0.17 <sup>a</sup>	1.45 ± 0.07 <sup>a</sup>	7.99 ± 0.01 <sup>c</sup>	8.24 ± 0.36 <sup>bc</sup>	0.88 ± 0.02 <sup>a</sup>	1644
	350	1246.34 ± 0.63 <sup>cd</sup>	134.52 ± 14.42 <sup>bc</sup>	95.48 ± 3.16 <sup>ab</sup>	61.83 ± 1.59 <sup>bc</sup>	55.11 ± 2.11 <sup>ab</sup>	14.15 ± 0.23 <sup>a</sup>	8.62 ± 0.01 <sup>b</sup>	3.03 ± 0.21 <sup>a</sup>	5.41 ± 0.59 <sup>bc</sup>	12.28 ± 0.23 <sup>d</sup>	0.78 ± 0.64 <sup>a</sup>	1620

Note: average ± standard deviation; a, b, c, d, e, f, g: values in columns marked with the same letters do not differ significantly at  $p \leq 0.05$  (Tukey's test, ANOVA).

Four isomers of dicaffeoylquinic acid (1,5-, 3,4-, 3,5-, and 4,5-dicaffeoylquinic acids) were identified in Jerusalem artichoke tubers in this study, which is consistent with the results reported by Kapusta et al. [37]. Here, 1,5-dicaffeoylquinic acid, 3,4-dicaffeoylquinic acid, and 3,5-dicaffeoylquinic acid accounted for approximately 25% of the identified polyphenolic compounds in *cv.* Violette de Rennes and for 16.5% of the identified polyphenolic compounds in *cv.* Waldspindel and Topstar, regardless of K fertilizer rate. In *cv.* Violette de Rennes, the content of 1,5-dicaffeoylquinic acid and 3,4-dicaffeoylquinic acid increased with a rise in K fertilization levels and was highest in response to the rate of 350 kg K ha<sup>-1</sup>. In *cv.* Waldspindel, the concentrations of the above compounds did not change considerably in response to increasing rates of K fertilizer. In *cv.* Topstar, the content of above components decreased when the K fertilizer rate was increased from 150 kg ha<sup>-1</sup> to 250 and 350 kg ha<sup>-1</sup>. The analyzed cultivars also contained neochlorogenic acid, which accounted for 3.5% of all polyphenolic compounds on average. The variations in the concentration of neochlorogenic acid across fertilizer treatments were cultivar-dependent, and they differed from those observed in the content of dicaffeoylquinic acids. Cryptochlorogenic acid was also identified in the analyzed Jerusalem artichoke cultivars. On average, cryptochlorogenic acid accounted for 1.2% of the identified polyphenolic compounds regardless of cultivar and K fertilizer rate. The content of cryptochlorogenic acid was highest in *cv.* Topstar and it more than doubled in response to a K fertilizer rate of 250 kg ha<sup>-1</sup>. The content of caffeoyl-glucoside acid and caffeic acid increased in all cultivars in response to a K fertilizer rate of 350 kg ha<sup>-1</sup>. The concentration of *p*-coumaroyl-quinic acid was highest in *cv.* Violette de Rennes, and it increased with a rise in K fertilizer rate. A reverse trend was observed in the remaining cultivars, which indicates that polyphenol synthesis is a varietal trait in Jerusalem artichoke.

### 3.3. Antioxidant Capacity

Antioxidant capacity ranged from 0.87 to 3.28  $\mu\text{mol Trolox kg}^{-1}$  DM in the ABTS radical scavenging activity assay (Table 4).

**Table 4.** The effect of potassium fertilizer rates on the antioxidant capacity of three Jerusalem artichoke cultivars ( $\mu\text{mol Trolox kg}^{-1}$ ).

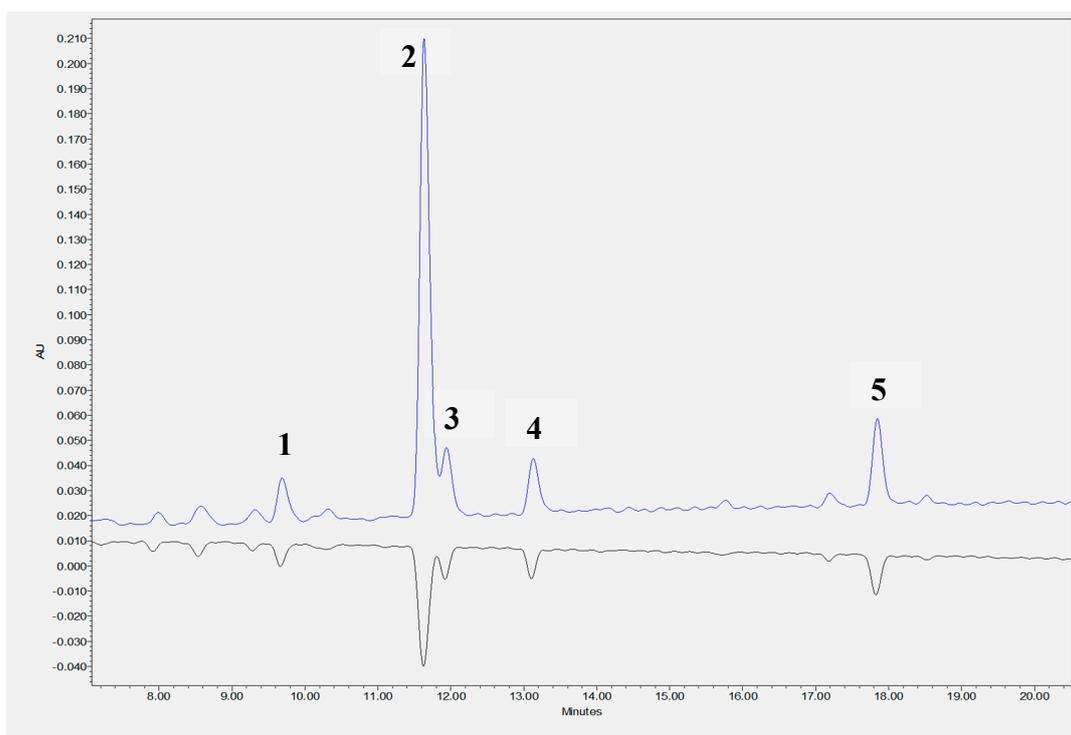
Cultivar	Rate (kg K ha <sup>-1</sup> )	TEAC ABTS	FRAP
<i>Violette de Rennes</i>	150	1.55 ± 0.08 <sup>ab</sup>	2.07 ± 0.09 <sup>de</sup>
	250	2.65 ± 0.21 <sup>cd</sup>	1.81 ± 0.1 <sup>cd</sup>
	350	3.28 ± 0.39 <sup>d</sup>	1.95 ± 0.08 <sup>cde</sup>
<i>Waldspindel</i>	150	0.88 ± 0.12 <sup>a</sup>	1.28 ± 0.12 <sup>b</sup>
	250	0.87 ± 0.12 <sup>ab</sup>	0.82 ± 0.02 <sup>a</sup>
	350	1.16 ± 0.09 <sup>ab</sup>	0.57 ± 0.02 <sup>a</sup>
<i>Topstar</i>	150	1.37 ± 0.08 <sup>ab</sup>	2.13 ± 0.06 <sup>e</sup>
	250	1.58 ± 0.14 <sup>b</sup>	0.59 ± 0.01 <sup>a</sup>
	350	2.45 ± 0.07 <sup>c</sup>	1.71 ± 0.09 <sup>c</sup>

Note: average ± standard deviation; a, b, c, d, e: values in columns marked with the same letters do not differ significantly at  $p \leq 0.05$  (Tukey's test, ANOVA).

Antioxidant capacity measured by TEAC ABTS assay was the highest in *cv.* Violette de Rennes and the lowest in *cv.* Waldspindel. Considerable differences in the antioxidant capacity of different Jerusalem artichoke cultivars were also reported by Catana et al. [42]. The antioxidant capacity of  *cvs.* Violette de Rennes, Waldspindel, and Topstar increased by approximately 53%, 24%, and 44%, respectively, when K fertilizer rate was increased from 150 kg ha<sup>-1</sup> to 350 kg ha<sup>-1</sup>. The content of polyphenolic compounds was correlated with antioxidant capacity measured in the ABTS assay only in *cv.* Violette de Rennes ( $r = 0.998$ ).

The chromatographic profile of phenolic components in Jerusalem artichoke before and after derivatization of the negative control (ABTS reagent) is presented in Figure 1. Chlorogenic acid exerted

the strongest effect on the antioxidant potential of Jerusalem artichokes, followed by 3,5-caffeoylquinic acid, 3,4-caffeoylquinic acid, 1,5-caffeoylquinic acid, and neochlorogenic acid.



**Figure 1.** Standard UV chromatograms (blue line) and on-line ABTS antioxidant profiles (black line) of Jerusalem artichoke. Peaks: 1: neochlorogenic acids; 2: chlorogenic acid; 3: 1,5-dicaffeoylquinic acid; 4: 3,4-dicaffeoylquinic acid; 5: 3,5-dicaffeoylquinic acid.

In summary, no significant correlations were found between the concentrations of individual polyphenolic compounds in Jerusalem artichoke tubers and the antioxidant capacity of the extracts determined spectrophotometrically in the ABTS radical scavenging assay.

On the other hand, the FRAP values indicated that the highest antioxidant capacity was noted for *cv.* Topstar in the treatment supplied with K fertilizer at 150 kg ha<sup>-1</sup>. The increase of the K content during fertilization led to the decrease in antioxidant capacity measured by FRAP. Thus, the ability of compounds able to reduce the Fe ion in Jerusalem artichoke can be moderated by the K levels.

#### 4. Conclusions

Based on the results obtained, it was concluded that among *cv.* Violette de Rennes, Waldspindel, and Topstar, the inulin accumulation was significantly higher in the early-maturing *cv.* Topstar. Higher rates of K fertilizer exerted the greatest influence on the inulin content of Jerusalem artichoke in this cultivar. This led to the increase of inulin content of 4.4 g 100 g<sup>-1</sup> when the K fertilizer rate was increased from 150 kg K<sub>2</sub>O ha<sup>-1</sup> to 350 kg K<sub>2</sub>O ha<sup>-1</sup>.

Eleven polyphenolic compounds were identified in 3 cultivars of Jerusalem artichoke. The content of polyphenolic compounds ranged from 1.5 to 1.8 g kg<sup>-1</sup> DM of tuber samples, and it was influenced by the rate of K fertilizer. Chlorogenic acid was the predominant phenolic acid in all cultivars, and it accounted for around 66.4% of the identified polyphenolic compounds in *cv.* Violette de Rennes and for around 77% of polyphenolic compounds in *cv.* Waldspindel and Topstar. Four isomers of dicaffeoylquinic acid were also identified in the evaluated tubers, and 1,5-dicaffeoylquinic acid was the predominant isomer. The content of the remaining compounds varied across cultivars and K fertilization treatments. Chlorogenic acid, 3,5-, 3,4-, 1,5-caffeoylquinic acids, and neochlorogenic acid had the strongest influence on antioxidant potential measured by the ABTS on-line profiling method.

Taking the above into consideration, fertilization with selected microelements of edibles, including Jerusalem artichoke, could be a new strategy for the improvement of the nutritional value of such plants. Nevertheless, the polyphenolic compounds are stress metabolites, and their content in the plants can be modified by the type of the fertilizer as well as the quantity applied; thus, numerous aspects should be considered in order to provide a thorough recommendation for a single polyphenolic component [43].

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## References

1. Georgescu, L.A.; Stoica, I. Studies concerning the dynamic of enzyme hydrolyze on the Jerusalem artichoke (*Helianthus tuberosus* L.) inulin. *Anal. Univ. Dunarea Galati VI Food Technol.* **2005**, *1*, 77–81.
2. Zaky, E.A. Physiological response to diets fortified with Jerusalem artichoke tubers (*Helianthus tuberosus* L.) powder by diabetic rats. *Am. Eurasian J. Agric. Environ. Sci.* **2009**, *5*, 682–688.
3. Cieřlik, E.; Geębusia, A. Topinambur (*Helianthus tuberosus* L.)—Bulwa o wlaściwościach prozdrowotnych. *Postę. Nauk Rol.* **2010**, *3*, 91–103. (In Polish)
4. Young-Jun, L.; Myoung-gi, L.; Seok-Yeong, Y.; Won-Byong, Y.; Ok-Hwan, L. Changes in physicochemical characteristics and antioxidant activities of Jerusalem artichoke tea infusions resulting from different production processes. *Food Sci. Biotechnol.* **2014**, *23*, 1885–1892.
5. Roberfroid, M.B.; Van Loom, J.; Gibson, G.R. The bifidogenic nature of chicory inulin and its hydrolysis products. *J. Nutr.* **1998**, *128*, 11–19. [[CrossRef](#)] [[PubMed](#)]
6. El-Hofi, A.A. Technological and biological uses of Jerusalem artichoke powder and resistant starch. *Ann. Agric. Sci. Moshtohor* **2005**, *43*, 279–291.
7. Roberfroid, M.B. Inulin-type fructans: Functional food ingredients. *J. Nutr.* **2007**, *137*, 2493–2502. [[CrossRef](#)]
8. Petkova, N.; Ivanov, I.; Denev, P.; Pavlov, A. Bioactive substance and free radical scavenging activities of flour from Jerusalem Artichoke (*Helianthus tuberosus* L.) tubers—A comparative study. *Turk. J. Agric. Nat. Sci.* **2014**, *2*, 1773–1778.
9. Tchoné, M.; Bärwald, G.; Annemüller, G.; Fleischer, L.G. Separation and identification of phenolic compounds in Jerusalem artichoke (*Helianthus tuberosus* L.). *Sci. Aliment.* **2006**, *26*, 394–408. [[CrossRef](#)]
10. Cieřlik, E.; Filipiak-Florkiewicz, A. Prospective usage of Jerusalem artichoke (*Helianthus tuberosus* L.) for producing functional food. *Żywność-Nauka Technologia Jakość* **2007**, *1*, 73–81. (In Polish)
11. Florkiewicz, A.; Cieřlik, E.; Filipiak-Florkiewicz, A. Wpływ odmiany i terminu zbioru na skład chemiczny bulw topinamburu (*Helianthus tuberosus* L.). *Żywność-Nauka Technologia Jakość* **2007**, *3*, 71–81. (In Polish)
12. Cieřlik, E.; Kopeć, A.; Praznik, W. Functional properties of fructan. In Proceedings of the Ninth Seminar on Inulin, Budapest, Hungary, 18–19 April 2002; Volume 27.
13. Mystkowska, I.; Zarzecka, K. Wartość odżywcza i prozdrowotna słonecznika bulwiastego (*Helianthus tuberosus* L.). *Post. Fitoter.* **2013**, *2*, 123–126. (In Polish)
14. Baldini, M.; Danuso, F.; Monti, A.; Amaducci, M.T.; Stevanato, P.; Mastro, G. Chichory and Jerusalem artichoke productivity in different areas of Italy, in relation to water availability and time of harvest. *Ital. J. Agron.* **2006**, *2*, 291–307. [[CrossRef](#)]
15. Góral, S. Zmienność morfologiczna i plonowanie wybranych klonów słonecznika bulwiastego –topinambur (*Helianthus tuberosus* L.). *Hodowla Roślin i Nasiennictwo* **1998**, *2*, 6–11. (In Polish)
16. Praznik, W.; Cieřlik, E.; Filipiak, A. The influence of harvest time on the content of nutritional components in tubers of Jerusalem artichoke (*Helianthus tuberosus* L.). In Proceedings of the Seventh Seminar on Inulin, Leuven, Belgium, 22–23 January 1998; pp. 154–157.

17. Sawicka, B. Wpływ nawożenia azotem na wartość biologiczną bulw *Helianthus tuberosus* L. *Roczniki Akademii Rolniczej w Poznaniu* **2000**, *313*, 447–451. (In Polish)
18. Matias, J.; Gonzales, J.; Cabanillas, J.; Royano, L. Influence of NPK fertilisation and harvest date on agronomic performance of Jerusalem artichoke crop in the Guadiana Basin (Southwestern Spain). *Ind. Crop. Prod.* **2013**, *48*, 191–197. [[CrossRef](#)]
19. Sawicka, B.; Kalembasa, D.; Skiba, D. Variability in macroelement content in the aboveground part of *Helianthus tuberosus* L. at different nitrogen fertilization levels. *Plant Soil Environ.* **2015**, *61*, 158–163. [[CrossRef](#)]
20. Gao, K.; Zhu, T.X.; Wang, Q.B. Nitrogen fertilization, irrigation, and harvest times affect biomass and energy value of *Helianthus tuberosus* L. *J. Plant Nutr.* **2016**, *39*, 1906–1914.
21. Stolzenburg, K. Anbau und Verwertung von Topinambur (*Helianthus tuberosus* L.). *Informationen für Pflanzenproduktion Sonderheft* **2002**, *1*, 10.
22. IUSS Working Group WRB. World Reference Base for Soil Resources. In *World Soil Resources Reports*, 2nd ed.; FAO: Roma, Italy, 2006.
23. Houba, V.J.G.; Van der Lee, J.J.; Novozamsky, I. Soil analysis procedure: other procedure. *J. Soil Sci. Plant Nutr.* **1995**.
24. Lachman, J.; Hamouz, K.; Orsák, M.; Pivec, V.; Hejtmánková, K.; Pazderů, K.; Čepl, J. Impact of selected factors—Cultivar, storage, cooking and baking on the content of anthocyanins in coloured-flesh potatoes. *Food Chem.* **2012**, *133*, 1107–1116. [[CrossRef](#)]
25. Nemš, A.; Peška, A.; Kucharska, A.Z.; Sokół-Łętowska, A.; Kita, A.; Drożdż, W.; Hamouz, K. Anthocyanin and antioxidant activity of snacks with coloured potato. *Food Chem.* **2015**, *172*, 175–182. [[CrossRef](#)] [[PubMed](#)]
26. Sustainable Chemistry Solutions, AOAC (Method 999.03), AACC (Method 32-32.01), CODEX (Typ III Method). In *Enzyme Sources Guide*; Megazyme International Ireland: Bray Business Park, Bray, Co.: Wicklow, Ireland, 2014; p. 11.
27. Topolska, K.; Filipiak-Florkiewicz, A.; Florkiewicz, A.; Ciešlik, E. Fructan stability in strawberry sorbets in dependence on their source and the period of storage. *Eur. Food Res. Technol.* **2017**, *243*, 701–709. [[CrossRef](#)]
28. Wojdyło, A.; Oszmiański, J.; Bielicki, P. Polyphenolic composition, antioxidant activity, and polyphenol oxidase (PPO) activity of quince (*Cydonia oblonga* Miller) varieties. *J. Agric. Food Chem.* **2013**, *61*, 2762–2772. [[CrossRef](#)] [[PubMed](#)]
29. Wojdyło, A.; Nowicka, P.; Laskowski, P.; Oszmiański, J. Evaluation of sour cherry (*Prunus cerasus* L.) fruits for their polyphenol content, antioxidant properties, and nutritional components. *J. Agric. Food Chem.* **2014**, *62*, 12332–12345. [[CrossRef](#)] [[PubMed](#)]
30. Re, R.; Pellegrini, N.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. *Free Radic. Biol. Med.* **1999**, *26*, 1231–1237. [[CrossRef](#)]
31. Benzie, I.F.; Strain, J.J. Ferric reducing/antioxidant power assay: Direct measure of total antioxidant activity of biological fluids and modified version for simultaneous measurement of total antioxidant power and ascorbic acid concentration. *Method Enzymol.* **1999**, *299*, 15–27.
32. Kusznierevich, B.; Piasek, A.; Bartoszek, A.; Namieśnik, J. The optimisation of analytical parameters for routine profiling of antioxidants in complex mixtures by HPLC coupled-postcolumn derivatisation. *Phytochem. Anal.* **2011**, *22*, 392–402. [[CrossRef](#)]
33. Tkacz, K.; Wojdyło, A.; Nowicka, P.; Turkiewicz, I.; Golis, P. Characterization *in vitro* potency of biological active fractions of seeds, skins and flesh from selected *Vitis vinifera* L. cultivars and interspecific hybrids. *J. Funct. Foods* **2019**, *56*, 353–363. [[CrossRef](#)]
34. Chekroun, M.B.; Amzile, J.; El Yachioui, M.; El Haloui, N.E.; Prevost, J. Qualitative and quantitative development of carbohydrate reserves during the biological cycle of Jerusalem artichoke (*Helianthus tuberosus* L.) tubers. *N. Z. J. Crop. Hortic. Sci.* **1994**, *22*, 31–37. [[CrossRef](#)]
35. Ciešlik, E.; Filipiak, A.; Filipiak-Florkiewicz, A. Wpływ terminu zbioru na zawartość węglowodanów w bulwach topinamburu (*Helianthus tuberosus* L.). *Żywność Człowieka i Metabolizm* **2003**, *30*, 1076–1080. (In Polish)
36. Sawicka, B. Słonecznik bulwiasty (*Helianthus tuberosus* L.)- Biologia, Hodowla, Znaczenie Użytkowe. *Wyd. UP Lublin* **2016**, 223. (In Polish)
37. Kapusta, I.; Krok, E.; Jamro, D.; Cebulak, T.; Kaszuba, J.; Salach, R. Identification and quantification of phenolic compounds from Jerusalem artichoke (*Helianthus tuberosus* L.) tubers. *J. Food Agric. Environ.* **2013**, *11*, 601–606.

38. Danilcenko, H.; Jariene, E.; Slepiewne, A.; Sawicka, B.; Zaldariene, S. The distribution of bioactive compounds in the tubers of organically grown Jerusalem artichoke (*Helianthus tuberosus* L.) during the growing period. *Acta Sci. Pol. Hortorum Cultus* **2017**, *16*, 97–107. [[CrossRef](#)]
39. Terzić, S.; Atagić, J.; Maksimo, I.; Zeremski, T.; Petrović, S.; Dedić, B. Influence of photoperiod on vegetation phases and tuber development in topinambur (*Helianthus tuberosus* L.). *Arch. Biol. Sci.* **2012**, *64*, 175–182. [[CrossRef](#)]
40. Kavalcova, P.; Bystricka, J.; Toth, T.; Volnova, B.; Kopernicka, M.; Harangozo, L. Potassium and its effect on the content of polyphenols in onion (*Allium cepa* L.). *J. Microbiol. Biotechnol. Food Sci.* **2015**, *4*, 74–77. [[CrossRef](#)]
41. Chen, F.; Long, X.; Liu, Z.; Shao, H.; Liu, L. Analysis of phenolic acids of Jerusalem artichoke (*Helianthus tuberosus* L.) responding to salt-stress by liquid chromatography/tandem mass spectrometry. *Sci. World J.* **2014**, *2014*, 1–8.
42. Catana, L.; Catana, M.; Iorga, E.; Lazar, A.G.; Lazar, M.A.; Teodorescu, R.; Asanica, A.; Belc, N.; Iancu, A. Valorification of Jerusalem artichoke tubers (*Helianthus tuberosus* L.) for achieving of functional ingredient with high nutritional value. *Sciendo* **2018**, *1*, 276–283. [[CrossRef](#)]
43. Heimler, D.; Romani, A.; Ieri, F. Plant polyphenol content, soil fertilization and agricultural management: A review. *Eur. Food Res. Technol.* **2017**, *43*, 1107–1115. [[CrossRef](#)]



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