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The Impact of Fertilization Regime on the Crop Performance and Chemical Composition of Potato (*Solanum tuberosum* L.) Cultivated in Central Greece

Spyridon A. Petropoulos [1,*], Ângela Fernandes [2,*], Nikolaos Polyzos [1], Vasileios Antoniadis [1], Lillian Barros [2] and Isabel C.F.R. Ferreira [2]

[1] Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 38446 Nea Ionia, Magnissia, Greece; niikpolyzos@gmail.com (N.P.); antoniadis@uth.gr (V.A.)
[2] Campus de Santa Apolónia, Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253 Bragança, Portugal; lillian@ipb.pt (L.B.); iferreira@ipb.pt (I.C.F.R.F.)
* Correspondence: spetropoulos@uth.gr (S.A.P.); afeitor@ipb.pt (Â.F.); Tel.: +30-2421-093-196 (S.A.P.); +35-1273-330-904 (Â.F.)

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Abstract: Potato cultivation is quite demanding in inorganic nutrients and adequate fertilization is a key factor for maximizing yield and producing tubers of high quality. In the present study, a field experiment was carried out to evaluate the effect of various forms of fertilization on crop performance and the nutritional value and chemical composition of two potato varieties (cv. Spunta and cv. Kennebec). For this purpose, five different fertilizer treatments were applied namely: control (C), standard fertilizer (T1), standard fertilizer + zeolite (T2), manure (T3) and slow release nitrogen fertilizer (T4). According to the results, it was observed that slow release treatment (T4) achieved the highest yield for both varieties, while the control treatment presented significantly lower yield compared to the studied fertilization regimes. The dry matter of leaves and shoots was higher in T1 treatment for cv. Kennebec and in T2 and T4 treatments for cv. Spunta, whereas the control treatment presented the highest dry matter content in tubers for cv. Kennebec and T2 and T3 treatments for cv. Spunta. A significant effect of the fertilization regime was also observed on the nutritional value of tubers and more specifically the protein, ash and fat content was increased by treatments T1 and T4, while carbohydrate content was also increased by T3 and T4 treatments for both varieties. Similarly, the total sugars, organic acids, β-carotene and lycopene content was increased in T3 treatment for the Spunta variety, while the antioxidant capacity showed a varied response depending on the fertilizer regime and the tested variety. In conclusion, the fertilization regime has a significant effect not only on the tuber yield but also on the quality of the final product and should be considered as an effective tool to increase the added value of potato crop.

Keywords: antioxidant activity; carbohydrates; carotenoids; manure; phenolic compounds; potato; slow release nitrogen fertilizer; *Solanum tuberosum* L.; zeolite

1. Introduction

Potatoes play an important role in human diet worldwide and for that reason they rank fourth as one the most consumed vegetable crops in the world [1]. The large per capita consumption can be easily justified because they are rich in carbohydrates, minerals but also contain a large amount of high quality of proteins, vitamin C, minerals and antioxidant activities [2]. Potato is one of the major vegetable crops cultivated throughout the southern Mediterranean, with Spain and Italy being the main producers, with 2.0 and 1.3 million tons of annual production, respectively [1]. However, during the last 10 years the farming sector has been facing a rapid decrease in total harvested area and total

production in potato crop (36.7% and 19.5%, respectively), which has been partially compensated by the increasing yields due to the introduction of new high yielding genotypes and improved farming practices [1].

Lately, there is an increased interest from potato growers in defining the optimal fertilization regimes in order to maximize total yield, while at the same time minimizing the production cost and maintaining high quality [3,4]. Optimizing the efficiency of nitrogen use has been suggested through various methods with the most common practice being the replacement of the single rate nitrogen fertilization through base dressing by multiple rates during the cultivation period through side dressings, depending on plant requirements and growth stage [5,6]. Moreover, nitrogen source (NH_4^+ or NO_3^-) can have a tremendous effect on potato growth and yield, while it can also affect nitrate content in tubers [7] and nitrogen use efficiency of the crop [8]. Other studies have shown that apart from nitrogen source, the time of application is equally important for tuber yield. In particular, NO_3^- nitrogen may induce higher yields than NH_4^+ nitrogen when applied before or during tuber formation, whereas after tuber formation NH_4^+ nitrogen was more efficient in terms of tuber yield [9]. Similarly, it has been suggested that application rates may also affect yield and according to many reports increased nitrogen rates could result in higher tubers yield [10,11], although tuber quality may also be affected [12,13], while excessive rates could induce late vegetation and decrease tuber bulking [8].

Considering that nitrogen is usually applied based on empirical standards, the irrational use of fertilizers is very common aiming at higher yields without considering the environmental impact from fertilizer production and the groundwater contamination through leaching [14,15]. Tuber quality is also an issue, since mineral fertilization may have a strong impact on the quality of potatoes [16], as for example nitrogen can present some serious effects on the dry matter, protein and starch content [4].

Zeolites are hydrated alkaline aluminosilicate crystals providing numerous benefits not only to crops but also to the soil. Almost 50 types of zeolite have been recorded, among which clinoptilolite is the most common type of zeolite generally used in agricultural systems [17]. Zeolites have a tendency to absorb NH_4^+ and K^+, while they also contain some of the most fundamental macro- and micro-nutrients a crop needs [18]. Likewise, zeolites present some serious positive effects to the crop by improving soil moisture and nitrogen availability and preventing nitrogen leaching, which leads to the prevention of quick nutrient loss and the facilitation of an adequate nutrient supply to crops [19]. According to Ghannad et al. [20] who studied the effect of different fertilizer programs on the quality and yield of potato, it was found that zeolite treatment as a fertilizer management practice increased the crop yield. Another suggested farming practice includes the combination of zeolite and compost which presents several advantages such as the improvement of water use efficiency and of soil properties, the increase of soil water holding capacity, and the reduction of soil and environmental pollution [21–23].

Apart from the acquired knowledge regarding crop needs in terms of macro- and micro-nutrient fertilization, further information is needed for defining the optimal fertilizing regimes for the yield and quality of potato crop within the context of eco-friendly farming management. Taking into consideration the information referred above, it is essential to examine and exploit new fertilizing tools such as zeolite and manure which may replace and/or substitute conventional fertilizers in order to achieve higher yield without compromising the quality of the final product. Therefore, the aim of the present study was to evaluate the effect of different fertilization regimes on total yield, quality characteristics and chemical composition of two potato varieties cultivated in central Greece.

2. Materials and Methods

2.1. Plant Material and Experimental Conditions

The experiments took place at the experimental field of the University of Thessaly in Velestino, Greece. Two commercial potato (*Solanum tuberosum* L.) varieties, namely Kennebec and Spunta, were

cultivated in a total area of 240 m^2 using whole Kennebec and Spunta variety tubers of approximately 80 g and 50 g weight, respectively, as planting material. Prior to planting, soil was configured in hills of approximately 20 cm in height. Planting of tubers was carried out manually on April 6th and 7th, 2016 with distances of 75 cm between hills and 30 cm within each hill and 8–10 cm depth. The experiment followed processing tomato and onion crops from previous growing periods. The soil was sandy clay loam (48% sand, 29% silt and 23% clay), the pH was 7.4, electrical conductivity (EC) was 1.4 dS/m, organic matter content was 1.3 g/100 g soil, total nitrogen content was 0. 85 g/kg, nitrate nitrogen was 9.8 mg/kg, potassium content was 2.0 $cmol_c$/kg, and Olsen P was 30 mg/kg [24]. The experiments wer+e carried out according to the split plot design using fertilization treatments as the main plots and varieties as the sub-plots. Each experimental plot consisted of six hills, three for each variety, while from each plot the two outer furrows were excluded from yield measurements and sampling. Plot dimensions were 4 m wide and 3 m long (12 m^2), with corridors of 1 m between them. Each fertilization treatment had four replicates and 20 plots at total have been used for the experiments.

Five fertilizer treatments were applied, namely: (i) Control (C) with no fertilizer added, (ii) standard fertilizer (T1) in amounts that allowed the application of 250 kg/ha of N in the form of ammonium sulfate (N-P-K: 21-0-0 + 24 S + 0.2 B; Yara S.A., Athens, Greece), (iii) standard fertilizer + zeolite (T2) in amounts that allowed the application of 250 kg/ha of N in the form of ammonium sulfate (N-P-K: 21-0-0; Yara S.A., Athens, Greece) and the addition of 3.3 kg of zeolite per plot, (iv) manure (T3) in amounts that allowed the application of 250 kg/ha of N (approximately 20 tons per ha) and (v) slow release nitrogen fertilizer with urease inhibitor (T4) in amounts that allowed the application of 250 kg/ha of N in the form of urea (N-P-K: 46-0-0; Nutrimore N-Plus, Gavriel S.A., Athens, Greece). In treatments T2 and T3, standard fertilizer was applied in three doses (base dressing and two side dressings), while manure (T3) and slow release nitrogen fertilizer (T4) were applied with base dressing. In all treatments, except for control (C), 150 and 300 kg/ha of P, K were added with base dressing in the form of triple phosphate (N-P-K: 0-48-0; Gavriel S.A., Athens, Greece) and potassium sulfate (N-P-K: 0-0-52; Gavriel S.A., Athens, Greece), respectively. Irrigation was applied regularly via a sprinkler irrigation system, while weed control and hilling were carried out manually with hoeing. Pests and pathogens were controlled with chemical management according to standard cultivation practices.

For dry matter content estimation, three whole plants were collected from each plot at 86 days after planting (DAP), then divided in shoots and leaves and dried in a forced-air oven at 72 °C to constant weight. Harvest of potato tubers took place on July 18-19, 2016 (105 DAP). Tubers from each plot were considered for yield estimation, while a batch sample of 15 tubers from each plot and each variety were used for chemical analyses. Dry matter content of tubers was determined in batch samples of 5 tubers from each plot similarly to shoots and leaves.

2.2. Chemical Analyses

Chemical composition sampling was achieved according to the method described by the authors [25]; chemicals and solvents were of analytical grade and purchased from common sources. Water was treated in a Milli-Q water purification system (TGI Pure Water Systems, Greenville, SC, USA). Samples were analyzed in terms of nutritional compounds (moisture, fat, ash, proteins and carbohydrates) according to the AOAC methods [26]. Briefly, moisture was determined by drying samples at 105 ± 5 °C until constant weight. Crude protein was evaluated by macro-Kjeldahl method ($N \times 6.25$) using an automatic distillation and titration unit (model Pro-Nitro-A, JP Selecta, Barcelona, Sapin) (AOAC 978.04), ash content was determined by incineration at 550 ± 10 °C (AOAC 923.03), and the crude fat was determined by extraction with petroleum ether using a Soxhlet apparatus (AOAC 920.85). Total carbohydrates were determined by difference according to the equation: Total carbohydrates (g/kg fw) = 100 − (g moisture + g fat + g ash + g proteins). Energy was determined according to the Atwater system following the equation: (kcal/kg fw) = 4 × (g proteins + g carbohydrates) + 9 × (g fat).

Free sugars were determined by an HPLC system coupled to a refraction index (RI) detector as previously described by Guimarães et al. [27]. The lyophilized powder sample (1.0 g) was spiked with

the melezitose as internal standard (IS, Matreya, State College, PA, USA), and was extracted with 40 mL of 80% aqueous ethanol at 80 °C for 30 min. The resulting suspension was centrifuged at 15,000× g for 10 min. The supernatant was concentrated at 40 °C (rotary evaporator) under reduced pressure and defatted three times with 10 mL of ethyl ether, successively. After concentration at 40 °C, the solid residues were dissolved in water to a final volume of 5 mL, and filtered through 0.2 μm nylon filters from Whatman for HPLC analysis. Sugar identification was made by comparing the relative retention times of sample peaks with standards. Data were analyzed using Clarity 2.4 Software. Quantification was based on the RI signal response of each standard and by using calibration curves obtained from the commercial standards of each compound. The results were expressed in g/kg of fresh weight (fw).

Organic acids were determined by ultra-fast liquid chromatography coupled with a photodiode array detector (PDA) as previously optimized and described by Pereira et al. [28]. Samples (2 g) were subjected to an extraction with meta-phosphoric acid (25 mL; 25 °C; 150 rpm; 45 min), and filtered through Whatman No. 4 paper and 0.2 μm nylon filters before injection. The organic acids were quantified by comparison of the area of their peaks recorded at 215 nm with calibration curves obtained from commercial standards (Matreya), of each compound. The results were expressed as g/kg of fw.

Fatty acids were determined after a transesterification procedure as described previously by Guimarães et al. [27] and using a gas chromatograph equipped with a split/splitless injector, a flame ionization detector (GC-FID) and a Macherey-Nagel column. Fatty acids (obtained after Soxhlet extraction) were methylated with 5 mL of methanol:sulphuric acid:toluene 2:1:1 (*v:v:v*), during at least 12 h in a bath at 50 °C and 160 rpm; then 3 mL of deionized water were added, to obtain phase separation; the FAME were recovered with 3 mL of diethyl ether by shaking in vortex, and the upper phase was passed through a microcolumn of sodium sulfate anhydrous, in order to eliminate the water; the sample was recovered in a vial with Teflon, and before injection the sample was filtered with 0.2 μm nylon filter from Whatman. Fatty acid identification was made by comparing the relative retention times of FAME peaks from samples with standards (reference standard mixture 37 (47885-U), Sigma (St. Louis, MO, USA). The results were recorded and processed using Clarity 4.0.1.7 Software and expressed as a relative percentage of each fatty acid.

To evaluate the antioxidant activity, hydroethanolic extracts were prepared; the lyophilized powder of samples (1 g) was stirred with ethanol:water (30 mL, 80/20, *v*/*v*) at 25 °C at 150 rpm for 1 h and filtered through Whatman no. 4 paper. The residue was then extracted with an additional portion of ethanol/water. The combined extracts were evaporated under reduced pressure (rotary evaporator Büchi R-210; Flawil, Switzerland), freeze-dried and lyophilized. The extracts were re-dissolved in ethanol:water (80:20, *v*/*v*) at a final concentration of 10 mg/mL (stock solution) and further diluted at different concentrations (in the range of 10–0.078 mg/mL) and stored at 4 °C for further use. Successive dilutions were made from the stock solution and submitted to in vitro assays already described by Barros et al. [29]. The sample concentrations (mg/mL) providing 50% of antioxidant activity or 0.5 of absorbance (EC_{50}) were calculated from the graphs of antioxidant activity percentages (DPPH,β-carotene/linoleate and thiobarbituric acid reactive substances (TBARS) assays) or absorbance at 690 nm (ferricyanide/Prussian blue assay) against sample concentrations. Trolox was used as a positive control.

The liposoluble pigments (total carotenoids content and chlorophylls) were estimated by a spectrophotometric procedure according to the method described by Nagata and Yamashita [30]. Samples (500 mg) was vigorously shaken with 10 mL of acetone/hexane mixture (4:6) for 1 min and filtered through Whatman No. 4 filter paper.; the absorbance of extracts was measured at 453, 505, 645 and 663 nm. The contents of total carotenoids and chlorophyll a and b were calculated according to the following equations, and further expressed in mg/kg fw: total carotenoids (mg/100 mL) = $0.216 \times A_{663} - 1.220 \times A_{645} - 0.304 \times A_{505} + 0.452 \times A_{453}$; chlorophyll a (mg/100 mL) = $0.999 \times A_{663} - 0.0989 \times A_{645}$ and chlorophyll b (mg/100 mL) = $-0.328 \times A_{663} + 1.77 \times A_{645}$.

Phenolic compounds were determined in the hydroethanolic extracts prepared above, which were redissolved in ethanol/water (80:20, *v*/*v*) to a final concentration of 15 mg/mL and filtered using

a 0.22 µm disposable filter disk. Further, were analyzed using an Ultimate 3000 ultra-performance liquid chromatography system (Thermo Scientific, Waltham, MA, USA) equipped with a diode array detector coupled to an electrospray ionization mass spectrometry detector as previously described by Bessada et al. [31]. A previously described solvent system with gradient was applied as follows: (A) 0.1% formic acid in water, (B) acetonitrile. An gradient elution was established: 15% B (0–5 min), 15% B to 20% B (5–10 min), 20–25% B (10–20 min), 25–35% B (20–30 min), 35–50% B (30–40 min), subsequent column re-equilibration with a flow rate of 0.5 mL/min. Double online detection was performed in the DAD (280 and 370 nm) and in a mass spectrometer (MS) connected via the DAD cell outlet. MS detection with electrospray ionization was performed in negative mode under hereby mentioned conditions: sheath gas (N2, 50 psi); source temperature 325 °C; spray voltage 5 kV; capillary voltage −20 V; tube lens offset voltage -66 V; collision energy 35 arbitrary units. The full scan data were collected from m/z 100 to 1500. Data acquisition and processing was conducted using an Xcalibur® data system. The individual compounds were identified by comparing their retention times, UV–visible spectra and MS fragmentation pattern with those obtained from the available commercial standards (Extrasynthesis, Genay, France), and also with data available from already reported studies. The phenolic compounds quantification was based on calibration curves obtained from available standards. The results were expressed as mg/kg fw.

2.3. Statistical Analysis

For chemical composition, three extractions were prepared and the analyses were performed in triplicate. For the statistical analysis, data were analyzed using two-way analysis of variance (two-way ANOVA) followed by the Tukey's HSD test ($p < 0.05$) and Student's *t*-test ($p < 0.05$) for means comparison using the Statgraphics 5.1.plus software (Statpoint Technologies, Inc., Warrenton, VA, USA).

3. Results and Discussion

Total yield of each variety in relation to the fertilizer regimes is presented in Table 1. There were statistically significant differences between the two varieties for all the tested fertilizer treatments. These differences could be attributed to seed (tuber) size, since it is well established that total yield is positively correlated with tuber size [32,33]. In our study, Kennebec variety seeds were larger than the Spunta ones, which explains the significant differences in yield. Regarding the varietal response to the fertilization regime, the treatment of slow release nitrogen fertilizer (T4) provided the highest yield for both varieties. Similarly to our study, Zareabyaneh and Bayatvarkeshi [34] studied the effects of slow-release nitrogen fertilizers on nitrate leaching and its distribution in soil profile, N-use efficiency, and the tuber yield in potato crop, and they reported that slow release nitrogen fertilizers resulted in higher yield than the urea treatment. A possible explanation for this result could be the lower nitrate leaching and the higher nitrate availability in the case where slow release fertilizers were used compared to conventional ureic fertilizers. In addition, the application of standard fertilizer, with or without zeolite added, resulted in significantly lower yield than the slow release treatment and higher yield than manure (T3) and the control treatment (C) for both varieties. However, according to Zebarth et al. [35] nitrogen accumulation and tuber yield are also associated with environmental factors such as the air temperature, the water availability, the growth stage and the intercepted irradiation and soil properties as well. Yield response to nitrogen fertilization is more related with tuber size which increases with increasing nitrogen rates and less with tuber number which shows varied response, while excessive nitrogen rates may have the opposite effect [36–39].

Apart from fertilizer rate, timing of nitrogen fertilization is equally important and appropriate recommendations for crop management are essential for achieving high tuber yields [40]. However, nitrogen source is also very important for the achievement of high yields since the form of the applied nitrogen and its availability may affect plant biomass partitioning and allocation of assimilates in tubers [41]. Mirdad [42], who carried out a field study comparing the impact of organic (chicken

manure) and mineral fertilizers on tuber yield of two potato cultivars (Nicola and Diamond), reported significant differences in tuber yield between the tested cultivars, although both of them showed the highest yield when moderate levels of organic (15 tons/ha) and mineral fertilization (300-150-150 kg/ha of N-P-K) were applied. Moreover, according to Wilkinson et al. [43] the use of fertilizers containing stabilized urea-nitrogen may increase tuber yield through the increased plant growth and nitrogen use efficiency compared to non-stabilized and conventional fertilizers.

Table 1. Total yield (kg/ha) of the studied potato varieties in relation to the fertilization regime.

Treatment	Kennebec	Spunta
C	15,275 ± 57 d*	10786 ± 81 d*
T1	22,633 ± 103 b*	12592 ± 103 b*
T2	22,619 ± 85 b*	12125 ± 92 b*
T3	20,186±64 c*	11586 ± 86 c*
T4	24,489 ± 93 a*	15433 ± 77 a*

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD. The asterisk symbol indicates significant differences between the varieties for the same fertilizer treatment, according to Student's *t*-test ($p < 0.05$).

Dry matter contents (%) of leaves, shoots and tubers are presented in Table 2. According to the results, statistically significant differences were observed between the fertilizer treatments and the studied varieties. Regarding the Kennebec variety, the highest amount of dry matter in leaves and tubers was achieved by control (C) and standard fertilizer treatment (T1), while the lowest one was occurred by treatments T1, T2 respectively. Different trends were observed in dry matter allocation for Spunta variety where the highest tuber DM content was observed for the T2 and T3 treatments, while T2 and T4 treatments resulted in the highest DM content in shoots and leaves, respectively. Overall, higher amounts of dry matter were observed in Spunta plant parts (leaves and shoots) regardless of the fertilization regime, whereas in tubers the highest dry matter content was observed in Spunta tubers and for T2 and T3 treatments, followed by T2 treatment.

Table 2. Dry matter (%) of leaves, shoots and tubers of the studied potato varieties in relation to the fertilization regime.

	Leaves	Shoots	Tubers
Kennebec C	16.7 ± 0.3 e	9.4 ± 0.7 f	23.0 ± 0.4 c
Kennebec T1	16.8 ± 0.3 e	10.0 ± 0.2 e	21.1 ± 0.6 g
Kennebec T2	14.6 ± 0.7 h	8.7 ± 0.4 h	21.5 ± 0.3 e
Kennebec T3	14.9 ± 0.2 g	8.7 ± 0.2 h	22.7 ± 0.6 d
Kennebec T4	15.8 ± 0.6 f	9.1 ± 0.5 g	21.3 ± 0.5f g
Spunta C	19.4 ± 0.6 c	12.9 ± 0.3 b	22.8 ± 0.4 c
Spunta T1	17.5 ± 0.3 d	12.7 ± 0.2 b	25.0 ± 0.5 b
Spunta T2	20.6 ± 0.4 b	14.1 ± 0.8 a	25.7 ± 0.3 a
Spunta T3	17.5 ± 0.3 d	11.9 ± 0.2 d	25.7 ± 0.3 a
Spunta T4	22.2 ± 0.7 a	12.4 ± 0.5 c	18.6 ± 0.6 h

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

These differences could be attributed to differences in tuber maturation earliness between the studied genotypes (recommendations of 105 DAP for harvest in the case Spunta and 110–130 DAP in the case of Kennebec) and the use of conventional nitrogen fertilizers (T1, T2 and T3 treatments) compared to slow release ones (T4), as well as to growing conditions that affected plant senescence (withering of aerial parts in the case of Spunta). According to Selladurai and Purakayastha [44], dry

matter content of potato plant tissues (shoots and tubers) may differ depending on the fertilizer regime and organic fertilizers could increase tuber dry matter, as it was observed in our study in the case of Spunta variety. Similarly, Mirdad [42] reported a significant interaction of genotype and fertilization regime effects on tuber and foliage dry weight. Moreover, dry matter content of tubers may affect the end use of the product with tubers having low values (18%–20%) of dry matter being more suitable for cooking and less susceptible to mechanical bruising, whereas tubers with high dry matter content (>20%) are suitable for processing [45]. Therefore, apart from the selection of the proper variety the adjustment of fertilization regime can be a cost-effective means to increase the high added of the final product through the regulation of tubers dry matter content [13,46].

The proximate composition and the energetic value of the studied potato varieties are presented in Table 3 showing a significant effect of the fertilization treatment and the genotype on the tested parameters. Kennebec plants treated with the standard fertilizer (T1) had the highest fat content 3.1 g/kg fw). Protein content was beneficially affected by T4 and T1 treatments in the case of Spunta variety (26.0 and 25.9 g/kg fw, respectively), followed by T1 treatment for Kennebec (2.7 g/kg fw). Ash and carbohydrates content was the highest in T1 and T3 treatments (13 and 221.2 g/kg fw, respectively) for Spunta variety, with the latter treatment (T3 for Spunta variety) having also the highest calorific value (987 kcal/kg fw). According to Naz et al. [47] who evaluated the effect of different levels of NPK fertilizers on the proximate composition of a potato crop grown at Abbottabad, fertilizer rates may have a significant effect on proximate composition of potato tubers, while similar results were reported by Ukom et al. [48] about the effect of nitrogen fertilizers on sweet potato crop. In addition, Ahmed et al. [49] reported a significant variation in carbohydrates and protein content under different nitrogen fertilization managements (different doses and sources of nitrogen), while the early study of Millard [50] indicated the significant effect of nitrogen fertilizers nitrogen and dry matter content of potato tubers.

Table 3. Nutritional value (g/kg fw) and energetic value (kcal/kg fw) of the studied potato varieties in relation to the fertilization regime (mean ± SD).

	Fat	Proteins	Ash	Carbohydrates	Energy
Kennebec C	1.9 ± 0.1 e	14.0 ± 0.6 g	10.0 ± 0.1 f	203.8 ± 0.4 b	888 ± 1 c
Kennebec T1	3.1 ± 0.1 a	22.7 ± 0.3 b	10.7 ± 0.5 d	174.9 ± 0.2 e	818 ± 1 f
Kennebec T2	2.7 ± 0.1 c	20.4 ± 0.4 d	10.3 ± 0.1 e	182.1 ± 0.4 d	834.0 ± 0.1 e
Kennebec T3	2.9 ± 0.1 b	19.42 ± 0.02 e	10.8 ± 0.7 d	193.5 ± 0.6 c	877 ± 1 d
Kennebec T4	2.6 ± 0.1 d	19.3 ± 0.3 f	11.2 ± 0.4 c	179.6 ± 0.6 de	819 ± 1 f
Spunta C	1.1 ± 0.1 g	19.5 ± 0.3 e	10.9 ± 0.2 d	196.1 ± 0.1 c	873 ± 1 d
Spunta T1	2.0 ± 0.1 e	25.9 ± 0.2 a	13 ± 2 a	209 ± 1 b	958 ± 4 b
Spunta T2	1.14 ± 0.04 g	22.17 ± 0.06 c	12.6 ± 0.3 b	178.5 ± 0.2 de	813 ± 1 f
Spunta T3	1.58 ± 0.06 f	22.2 ± 0.4 c	12.5 ± 0.4 b	221.2 ± 0.7 a	987 ± 1 a
Spunta T4	0.63 ± 0.02 h	26.0 ± 0.6 a	8.72 ± 0.05 g	148.7 ± 0.6 f	704.4 ± 0.5 g

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

The free sugars composition results are listed in Table 4. Sucrose, glucose and fructose were the only detected sugars in both varieties and for all the fertilizer treatments with great variation being detected. The same sugars were detected by Galdón [51] who also indicated the variability in sugars composition among different potato cultivars. Standard fertilizer (T1) resulted in the highest content of glucose, fructose and total sugars content in the case of Spunta variety (3.3, 0.78 and 13.7 g/kg fw), while sucrose content was the highest in T3 treatment for the same variety (11.4 g/kg fw). On the other hand, the lowest contents of the detected sugars were observed in Kennebec variety and the control (0.3 and 0.06 g/kg fw of glucose and fructose, respectively) and T1 treatments (2.33 and 3.1 g/kg fw of sucrose and total sugars, respectively). Based on these results, the standard fertilizer treatment increased the reducing sugars content compared to the rest of the fertilizer treatments in Spunta potatoes suggesting

a lower nitrogen availability, since according to De Wilde [52] lower nitrogen availability resulted in higher content of reducing sugars (fructose and glucose) in three potato varieties, especially under nitrogen deprivation (no nitrogen). The fact that in our study the tested cultivars showed a different reducing sugars content in the control treatment where no nitrogen was added could be associated with tuber maturity at the day of harvest or tuber size [53], since maturation is a complex process involving several parameters which usually do coincide e.g., senescence, sin set, dry matter accumulation and decrease of sucrose content [54–56]. Sugars composition fluctuates during the tuber development with high levels of fructose being detected in immature tubers, then reducing sugars content reduces during development and increases again to moderate levels just before maturation [57]. Sucrose content is an index of tuber maturity and the lower the content the more mature the tuber is [58,59]. Moreover, varietal differences in free sugars composition of tubers have been previously reported by Choi et al. [60] and Silva et al. [61]) which supports the observed variation in our study. In terms of quality, high free sugars content is not a desirable feature for potatoes destined for processing e.g., dehydrated or fried products, since it affects the taste of the final product, while high sucrose content at harvest is not suggested for storing tubers intended for processing [62]. Moreover, high reducing sugars content is also a negative feature for potato processing, since they are correlated with acrylamide, a carcinogenic compound formed in the Maillard reaction during processing [63,64]. Therefore, it seems that the application of slow release fertilizers induced maturity of Spunta variety tubers as also indicated by the low dry matter content (see results in Table 2), while it also enhanced their suitability for processing and storage.

Table 4. Composition in sugars (g/kg fw) of the studied potato varieties in relation to the fertilization regime (mean ± SD).

	Fructose	Glucose	Sucrose	Total Sugars
Kennebec C	0.06 ± 0.01 e	0.3 ± 0.1 f	4.00 ± 0.02 e	4.37 ± 0.06 f
Kennebec T1	0.155 ± 0.004 c	0.6 ± 0.1 cd	2.33 ± 0.01 i	3.1 ± 0.1 i
Kennebec T2	0.18 ± 0.01 c	0.8 ± 0.1 b	3.8 ± 0.2 f	4.7 ± 0.3 e
Kennebec T3	0.09 ± 0.04 d	0.56 ± 0.01 cd	3.30 ± 0.07 g	3.95 ± 0.04 g
Kennebec T4	0.18 ± 0.04 c	0.5 ± 0.1 de	5.13 ± 0.05 c	5.81 ± 0.06 c
Spunta C	0.09 ± 0.01 d	0.67 ± 0.05 bc	3.82 ± 0.03 f	4.58 ± 0.03 ef
Spunta T1	0.78 ± 0.05 a	3.3 ± 0.3 a	9.6 ± 0.1 b	13.7 ± 0.5 a
Spunta T2	0.07 ± 0.01d e	0.399 ± 0.002 e	4.8 ± 0.1 d	5.2 ± 0.1 d
Spunta T3	0.23 ± 0.01 b	0.6 ± 0.1 cd	11.4 ± 0.2 a	12.3 ± 0.4 b
Spunta T4	0.067 ± 0.008 de	0.62 ± 0.02 cd	2.59 ± 0.01 h	3.27 ± 0.02 h

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

The organic acids composition in relation to fertilizer regime and genotype is presented in Table 5. The main detected organic acids were citric, oxalic and malic acid, followed by ascorbic acid and traces of fumaric acid, while total organic acids content ranged between 7.5 and 11.96 g/kg fw. Citric and malic acid were also reported as the main organic acids by Lisińska and Aniołowski [65], while Wichrowska et al. [66] and Bushway et al. [67] detected tartaric, fumaric, oxalic, citric, ascorbic and malic acid with significant varietal differences in individual organic acids content. Significant differences in organic acids composition between various potato cultivars were observed by Galdón et al. [51], who also highlighted the interrelation of organic acids and sugars content, since the former are converted to sugars during tuber maturation. Organic acids composition of tubers depends on maturity stage and the content of the main compounds such as citric and malic acid fluctuates and reduces with maturation, respectively [57]. Moreover, a varied response of the tested varieties to fertilization regime was observed in the present study, with significant differences in individual and total organic acids content among the various treatments. The application of slow release nitrogen (T4) and standard (T1) fertilizers resulted in the highest oxalic and malic acid content for Spunta variety, respectively,

while manure application (T3) increased ascorbic and citric acid content for the same variety. Likewise, manure treatment (T3) increased ascorbic acid content for Kennebec potatoes, while T1 treatment resulted in the highest citric and total organic acids content. According to Jadhav and Andrew [68], nitrogen fertilization may affect organic acids content and acidity of tubers, as well as the quality of potato processing products, while Hamouz et al. [69] suggested that increasing rates of nitrogen fertilization resulted in a decrease of ascorbic acid content. Therefore, high citric acids content is beneficial to potato quality due to the reduced discoloration after cooking through the chelation of free Fe cations [70]. Moreover, Mozafar [71] reported that excessive nitrogen rates may have a variable effect on the ascorbic acid content of food plants such as potato. On the other hand, Boydston et al. [72] did not observe statistical differences in the ascorbic acid content under different nitrogen rate levels, but also noticed a significant year effect indicating the variable environmental effect.

Table 5. Composition in organic acids (g/kg fw) of the studied potato varieties in relation to the fertilization regime (mean ± SD).

	Oxalic Acid	Malic Acid	Ascorbic Acid	Citric Acid	Total Organic Acids
Kennebec C	0.020 ± 0.001 j	1.5 ± 0.1 g	0.160 ± 0.001 b	5.8 ± 0.1 e	7.5 ± 0.1 j
Kennebec T1	1.54 ± 0.02 c	1.66 ± 0.04 f	0.150 ± 0.001 c	8.61 ± 0.01 a	11.96 ± 0.07 a
Kennebec T2	1.10 ± 0.01 d	1.21 ± 0.01 hi	0.150 ± 0.001 c	6.12 ± 0.02 d	8.58 ± 0.03 g
Kennebec T3	0.440 ± 0.007 i	1.22 ± 0.01 h	0.17 ± 0.01 a	6.08 ± 0.03 d	7.91 ± 0.05 i
Kennebec T4	0.880 ± 0.001 e	1.19 ± 0.01 i	0.160 ± 0.001 b	7.05 ± 0.01 b	9.28 ± 0.01 f
Spunta C	0.560 ± 0.003 g	2.33 ± 0.01 c	0.070 ± 0.001 f	5.2 ± 0.3 g	8.1 ± 0.3h
Spunta T1	1.72 ± 0.02 b	3.25 ± 0.02 a	0.060 ± 0.001 g	6.2 ± 0.1 d	11.2 ± 0.1 c
Spunta T2	0.71 ± 0.02 f	2.25 ± 0.02 d	0.110 ± 0.001 d	6.4 ± 0.1 c	9.5 ± 0.2 e
Spunta T3	0.50 ± 0.02 h	2.05 ± 0.01 e	0.170 ± 0.001 a	8.65 ± 0.01 a	11.37 ± 0.05 b
Spunta T4	1.96 ± 0.01 a	2.86 ± 0.01 b	0.100 ± 0.001 e	5.5 ± 0.1 f	10.5 ± 0.1 d

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer; tr: traces. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

The antioxidant properties of the studied samples were evaluated with four different assays and the results are presented in Table 6. The highest antioxidant activity for all the assays was recorded in extracts from the Spunta variety, except for the DPPH assay where extracts from Kennebec tubers (T3 treatment) had the lowest EC_{50} values (5.43 mg/mL). Similarly, for the reducing power assay the highest antioxidant activity was detected for Spunta varieties that received T2 treatment, while the extracts from the control, T2 and T4 treatments showed the highest activity for the β-carotene/linoleate and the lipid peroxidation (TBARS) assays. According to the literature, fertilization rates may affect antioxidant properties of colored-flesh potato tubers through the increase of polyphenols content such as chlorogenic acid and anthocyanins [16]. In contrast, Boydston et al. [72] estimated the antioxidant capacity of two potato varieties without recording any significant differences for the different tested nitrogen rates. Moreover, Seijo-Rodríguez et al. [73] evaluated the antioxidant activity and total phenols and flavonoids content in tubers of 35 potato varieties with varied skin and flesh color and reported a great variation in the tested parameters among the tested varieties, as well a strong correlation of antioxidant activities with polyphenols content. Similarly, Andre et al. [74] found a strong correlation between the total phenolics content and the hydrophilic antioxidant capacity of 74 Andean potato cultivars. However, several other bioactive compounds such as carotenoids and ascorbic acid may have a synergistic effect on the overall antioxidant activity of potato tubers making it difficult to unravel the impact of fertilizers [16,75].

Table 6. Antioxidant properties (EC_{50}; mg/mL) of the studied potato varieties in relation to the fertilization regime.

	Reducing Power	Radical Scavenging Activity		Lipid Peroxidation Inhibition
	Ferricyanide/Prussian Blue	DPPH Scavenging Activity	β-Carotene/Linoleate	TBARS
Kennebec C	5.14 ± 0.03 e	8.1 ± 0.2 d	4.05 ± 0.08 a	0.77 ± 0.05 a
Kennebec T1	5.30 ± 0.02 d	7.39 ± 0.02 g	3.58 ± 0.06 c	0.71 ± 0.04 b
Kennebec T2	5.89 ± 0.07 c	7.6 ± 0.1 f	3.31 ± 0.04 d	0.73 ± 0.01 b
Kennebec T3	6.5 ± 0.1 b	5.43 ± 0.03 j	3.7 ± 0.3 b	0.67 ± 0.02 c
Kennebec T4	6.7 ± 0.1 a	8.5 ± 0.2 b	3.00 ± 0.05 e	0.76 ± 0.01 a
Spunta C	3.13 ± 0.03 h	8.6 ± 0.2 a	1.9 ± 0.1 h	0.42 ± 0.04 ef
Spunta T1	3.18 ± 0.01 g	7.21 ± 0.05 h	2.34 ± 0.04 f	0.44 ± 0.02 de
Spunta T2	3.06 ± 0.02 i	8.19 ± 0.03 c	1.94 ± 0.03 h	0.41 ± 0.01 f
Spunta T3	3.81 ± 0.01 f	8.02 ± 0.07 e	2.1 ± 0.1 g	0.45 ± 0.01 d
Spunta T4	3.19 ± 0.01 g	6.6 ± 0.2 i	1.89 ± 0.05 h	0.42 ± 0.02 ef

C: Control, T1: Standard Fertilizer, T2: Standard Fertilizer + Zeolite, T3: Manure, B: Slow release nitrogen fertilizer. Means values and standard deviations in columns with different letters are significantly different at $p < 0.05$ according to Tukey's HSD.

The composition of total carotenoids content and chlorophylls in the tested potatoes varieties is presented in Table 7. Manure treatment (T3) benefited total carotenoids content in Kennebec and Spunta tubers. Regarding chlorophylls content, the control treatment resulted in the highest content of chlorophyll a and b for the Kennebec and Spunta variety, respectively.

Table 7. Total carotenoids content and chlorophylls composition (mg/kg fw) of the studied potato varieties in relation to the fertilization regime.

	Carotenoids	Chlorophyll a	Chlorophyll b
Kennebec C	64.3 ± 0.3 b	1.420 ± 0.001 a	0.90 ± 0.01 a
Kennebec T1	46.5 ± 0.1 d	0.381 ± 0.001 e	0.601 ± 0.002 e
Kennebec T2	62.2 ± 0.1 b	1.156 ± 0.002 d	0.65 ± 0.01 d
Kennebec T3	66.5 ± 0.1 a	1.234 ± 0.001 c	0.728 ± 0.001 c
Kennebec B	59.3 ± 0.1 c	1.313 ± 0.004 b	0.83 ± 0.01 b
Spunta C	52.2 ± 0.1 b	0.751 ± 0.007 a	1.176 ± 0.004 a
Spunta T1	42.7 ± 0.0 c	0.515 ± 0.004 c	0.67 ± 0.01 d
Spunta T2	36.5 ± 0.0 d	0.439 ± 0.003 d	0.572 ± 0.002 e
Spunta T3	57.2 ± 0.1 a	0.631 ± 0.006 b	1.040 ± 0.01 b
Spunta B	41.2 ± 0.1 c	0.466 ± 0.002 d	0.758 ± 0.002 c

C: Control; T1: Standard Fertilizer; T2: Standard Fertilizer + Zeolite; T3: Manure; T4: Slow release nitrogen fertilizer. Mean values in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

Like in our study, the application of N-P-K fertilizers did not show any significant effects on carotenoids content of nine potato varieties, whereas a significant variation was observed among the tested varieties [76]. Similar results were reported by Tierno et al. [77] who also observed significant differences in total carotenoids content (1.12 to 11.9 μg lutein equivalents per g dw) of six potato cultivars and ten breeding lines, while Burmeister et al. [78] suggested a similar range of carotenoids for color-fleshed potatoes (2.57 to 14.77 μg of β-carotene equivalents per g dw). In contrast, Ukom et al. [48] evaluated the carotenoids content of selected sweet potato varieties as influenced by different levels of nitrogen fertilizer and they observed an increasing trend for β-carotene with increasing nitrogen levels, although a varied response among the tested cultivars was reported. Regarding chlorophyll content, most of the studies refer to chlorophyll in leaves which increased with increasing nitrogen fertilizer and manure rates, while a genotype effect was also observed [79,80].

However, according to Griffiths et al. [81], chlorophyll content in tubers is closely associated with the physiological maturity of tubers and the genotype with significant variation being observed.

Fatty acids composition in relation to the fertilization regime and the studies variety is presented in Table 8. Twenty fatty acids were detected in all the tested samples (Figure 1), with palmitic acid being the most abundant one (43.67%–52.94%), followed by stearic (11.88%–16.0%), linoleic (9.96%–20.29%), oleic (2.21%–7.56%), behemic (2.30%–3.74%), and arachidic acid (1.96–2.90%). Saturated fatty acids was the most abundant class of fatty acid (69.8%–78.1%), followed by polyunsaturated (15.80%–26.16%) and monounsaturated fatty acids (3.88–9.27%). Similar results were reported by Yang and Bernards [82] who also suggested that new fatty acids can be formed after wounding and the resulting suberization, while Uri et al. [83] detected palmitic and stearic as the main fatty acids in six potato cultivars. In contrast, Camire et al. [84] reported that polyunsaturated fatty acids were the most abundant class followed by saturated and monounsaturated ones (0.058, 0.035 and 0.003 g/100 g fw, respectively). Moreover, Galliard [85] identified linoleic as the main fatty acid, while they suggested the impact of genotype and maturation stage on fatty acid composition of tubers [86]. Therefore, the contrasting results could be attributed to differences in the studied genotypes and tubers maturity, as well as to extraction protocols. Regarding the effect of fertilization regime, a varied response was observed between the two varieties without specific trends being noticed.

Table 8. Fatty acids composition (%) of the studied potato varieties in relation to the fertilization regime (mean ± SD).

	Kennebec C	Kennebec T1	Kennebec T2	Kennebec T3	Kennebec T4	Spunta C	Spunta T1	Spunta T2	Spunta T3	Spunta T4
C6:0	0.54 ± 0.02 d	0.347 ± 0.004 h	0.56 ± 0.05 c	0.371 ± 0.004 g	0.505 ± 0.008 e	1.23 ± 0.05 a	0.40 ± 0.01 f	0.54 ± 0.03 d	0.53 ± 0.03 d	0.58 ± 0.01 b
C8:0	0.151 ± 0.007 e	0.17 ± 0.01 c	0.138 ± 0.005 f	0.113 ± 0.009 g	0.16 ± 0.01 d	0.81 ± 0.02 h	0.117 ± 0.004 g	0.120 ± 0.008 g	0.19 ± 0.01 b	0.213 ± 0.001 a
C10:0	0.163 ± 0.001 d	0.146 ± 0.006 f	0.195 ± 0.005 c	0.092 ± 0.004 h	0.15 ± 0.01 ef	1.55 ± 0.08 e	0.202 ± 0.005 c	0.128 ± 0.006 g	0.35 ± 0.03 a	0.258 ± 0.004 b
C12:0	0.26±0.02 f	0.32 ± 0.02 c	0.38 ± 0.02 b	0.300 ± 0.001 d	0.304 ± 0.003 d	1.05 ± 0.01 a	0.289 ± 0.005 e	0.166 ± 0.008h	0.29 ± 0.02 e	0.176 ± 0.006 g
C14:0	0.988 ± 0.001 e	1.12 ± 0.03 c	1.10 ± 0.04 cd	0.948 ± 0.008 f	1.07 ± 0.01 d	2.76 ± 0.07 a	0.959 ± 0.004 f	0.904 ± 0.008 g	1.18 ± 0.02 b	1.00 ± 0.01 e
C15:0	0.732 ± 0.002 g	0.94 ± 0.02 b	0.76 ± 0.03 f	0.76 ± 0.01 f	0.84 ± 0.02 d	1.03 ± 0.02 a	0.819 ± 0.006 e	0.71 ± 0.01 h	0.69 ± 0.01 i	0.88 ± 0.02 c
C16:0	51.20 ± 0.34 c	46.0 ± 0.4 h	43.67 ± 0.33 j	49.10 ± 0.13 e	52.5 ± 0.3 b	44.79 ± 0.01 i	46.33 ± 0.21 g	46.6 ± 0.2 f	51.02 ± 0.08 d	52.94 ± 0.01 a
C16:1	0.32 ± 0.01 a	0.27 ± 0.01 c	0.24 ± 0.01 d	0.279 ± 0.004 c	0.298 ± 0.008 b	0.25 ± 0.02 d	0.194 ± 0.006 f	0.21 ± 0.01 e	0.184 ± 0.004 f	0.22 ± 0.01 e
C17:0	1.06 ± 0.03 c	1.05 ± 0.01 c	0.94 ± 0.03 e	0.91 ± 0.05 f	1.05 ± 0.04 c	1.02 ± 0.03 d	1.34 ± 0.05 a	1.06 ± 0.07 c	1.21 ± 0.03 b	1.02 ± 0.07 d
C18:0	13.58 ± 0.04 e	12.83 ± 0.01 g	16.0 ± 0.2 a	13.4 ± 0.1 f	13.5 ± 0.2 e	15.87 ± 0.07 a	13.99 ± 0.11 c	13.79 ± 0.07 d	14.71 ± 0.07 b	11.88 ± 0.09 h
C18:1n9c	3.32 ± 0.04 b	2.86 ± 0.02 c	2.56 ± 0.06 e	2.63 ± 0.01 d	2.68 ± 0.009 d	7.56 ± 0.02 a	2.50 ± 0.01 f	2.21 ± 0.03 g	3.32 ± 0.04 b	2.49 ± 0.06 f
C18:2n6c	13.87 ± 0.01 c	13.22 ± 0.04 d	13.3 ± 0.1 d	9.96 ± 0.02 i	10.29 ± 0.05 h	12.00 ± 0.01 g	17.24 ± 0.01 b	20.29 ± 0.03 a	12.49 ± 0.06 f	12.7 ± 0.1 e
C18:3n3	1.66 ± 0.05 c	1.56 ± 0.01 d	1.39 ± 0.02 e	1.01 ± 0.06 g	1.25 ± 0.07 f	1.70 ± 0.01 c	2.75 ± 0.03 b	3.28 ± 0.02 a	1.65 ± 0.02 c	1.65 ± 0.06 c
C20:0	2.37 ± 0.06 c	2.36 ± 0.12 c	2.42 ± 0.07 c	2.40±0.09 c	2.64 ± 0.01 b	1.96 ± 0.01 g	2.25 ± 0.05 d	2.01 ± 0.03 f	2.17 ± 0.06 e	2.9 ± 0.2 a
C20:3n3+C21:0	1.8 ± 0.1 a	1.88 ± 0.01 a	1.49 ± 0.01 b	1.46 ± 0.03 b	1.84 ± 0.01 a	1.03 ± 0.01 d	1.5 ± 0.1 b	1.50 ± 0.09 b	1.41 ± 0.05 c	1.46 ± 0.01 b
C20:5n3	1.52 ± 0.02 g	4.27 ± 0.01 b	4.3 ± 0.2 b	4.72 ± 0.01 a	2.44 ± 0.05 c	1.10 ± 0.04 h	1.96 ± 0.01 e	1.13 ± 0.04 h	1.65 ± 0.05 f	2.34 ± 0.02 d
C22:0	3.24 ± 0.09 d	3.1 ± 0.2 e	3.03 ± 0.01 f	3.4 ± 0.1 c	3.74 ± 0.01 a	2.3 ± 0.1 h	3.16 ± 0.08 de	2.79 ± 0.02 g	3.5 ± 0.1 b	3.19 ± 0.16 d
C22:1n9	1.9 ± 0.1 e	6.14 ± 0.06 b	6.2 ± 0.1 b	6.35 ± 0.11 a	3.11 ± 0.07 c	1.06 ± 0.01 g	2.7 ± 0.1 d	1.45 ± 0.03 f	2.03 ± 0.05 e	2.8 ± 0.3 d
C23:0	0.90 ± 0.04 c	0.98 ± 0.04 b	0.822 ± 0.001 d	0.77 ± 0.07 e	1.06 ± 0.05 a	0.60 ± 0.05 g	0.893 ± 0.008 c	0.669 ± 0.008 f	0.89 ± 0.04 c	0.98 ± 0.04 b
C24:0	0.47 ± 0.01 d	0.482 ± 0.006 c	0.48 ± 0.02 c	0.481 ± 0.008 c	0.581 ± 0.001 a	0.35 ± 0.01 g	0.417 ± 0.008 ef	0.42 ± 0.02 e	0.512 ± 0.001 b	0.41 ± 0.02 f
Total SFA (% of total FA)	75.7 ± 0.2 d	69.8 ± 0.1 i	70.5 ± 0.1 h	73.60 ± 0.06 f	78.1 ± 0.1 a	75.3 ± 0.1 e	71.2 ± 0.2 g	69.94 ± 0.03 i	77.27 ± 0.01 b	76.4 ± 0.4 c
Total MUFA (% of total FA)	5.5 ± 0.2 d	9.27 ± 0.05 a	9.0 ± 0.2 b	9.3 ± 0.1 a	6.1 ± 0.1 c	8.87 ± 0.04 b	5.3 ± 0.1 e	3.88 ± 0.06 f	5.53 ± 0.01 d	5.5 ± 0.2 d
Total PUFA (% of total FA)	18.84 ± 0.04 e	20.93 ± 0.04 c	20.51 ± 0.06 d	17.15 ± 0.05 g	15.8 ± 0.1 h	15.83 ± 0.05 h	23.5 ± 0.1 b	26.19 ± 0.04 a	17.20 ± 0.01 g	18.1 ± 0.2 f

Caproic acid (C6:0); Caprylic acid (C8:0); Capric acid (C10:0); Lauric acid (C12:0); Myristic acid (C14:0); Pentadecylic acid (C15:0); Palmitic acid (C16:0); Palmitoleic acid (C16:1); Margaric acid (C17:0); Stearic acid (C18:0); Oleic acid (C18:1n9); Linoleic acid (C18:2n6c); α-Linolenic acid (C18:3n3); Arachidic acid (C20:0); Eicosatrienoic acid (C20:3n3); Heneicosylic acid (C21:0); Eicosapentaeonic acid (C20:5n3); Behenic acid (C22:0); Erucic acid (C22:1n9); Tricosylic acid (C23:0); Lignoceric acid (C24:0); SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids; n6/n3: omega-6/omega-3 fatty acids. Mean values in the same row followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

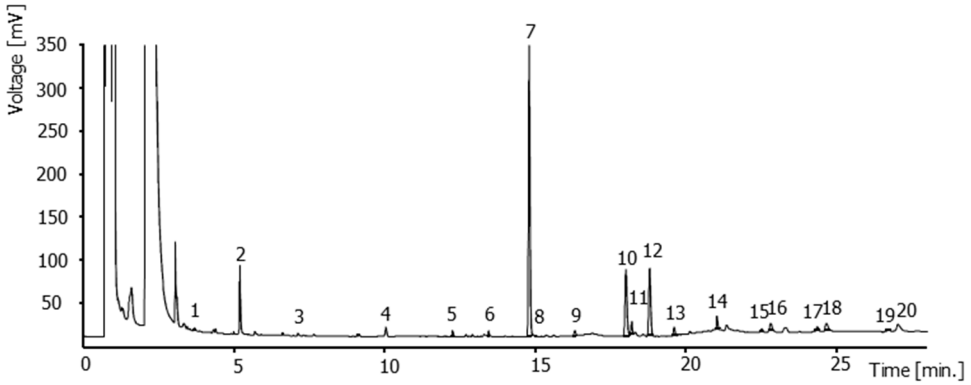

Figure 1. Individual profile of fatty acids of Kennebec T1: 1—C6:0; 2—C8:0; 3—C10:0; 4—C12:0; 5—C14:0; 6—C15:0; 7—C16:0; 8—C16:1; 9—C17:0; 10—C18:0; 11—C18:1n9c; 12—C18:2n6c; 13—C18:3n3; 14—C20:0; 15—C20:3n3+C21:0; 16—C20:5n3; 17—C22:0; 18—C22:1n9; 19—C23:0; 20—C24:0.

The analysis of phenolic compounds showed the presence of a single polyphenol, namely 5-O-caffeoylquinic acid or chlorogenic acid (Table 9; Figure 2).

Table 9. Quantification of the phenolic compounds (mg/kg fw) present in the studied potato varieties in relation to the fertilization regime (mean ± SD).

Treatment	5-*O*-Caffeoylquinic Acid
Kennebec C	46 ± 1 f
Kennebec T1	48 ± 1 e
Kennebec T2	41.5 ± 0.1 h
Kennebec T3	65 ± 2 c
Kennebec T4	54 ± 2 d
Spunta C	77 ± 3 b
Spunta T1	86 ± 2 a
Spunta T2	43 ± 1 g
Spunta T3	52 ± 2 e
Spunta T4	42 ± 2 gh

Standard calibration curves: 5-*O*-Caffeoylquinic acid (y = 168823x − 161172, R^2 = 0.999). 5-*O*-Caffeoylquinic acid (Rt: 7.0 min; λmax: 324 nm; $[M-H]^-$ m/z at 353; MS^2: 191(100),179(50),161(23),135(10)). Means in the same column followed by different Latin letters are significantly different at $p < 0.05$ according to Tukey's HSD.

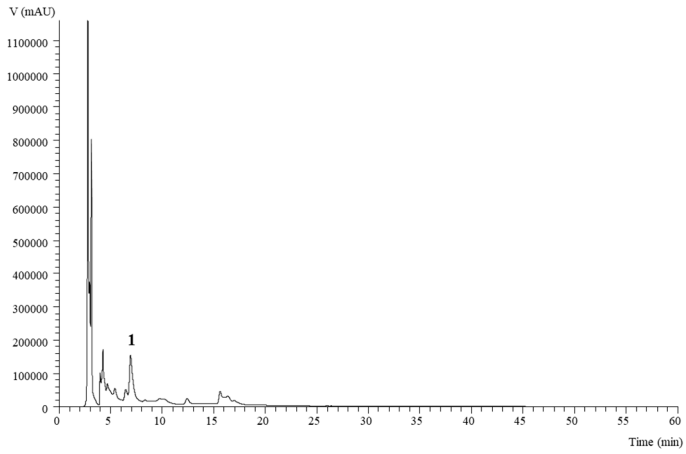

Figure 2. Individual profile of phenolic compounds in Spunta T1. 1-5-*O*-caffeoylquinic acid.

This compound was identified taking into account the chromatographic characterization with the commercial standard. Chlorogenic acid was the main or the only polyphenol in tuber flesh detected

in variable amounts depending on the genotype and flesh color [74,77,87,88]. The highest amount of chlorogenic acid were detected in extracts obtained from Spunta tubers subjected to the control and T1 treatment. The reports in the literature suggest a negative correlation of phenolic compounds content and nitrogen fertilization [16,89,90], while no differences were observed when different farming systems (conventional and organic cultivation) were compared [91]. In contrast, Lugasi et al. [88] did not observe any effect of nitrogen fertilization on phenolic compounds content, while they reported chlorogenic acid content within the range of 6.0 and 22.3 mg/kg fw. Similarly, Hamouz et al. [92] suggested that increasing rates of Mg and K may result in a decreased content of phenolic compounds of two potato varieties.

4. Conclusions

Based on the results of the present study, it can be concluded that the form of the fertilizers applied and the variety can significantly affect the yield and the chemical composition of potato crop, determining the end use of the product. In terms of yield, the importance of providing the necessary inorganic nutrients is pivotal for achieving high yields, while the timing of fertilizer application is also an important factor. In our study, the application of slow release nitrogen fertilizers resulted in the highest yield. The addition of nitrogen also affects the dry matter content of tubers, which is related to the maturity and the storage suitability of the final products. Chemical composition and antioxidant activity of tubers were also affected by the fertilization regime, although a varied response was observed between the tested varieties. Overall, based on the results of this study the fertilizer regimes varied in the forms of nitrogen are important for the effectiveness of fertilizers use, as expressed by tubers yield, as well as for the quality and the end use of the final product.

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