The Contribution of Soil Tillage and Nitrogen Rate to the Quality of Maize Grain

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Abstract: A soil tillage system adjusted to the soil type and agro-ecological conditions, together with the optimal nutrient supply, is a prerequisite for high maize (*Zea mays* L.) yield. However, there is little knowledge about the influence of soil tillage and nitrogen (N) rates on maize grain quality. A study was initiated in 1978 in Zemun Polje, Belgrade, Serbia, on the chernozem soil type. The effects of three N rates—0, 180 and 240 kg N ha^{-1}—within three tillage practices—no-tillage, reduced and conventional tillage—and their influence on grain yield (GY) and the content of proteins, starch, oil, total tocopherols and carotenoids, phytic phosphorus (Phy), glutathione (GSH), phenols and inorganic P (Pi) in maize grain were analysed in the period 2016–2018. Differences in maize GY were 2.57 and 3.01 t ha^{-1} for reduced- or no-tillage, respectively, in comparison to conventional tillage. Conventional tillage and higher N rates contributed to the increase in maize yield and the grain nutritional quality with regard to the increased level of proteins, GSH and Phy. On the other hand reduced inputs were beneficial only for grain quality, in relation to the increase in tocopherols and phenols.

1. Introduction

Maize (*Zea mays* L.) is the second largest crop, after wheat, with around 25% in the total cereal production within the European Union [1]. Maize production prevails in Serbia and probably will be more upgraded, together with animal stock production and the bio-fuel industry development. Despite the large production area, the average yields have not yet reached genetic potential and, besides innovations in breeding technology, some cropping practices such as the crop rotation, soil tillage and fertilisation, have to be additionally improved [2]. Alongside rice, wheat and soya bean, maize is an important staple food plant as it provides, either directly or indirectly (as feed grain), approximately 2/3 of the calories and protein consumed by humans and animals [3].

Its biomass and grain have many different purposes and can be used for the production of various raw materials in industry, as feed and food, etc. [4]. Due to its composition, maize grain is utilised in various ways. The increased amount of proteins, vitamins and some antioxidants, such as phenols, tocopherols and carotenoids, is a desirable and valuable trait.

The soil tillage system is an essential maize-growing practice for successful production. Tillage systems can significantly influence the yield and nutritional quality of maize through their effects on soil moisture, temperature, aeration and nutrient availability. Under variable climatic conditions and frequent occurrences of dry years, soil tillage adjusted to the soil type and agro-ecological conditions, can contribute to the water preservation and the achievement of higher yields [5]. Systems of reduced

tillage, particularly direct sowing, have entered widespread use in North America [6], Australia [7], South America and in Europe [8] due to their advantages in reducing soil erosion, conserving soil moisture, improving soil organic matter, and reducing labour, fuel and machinery costs. However, a shift towards minimum tillage tends to decrease nutrient concentration in crops, especially N, which can be overcome through the use of higher N rates [9]. Under the agro-ecological conditions of central Serbia, the highest maize yields are achieved with the conventional soil tillage system with 20–25 cm deep autumn ploughing and a single pass soil preparation in spring as 10–12 cm shallow tillage [10,11]. The results of a long-term experiment in the period 2005–2016 showed that the grain yield of maize was 10.0, 8.3 and 7.0 t ha^{-1} under conventional, reduced and no-tillage, respectively, while in dry years, the maize grain yield was higher under reduced than conventional tillage [11]. Studies performed by other authors also underlined the effects of different tillage systems on maize grain yield and its components [12,13].

The application of fertilisers, particularly of N, is the second prerequisite for successful maize production. The most important contribution to increased N use efficiency can be achieved through progress in breeding [14]. Compared with genetic improvement, agronomic management can more strongly influence N use efficiency through the right source, time, place and rate of fertiliser application [15,16]. The evidence showed that kilogram of maize grain yield per kilogram of N applied as a fertiliser was 54.6 in the EU, while the average amount of N applied per ha was 123 kg; however this ratio was 60.2 (163 N kg ha^{-1}) in the USA, and even 87.2 (76 N kg ha^{-1}) in Argentina [17]. Results gained by Singh et al. [18] showed that maize yields had increased from 10.5 t ha^{-1} (at the 0 kg N ha^{-1}) to 11.5 t ha^{-1} (at the highest N level of 202 kg N ha^{-1}). Nonetheless, the achievement and conduct of the good agronomic management of N fertilisers is usually determined by other practices such as the crop rotation, soil tillage systems or irrigation. The results obtained in trials with different N rates conducted in 32 irrigated maize fields in southern Nebraska, USA, pointed out that the economically optimal N rate for maize-following-maize rotations was 171 kg N ha^{-1}, giving a grain yield of 14.9 t ha^{-1}, while for maize-following-soybean rotations, this rate and the grain yield were 122 kg N ha^{-1} and 14.5 t ha^{-1}, respectively [19].

Besides the yield increase, the N application rate influences the nutrient composition of maize grain, especially in terms of protein and starch contents [20]. Maize grain, like the grain of all cereals, is high in starch (approximately 75%, on dry basis). Starch basically provides energy, and during seed germination it is a source of sugar for the developing germ. When used as a source of energy, maize can be prepared in various ways. On the contrary, maize grain contains an insufficient amount of proteins and it is deficient in the essential amino acids, such as lysine and tryptophan [21]. The protein content, and particularly the content of amino acids, lysine and tryptophan, significantly increased with increases in the N rate [18] due to the preferential deposition of zein over other endosperm proteins [22]. Nevertheless, high N rates usually decrease maize oil, and particularly the starch content [23]. The oil content did not vary significantly with N rates, while the starch content and extractable starch decreased significantly as the N rate increased [18]. The highest extractable starch level of 72.1% occurred on the plots without N application, while the lowest extractable starch occurred on plots receiving 202 kg N ha^{-1} [18]. Carotenoids and tocopherols are essential vitamins and bioactive substances with a protective role for human health due to their antioxidant activity [24,25]. Results obtained in a recent study, [26], have shown that foliar fertiliser with 3% of total N *w/w* had a significant influence on the content of antioxidants in sweet maize kernel.

The aim of the study was to investigate the effects of N rates on maize yield within different soil tillage systems and to determine the optimal combination of tillage practice-no-till, reduced and conventional tillage, and the N rate for high grain yield, and contents of proteins, starch, oil, total tocopherols and carotenoids, phytic and inorganic P, glutathione, and phenols in order to make maize grain more benefical.

2. Materials and Methods

2.1. Experimental Site and Soil Properties

The long-term trial was set up at the Maize Research Institute, Zemun Polje, in the vicinity of Belgrade (Latitude: 44°52′ N, Longitude: 20°20′ E, Altitude: 110 m) in 1978. The effects of three tillage systems: no-tillage, reduced and conventional tillage, and three fertiliser rates on maize yield and grain quality, were observed in the 2016–2018 period. The trial was performed on a chernozem [27], whose properties were analysed by the following methods: soil pH in KCl was determined in a 1:2.5 soil^{-1} M KCl suspension after a half-hour equilibration period, $CaCO_3$ was determined by the Scheibler calcimeter method, organic matter content by Kotzmann's method, total N by the Kjeldahl method and available phosphorus (P_2O_5) and potassium (K_2O) content by the standard AL-method according to Egner-Riehm. The 32% of clay, 15% of silt and 53% of sand were established in the 0–30 cm soil layer. Soil contained 4.3%, 3.6% and 3.3% OM in no-till, reduced and conventional tillage, respectively, in 2016, whereas the corresponding values in 2017 and 2018 amounted to 4.2%, 3.4% and 3.2% OM, and 4.8%, 3.7% and 4.4% OM, respectively. The content of total N was 0.52%, 0.12% and 0.21% in no-till, reduced and conventional tillage in 2016; 0.59%, 0.30% and 0.20%, respectively, in 2017, and 0.85%, 0.60% and 0.54%, respectively, in 2018. Available P and extractable K were 14 mg and 31 mg per 100 g of soil, respectively, in 2016, while total $CaCO_3$ amounted to 9.7%, and pH in KCl was 7.8.

2.2. Experimental Details

Winter wheat (*Triticum aestivum* L.) was a preceding crop, sown in autumn and harvested in July each year. The no-till, reduced and conventional tillage treatments were placed on the same area every second year after winter wheat within the double crop rotation. Winter wheat was harvested by harvester Claas Lexion 450 (Claas Grouppe, Harsewinnel, Gemany), and straw residues were left on the soil surface. The maize hybrid ZPSC 606 (FAO 600; Maize Research Institute Zemun Polje, Belgrade, Serbia) was sown on April 15, 26 and 27 in 2016, 2017, and 2018, respectively. This is the hybrid with a high yield potential, high density tolerance, medium height, lower cob position, and with a growth period of 120–125 days. The sowing density was 60,606 plants ha^{-1}, with an inter-row distance of 75 cm and within-row plant distance of 22 cm.

The experiment was set as a split-split-plot block design with four replications. The main treatments were three tillage (T) systems: T1-no-tillage, T2–reduced, and T3-conventional tillage. In the no-tillage treatment, maize seeds were directly sown in the upper soil layer of 5–7 cm, directly by a special, John Deere 7200 seeder (John Deere, Moline, Illinois, USA). In the reduced tillage treatment, soil tillage was performed to a depth of 8–10 cm, with a rotary tiller-rotovator TF-145 (FPM Deljanin, Kuršumlija, Serbia) in autumn. Sowing was conducted in spring after the seedbed preparation (10–12 cm) performed with a conventional drill Majevica 454,200 4RK (Majevica, Bačka Palanka, Serbia). The conventional tillage treatment consisted of the following: shallow ploughing, immediately after wheat harvest to the depth of 10–15 cm; primary tillage (ploughing) to the depth of 25–30 cm in autumn; and the seedbed preparation (10–12 cm) in spring. The N fertiliser was applied in spring, prior to sowing in three rates (subplots): N1–0 kg N ha^{-1}; N2–180 kg N ha^{-1} and N3-240 kg N ha^{-1} within each tillage treatment as the main plot. The N fertilizer Urea with 46% N (carbamide, Agromarket, Kragujevac, Serbia), was applied by a spreader MR 300 (Agroart, Stara Pazova, Serbia) prior to sowing in all treatments of soil tillage. The application of N fertilizer application was done in accordance with weather forecasting predicting rain, which served for the N incorporation with gravitational water into soil. Fertilisers in the amounts of 50 kg P ha^{-1} and 50 kg K ha^{-1} were applied in autumn in N2 and N3 treatments. The elementary plot size was 21 m^2. The whole area was treated with the pre-emergence herbicide mixture for grass and broadleaf weed control. The application was performed at the recommended rates of Dual Gold 960 (Syngenta International AG, Basel, Switzerland) + Radazin TZ 500 (Iskra Chemical Industry, Zelina, Croatia), 960 + 500 g ha^{-1}, respectively (a.i.: S-metolachlor (*2-chloro-N-[2-ethyl-6-methylphenyl]-N-[(2S)-1-methoxypropan-2-yl]acetamide*)

+ terbuthylazine (*2-N-tert-butyl-6-chloro-4-N-ethyl-1,3,5-triazine-2,4-diamine*)), applied in recommended rates (960 + 500 g ha^{-1} a.i.) with a hand-held sprayer calibrated to deliver 15 L at 300 kPa with a flat-fan nozzle (1.4 mm E 04-80, TeeJeet Technologies, Springfield, IL, USA).

2.3. Sampling and Analysis

The maize grain yield (GY, t ha^{-1}) was determined for each plot at the end of the maize-growing period and adjusted to 14% moisture content. The contents of proteins, oil and starch were determined with an NIR analyser Infraneo (Chopin, France). Then, grains were milled (particle size < 500 μm) using a laboratory mill SJ 500 (MetronGroup, Novi Sad, Serbia) and the concentrations of carotenoids (lutein, zeaxanthin and β-carotene) and tocopherols (α-T, β+γ-T, δ-T) were determined by HPLC (Dionex UltiMate 3000 liquid chromatography system-Thermo Scientific, Germany) by the method proposed by Mesarović et al. [28]. The content of carotenoids was expressed as a sum of concentrations of lutein, zeaxanthin and β-carotene. The tocopherols content was presented as a sum of concentrations of α-tocopherol, β+γ-tocopherol and δ-tocopherol. The content of phytic phosphorus (Phy) and inorganic phosphorus (P$_i$) was determined by the method of Dragičević et al. [29], total glutathione (GSH) by the method of Sari-Gorla et al. [30], while water-soluble phenolics were measured by the method of Simić et al. [31] and expressed in μg of *3-hydroxy-4-methoxycinnamic acid* g^{-1}. All analyses were done in three separate measurements and expressed as a mean value ± standard deviation (SD).

2.4. Statistical Analysis

The four-replicate experiment was set up according to the three-factorial randomized complete-block system design. The obtained data were statistically processed by ANOVA (F test), using STATISTICA 10 (StatSoft, Tulsa, OK, USA), while differences between means were tested by the least significant difference (LSD) test. The $p < 0.05$ and $p < 0.01$ were set as significance levels. The responses of the studied variables to the year of investigation, soil tillage system and a fertiliser rate were analysed using the correlation analysis (Pearson's coefficients) with the structure of the analysis of variance. The interdependence among the GY and its components—proteins, starch, oil, total tocopherols and carotenoids—as well as the content of Phy, GSH, soluble phenols and P$_i$ in the grain was processed by the principal component analysis (PCA) in SPSS 15.0 for the Windows evaluation version (SPSS Inc., Chicago, IL, USA).

2.5. Meteorological Conditions

Based on the precipitation sum during the maize-growing season, both seasons, 2018 and 2016, were favourable for maize cultivation. On the contrary, 2017, with dry spells during July and August with average temperatures of 25.5 and 25.8 °C, respectively (Figure 1), was the least favourable season for maize cultivation.
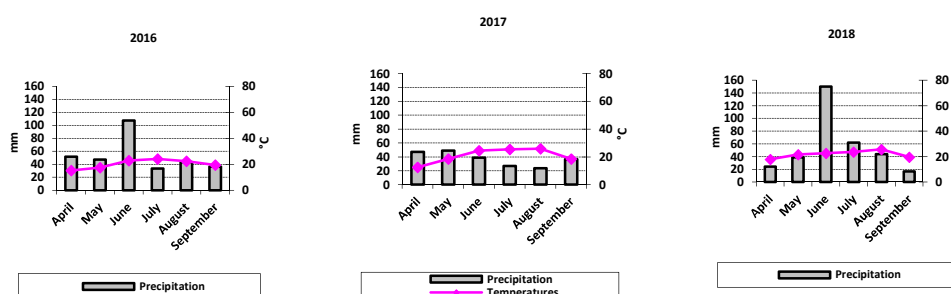

Figure 1. Walter and Lieth [32] climate diagram for the maize-growing seasons of 2016, 2017 and 2018.

3. Results

3.1. Response of Maize Parameters to the Year, the Soil Tillage System and the Fertiliser Rate

The obtained results pointed out the significant importance of both, the soil tillage system and the N rate on maize grain quantity and quality, Table 1. The results of the ANOVA showed that the year of investigation also had remarkable effects on both the maize productivity and the grain composition. Moreover, GY and the starch content were very significantly influenced by all investigated parameters and their interactions. Other parameters were determined by the influence of the interactions between soil tillage systems, N rate and the year (Y × T, Y × N, T × N and Y × T × N; Supplementary Tables S1 and S2).

Table 1. Analysis of variance (F values) for the effect of the year (Y), tillage system (T), N rate (N) and their interactions on grain yield (GY) and quality parameters of maize grain.

Source of Variation	d.f.	GY (t ha^{-1})	Proteins (%)	Starch (%)	Oil (%)	Carot (µg g^{-1})	Tocopher. (µg g^{-1})	P$_i$ (mg g^{-1})	GSH (nmol g^{-1})	Phenol (µg g^{-1})	Phy (mg g^{-1})
Y	2	103.73 **	1.53	17.77 **	104.87 **	135.50 **	0.95	0.90	174.31 **	56.89 **	24.69 **
T	2	9.37 **	13.49 **	8.38 **	3.57 *	4.06 *	1.40	8.08 **	0.19	6.10 **	0.49
Y × T	8	56.63 **	5.28 **	8.98 **	58.79 **	76.83 **	3.79 **	4.16 **	50.87 **	18.11 **	13.42 **
N	2	5.06 **	27.46 **	15.58 **	2.60	2.79	13.41 **	3.92 *	1.53	0.56	1.55
Y × N	8	37.85 **	8.87 **	12.88 **	31.45 **	46.32 **	5.90 **	5.84 **	60.83 **	14.79 **	9.93 **
T × N	8	4.36 **	20.67 **	9.16 **	1.86	2.12 *	4.81 **	3.78 **	0.52	0.72	2.91 **
Y × T × N	26	45.60 **	16.81 **	12.98 **	36.50 **	665.82 **	310.97 **	16.57 **	38.27 **	8.44 **	28.56 **

Carotenoids (Carot) = content of lutein+ zeaxanthin + β-carotene; tocopherols (Tocopher) = content of α-T + β+γ- T + δ-T; phytic P (Phy), glutathione (GSH), phenols, and inorganic P (P$_i$) in maize grain; ** Significant at the 1% probability level; * Significant at the 5% level; df: degrees of freedom.

3.2. The Effect of the Year

Significantly higher GY was recorded in 2016 and 2018 than in 2017, with both years having a favourable level of precipitation, Table 2; Supplementary Table S3. On average, GY was nearly three times higher in 2016—9.92 t ha^{-1} (100.00%) and 2018-8.60 t ha^{-1} (86.7%)—than in 2017—3.47 t ha^{-1} (35.0%). Similarly, the oil content showed the same trend and was very significantly higher in 2016 and 2018 than in 2017 (4.47, 3.92 and 3.73%), as well as GSH (2992.7, 2732.7 and 1896.2 nmol g^{-1}) and soluble phenols (342.29, 278.31 and 148.84 µg g^{-1}). The content of proteins was higher in 2016 (9.2%) in comparison to the remaining two years, 2017-9.1% and 2018-9.0%, as well as the content of P$_i$ (0.35, 0.34 and 0.34), but differences were not significant. Total carotenoids and tocopherols had the highest values in 2018, while Phy has the highest level in maize grain in 2017, compared to the other two years. The growing season caused high and significant variations in phenols in maize grain, and the highest value was obtained in 2016 (342.29 µg g^{-1}), the medium in 2018 (278.31 µg g^{-1}) and the lowest in 2017 (148.84 µg g^{-1}).

Table 2. Effects of the year (Y), tillage system (T), and N rate (N) on grain yield (GY) and quality parameters of maize grain.

Investigated Factors	GY (t ha^{-1})	Proteins (%)	Starch (%)	Oil (%)	Carot (µg g^{-1})	Tocopher. (µg g^{-1})	P$_i$ (mg g^{-1})	GSH (nmol g^{-1})	Phenols (µg g^{-1})	Phy (mg g^{-1})
2016	9.92 [a]	9.23	72.06 [a]	4.47 [a]	34.77 [b]	43.54	0.35	2992.70 [a]	342.29 [a]	3.16 [b]
2017	3.47 [b]	9.11	70.90 [b]	3.73 [b]	28.78 [c]	42.33	0.34	1896.20 [c]	148.84 [c]	3.57 [a]
2018	8.60 [a]	8.96	72.48 [a]	3.92 [b]	38.19 [a]	44.24	0.34	2732.70 [b]	278.31 [b]	3.23 [b]
LSD $_{0.05}$	2.005	0.6482	1.165	0.225	2.455	5.935	0.033	260.4	78.40	0.262
T1	6.18	9.15 [ab]	71.94	4.13	33.23	43.68	0.34 [ab]	2569.50	271.00	3.18
T2	6.62	8.72 [b]	72.34	4.09	32.87	44.35	0.36 [a]	2495.70	245.40	3.37
T3	9.19	9.43 [a]	71.15	3.90	35.64	42.08	0.33 [b]	2556.40	253.00	3.41
LSD $_{0.05}$	3.186	0.586	1.252	0.377	4.475	5.909	0.031	540.2	112.6	0.301
N1	6.00	8.61 [b]	72.64 [a]	4.14	32.60	46.68 [a]	0.36 [a]	2416.50	266.40	3.28
N2	7.54	9.15 [a]	71.69 [ab]	4.04	34.02	43.28 [ab]	0.34 [ab]	2579.50	262.60	3.28
N3	8.45	9.53 [a]	71.10 [b]	3.94	35.12	40.15 [b]	0.33 [b]	2625.50	240.40	3.39
LSD $_{0.05}$	3.304	0.533	1.184	0.380	4.526	5.344	0.032	533.5	112.6	0.313

Carotenoids (Carot) = content of lutein+ zeaxanthin + β-carotene; tocopherols (Tocopher) = content of α-T + β+γ- T + δ-T; phytic P (Phy), glutathione (GSH), phenols, and inorganic P (P$_i$) in maize grain. Different letters indicate significant differences according to LSD test at $p < 0.05$.

3.3. The Importance of the Soil Tillage System

The highest GY was obtained within the conventional soil tillage system—9.19 t ha^{-1}, Table 2. On average for all years, the remaining two systems of soil tillage, no-till and reduced tillage, gave the lower GY by nearly 3, 6.62 and 6.18 t ha^{-1}, respectively (Supplementary Table S3). Together with GY, proteins and carotenoids were the highest under conventional soil tillage, and differences were significant in case of proteins. The content of oil was the lowest in conventional tillage (3.90%) in comparison to reduced (4.09%) and no-tillage (4.13%). The phenols content decreased with soil tillage intensification from 271.00 µg g^{-1} in no-tillage to 245.00 µg g^{-1} in reduced tillage, even though differences were not significant. Furthermore, the content of total tocopherols was the highest in reduced tillage (44.35 µg g^{-1}), lower in no-tillage (43.68 µg g^{-1}) and the lowest in conventional tillage (42.08 µg g^{-1}), although differences were not significant (LSD$_{0.05}$ = 5.909). On the contrary, Phy had the highest values in conventional tillage (3.41mg g^{-1}). The content of carotenoids in conventional tillage was higher (35.64 µg g^{-1}) when compared to reduced (32.87 µg g^{-1}) or no-tillage (33.23 µg g^{-1}).

3.4. Contribution of the N Rate

The application of N fertiliser, especially the highest amount (N3), increased GY, as well as the concentration of proteins, total carotenoids, GSH and Phy, Table 2. On average, for three years, GY was higher by 10.8% and 29.0% in the N3 (8.45 t ha^{-1}) than in N2 (7.54 t ha^{-1}) and N1 (6.00 t ha^{-1}) treatment, respectively (Supplementary Table S4). At the same time, with increasing N rate, the protein content in maize grains significantly increased from 8.61% to 9.53%. On the other hand, the content of starch was significantly and negatively, while oil content was insignificantly, and also negatively, affected by the N application, 72.64% and 4.14%, respectively, and were the highest in the N1 variant, without fertiliser application. N treatments expressed various and significant effects on tocopherols and P$_i$ accumulation, with the highest average values also obtained in N1, 46.68 and 0.36 µg g^{-1}, respectively. The N3 treatment insignificantly lowered the phenol content in maize grain, from 266.40 to 240.40 µg g^{-1}, while the Phy content was the highest in the N3 treatment (3.39 µg g^{-1}).

3.5. The Effectiveness of the Interactions between the Year, Soil Tillage System and the N Rate

The interaction of the soil tillage system and the N rate with the year of investigation very significantly influenced all investigated parameters, Table 1. However, the interaction effects of tillage and the N rate were found to be significant for the majority of tested parameters but not for the GSH, phenols and Phy content, Table 3. The highest GY was obtained in the conventional system of tillage and with the N3 level of fertiliser application, 9.57 t ha^{-1}; the content of proteins increased when a higher level of N was applied and the highest value was obtained in the T3N3 treatment-9.63%, while the starch concentration reached the maximum in the T2N1 treatment-73.18%, Table 3. The contents of both starch and oil were higher in the N1 treatment in all three tillage systems. The highest content of total carotenoids was recorded in maize grain in conventional tillage and the increased level of N, T3N2-36.90 and T3N3-35.91 µg g^{-1}, respectively. Tocopherols very significantly varied under the influence of soil tillage and the N level; they were reduced with increased N levels and the intensity of soil tillage. Thus, the highest amount of total tocopherols in maize grain was in T1N1-47.87 (µg g^{-1}) and T2N1-47.86 (µg g^{-1}). P$_i$ was the highest in T2N1-0.37; GSH did not significantly vary in dependence on the tillage system and the N level, as well as phenols, but they had the highest level in T3N3-2709.50 nmol g^{-1} and in T1N3 and T3N2 −284.50 and 282.80 µg g^{-1}, respectively. The content of Phy reached the highest values in T3N3-3.63 mg g^{-1}.

3.6. Interdependencies between GY and Quality Components in Grain

The significant correlations between GY and grain quality traits influenced by soil tillage systems and the N rate are shown in Table 4. GY was positively and highly correlated with the protein content

in T2 (r = 0.542) and N1 (r = 0.832). On the contrary, in T3 and N3, GY was significantly and positively connected with the starch content (r = 0.46 and r = 0.620).

Table 3. Interaction effects of soil tillage system (T) and nitrogen rate (N) on grain yield (GY) and quality parameters of maize grain.

Soil Tillage/ N Level		GY (t ha^{-1})	Proteins (%)	Starch (%)	Oil (%)	Carot. (µg g^{-1})	Tocopher. (µg g^{-1})	Pi (mg g^{-1})	GSH (nmol g^{-1})	Phenols (µg g^{-1})	Phy (mg g^{-1})
	N1	4.76 [a]	8.53 [a]	72.98 [b]	4.25 [b]	31.89 [a]	47.87 [b]	0.36 [b]	2459.20	258.80	3.19
T1	N2	6.43 [ab]	9.35 [bc]	71.75 [ab]	4.18 [ab]	33.34 [ab]	42.72 [ab]	0.35 [ab]	2670.00	269.70	3.18
	N3	7.36 [ab]	9.57 [c]	71.27 [a]	3.96 [ab]	34.47 [ab]	40.44 [a]	0.33a	2579.20	284.50	3.15
	N1	4.58 [a]	8.29 [a]	73.18 [b]	4.16 [ab]	31.82 [a]	47.86 [b]	0.37 [b]	2348.20	265.70	3.33
T2	N2	6.85 [ab]	8.46 [a]	72.72 [b]	4.13 [ab]	31.83 [a]	46.13 [b]	0.35 [ab]	2551.00	235.20	3.38
	N3	8.43 [b]	9.41b [c]	71.12 [a]	3.99 [ab]	34.98 [ab]	39.08 [a]	0.36 [b]	2587.80	235.40	3.40
	N1	8.67 [b]	9.01 [b]	71.77 [ab]	4.03 [ab]	34.10 [ab]	44.30 [ab]	0.34 [ab]	2442.10	274.70	3.33
T3	N2	9.34 [b]	9.65 [c]	70.78 [a]	3.81 [a]	36.90 [b]	41.00 [ab]	0.32 [a]	2517.50	282.80	3.27
	N3	9.57 [b]	9.63 [c]	70.91 [a]	3.88 [ab]	35.91 [ab]	40.95 [ab]	0.32 [a]	2709.50	201.40	3.63
LSD $_{0.05}$		3.064	0.4143	1.053	0.3741	4.421	5.233	0.0298	546.10	113.40	0.294

Maize grain yield (GY); total carotenoids (Carot.) = content of lutein+ zeaxanthin + β-carotene); total tocopherols (Tocopher) = content of α-T + $\beta+\gamma$- T + δ-T; inorganic P (Pi); glutathione (GSH); phenols and phytic P (Phy). Different letters indicate significant differences according to LSD-test at p < 0.05.

Table 4. Correlation coefficients (Pearson's correlation) for interdependence between GY and investigated quality parameters in dependence on the soil tillage system and the N rate.

Maize Grain Parameters	Tillage System			Fertilisation Rate		
	T1	T2	T3	N1	N2	N3
Proteins (%)	0.12	0.54 *	0.27	0.83 *	0.21	−0.19
Starch (%)	0.29	0.12	0.46 *	−0.09	0.30	0.62 *
Oil (%)	0.71 *	0.47 *	0.69 *	0.42 *	0.47 *	0.76 *
Carotenoids (µg g^{-1})	0.61 *	0.90 *	0.76 *	0.72 *	0.74 *	0.82 *
Tocopherols (µg g^{-1})	0.33	−0.30	−0.10	0.28	0.01	−0.40 *
P$_i$ (mg g^{-1})	−0.22	0.01	0.40 *	−0.30	−0.57 *	0.57 *
GSH (nmol g^{-1})	0.93 *	0.90 *	0.93 *	0.80 *	0.74 *	0.94 *
Phenols (µg g^{-1})	0.88 *	0.64 *	0.72 *	0.74 *	0.80 *	0.63 *
Phy (mg g^{-1})	−0.74 *	−0.77 *	−0.24	−0.71 *	−0.74 *	0.04

Total carotenoids (Carot) = content of lutein+ zeaxanthin + β-carotene); total tocopherols (Tocopher) = content of α-T + $\beta+\gamma$- T + δ-T; inorganic P (Pi); glutathione (GSH); phenols and phytic P (Phy). * Significant at 0.05 level, Pearson's correlation.

The oil content in maize grain significantly increased together, with yield increasing in all treatments, especially in T1 (0.71%), T3 (0.69%) and N3 (0.76%). The content of carotenoids was also significantly increased, with a yield increase in all treatments, especially in T2 (r = 0.904) and N3 (r = 0.823). The GSH content was positively and significantly correlated with all tillage systems and the application of higher N rates and GY increasing, while the content of total tocopherols decreased when GY increased. The values of phenols simultaneously increased with GY, especially in T1 (r = 0.88) and N2 (r = 0.80). Phy was negatively and significantly correlated with GY in T1, T2, N1 and N2, while P$_i$ was correlated with the GY increase in T3 (0.40) and N3 (0.57).

The Principal Component Analysis expressed that the PC1 and PC2 axes participated with 66.2% and 18.9%, respectively, in total variability. Among the tested parameters, grain yield, protein content, and total carotenoids were positively and significantly correlated with PC1, while starch, oil, total tocopherols and P$_i$ significantly but negatively correlated with the same axis. Phy correlated significantly and positively with PC2, and phenols correlated negatively with it, Figure 2.

Figure 2 reveals that the highest variation in the content of the soluble phenols was in T1-N2 and T3-N1 combinations. Nevertheless, T1-N1 and T2-N1, as well as T2-N2 (but to a lesser extent), mainly contributed to the variation in starch, oil, Pi and tocopherol concentrations. The T2-N3 combination and the T3-N3 combination, to a slight degree, expressed the impact on the variation in Phy and GSH contents and, to some extent, on GY. The content of proteins and carotenoids varied to a smaller extent, mainly in T1-N3 and T3-N2 combinations.
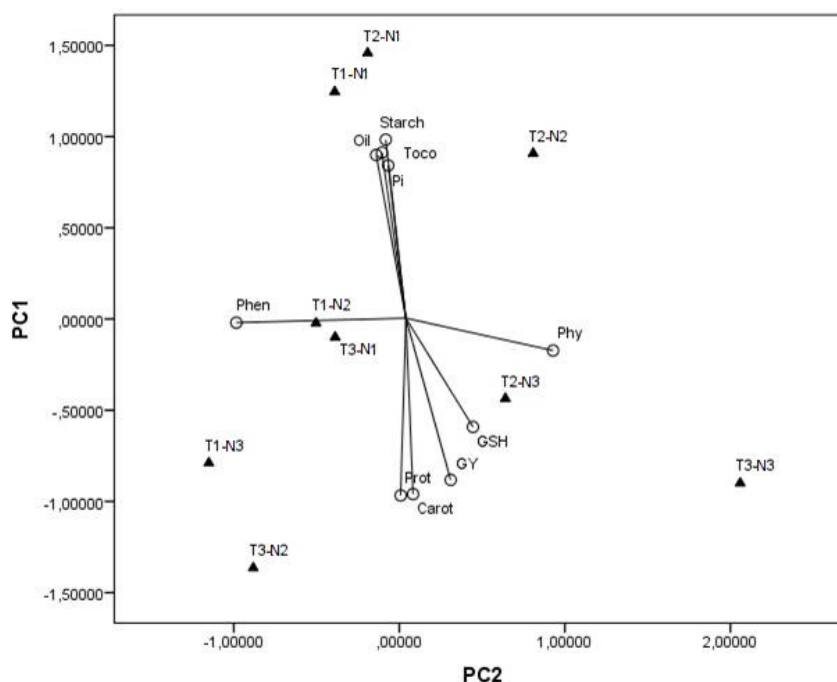
Figure 2. Principal Component Analysis for grain yield (GY), proteins (Prot), starch, oil, carotenoids (Carot), tocopherols (Toco), phytic P (Phy), phenols (Phen) and glutathione (GSH) in maize grain affected by different soil tillage systems and fertiliser rates: T1—no tillage, T2—reduced tillage, T3—conventional tillage; N1–without fertilization; N2-180 kg N ha^{-1} and N3-240 kg N ha^{-1}.

4. Discussion

4.1. The Effects of Meteorological Conditions on the Maize Yield and its Qualitative Parameters

Maize GY and its quality parameters were significantly influenced by the meteorological conditions. The significantly higher yield, $p < 0.05$, was recorded in years with a sufficient amount of precipitation, compared the yield recorded in the dry year, which was particularly present during anthesis and the grain-filling period. With the increased GY in years with a sufficient amount of precipitation, 2016 and 2018, the content of oil in grain has the opposite trend as a well-known rule [33]. Previous studies showed that stressful environments were largely associated with variations in maize grain oil, as well as total and extractable starch contents, while they were less associated with variation in the protein content, which implies that breeding for feedstock, i.e. greater protein content could be conducted across environments [34]. The highest phenol content was achieved in more favourable years, while the lowest concentration was detected in the dry 2017 [35]. The growing season affected concentrations of soluble phenols, and insignificantly influenced variations in the content of total tocopherols [36]. Phenolic compounds are important for human health. As pronounced antioxidants, they have an important role in plant metabolism, and their higher concentrations in maize grain could be a desirable trait [37]. Moreover, the highest GSH concentration was established in 2016 and then in 2018, which were favourable years for maize growth. This is not in agreement with the results obtained by May et al. [38] who concluded that the increased GSH content was associated with the adaptation of the plant to stress, such as high temperatures, but they mainly considered GSH alterations in plant leaves, not in grain.

4.2. Soil Tillage Effects on Maize Yield and Nutritive Components of the Grain

Deep soil tillage reduces soil compaction, leading to improved soil physical properties and, therefore, higher maize yields [12]. Soil disturbance usually improves the aeration and mineralisation of organic matter, thus increasing N availability [39]. Even more, sub-soiling treatment can improve

the distribution of the denser maize root system through the soil profile, playing a crucial role in crops' ability to access nutrients and water, which resulted in significantly greater post-silking biomass and GY compared to the reduced and no-tillage [12]. Merhij et al. [40] explained that maize grown under drought conditions, with a no-till system, had increased indoleacetic acid (IAA) concentration, while maize grown with conventional tillage system had the increased abscisic acid (ABA), which affected the plant growth, i.e., its ability to absorb and manage water, thus could be reflected in grain yield and grain composition. On the other hand, Houx et al. [41] established that tillage mainly influenced maize GY and was not a dominant factor that affected the grain composition, but one has to bear in mind that the experiment was based on the removal of mineral nutrients by grain yield. According to the results of Malhi et al. [9], minimum tillage tends to decrease the nutrient concentration in crops, especially N, which is most probably caused by an increase in N immobilisation. This effect can be surpassed with higher N rates or the inclusion of straw-retained practice, which contributes to N mineralisation due to increased organic matter in the soil. The results of the long-term experiment, 2005–2016, showed that differences between conventional and reduced or no-tillage in GY were 1.7 and 1.3 t ha^{-1}, respectively, while in some drier years, the maize GY was higher under conditions of reduced than in conventional tillage [11]. Studies done by Wasaya et al. [13] also proved the advantage of deep tillage for a higher maize yield achievement and improvement in grain quality, especially in the protein content. A positive correlation was established between total soil N and total protein content, which suggests that more intensive soil tillage has, along with more favourable soil physical and chemical properties, a beneficial effect on the plant N metabolism, and thus protein content, in maize grain can be achieved [42].

4.3. Effects of N Levels on the Maize Yield and the Grain Composition

The efficient agronomic management of N fertilisers is usually determined by other practices such as crop rotation, systems of soil tillage or irrigation, etc., and is also significantly related to the meteorological conditions of the year. According to results of Wang et al. [43], the N application significantly increased maize grain yields by 26.8% during the wet year, but only increased yields by 5.4% during the dry year. It was obvious that higher fertiliser rates, for instance rates in the N3 treatment, expressed a positive impact on GY, together with the increase in the concentration of important grain components, such as proteins, carotenoids, GSH and Phy. Kaplan et al. [44] proved that the increased N level was an important factor, not just for GY, but also for starch and phytate accumulation in grain. In Serbia, maize is usually rotated with winter wheat, but a more prominent practice requires legume crops in the rotation in order to improve soil physical and chemical properties and to increase the maize yield and the protein content in grain [45]. Dobermann et al. [19] conducted detailed N rate trials in 32 irrigated maize fields in southern Nebraska, USA, and pointed out that the economically optimal N rate for maize-following-maize rotations was 171 kg N ha^{-1}, giving GY of 14.9 t ha^{-1}, while, for maize-following-soybean rotations, this rate was 122 kg N ha^{-1} giving a yield of 14.5 t ha^{-1}. The higher the amount of N fertiliser applied, the greater the protein content in maize grains is [20], even though the correlation between GY and protein content for the higher N rate was negative ($r = -0.193$), indicating that the application of 240 kg N ha^{-1} was more directed towards GY increase than protein content increase in maize grain. Contrary to proteins, the starch content was negatively affected by the greater N application [46] and was the highest in the N1 treatment without the N fertiliser, 72.64%. Results of the study carried out by Singh et al. [18] showed that maize GY increased from 10.5 t ha^{-1} with no N application, to 11.5 t ha^{-1} at the higher N3 level of 202 kg N ha^{-1}.

Fertilisation treatments expressed various effects on the accumulation of tocopherols, P$_i$ and phenols, with the highest average values obtained in N1 (46.68 µg g^{-1}, 0.36 mg g^{-1} and 266.40 µg g^{-1}, respectively). The same trend has been observed for the oil content in maize grain, which was also the highest in the N1 (4.14%), treatment with the lowest grain yield achieved. Similar to these results, Langenkämper et al. [47] reported that higher N rates negatively affected phenol concentration in wheat grains, while Ma et al. [48] noticed a higher phenolic content when an increased amount of the N

fertiliser had been applied. This means that N fertilization could affect the accumulation of phenols in grain, but it is a complex trait that involves other factors. According to the generally accepted concept of the competition between phenolic compounds and proteins for their common precursor, L-phenylalanine, N at higher concentrations could inhibit the synthesis, and thus the accumulation, of phenolic compounds via increased phenylalanine biosynthesis towards proteins [49]. This means that the metabolism of phenolic compounds can be easily modified by the application of different N levels, i.e., with the low N rates, thus increasing the synthesis of phenolic compounds [50]. Moreover, N can adversely affect the activity of the phenylalanine ammonium-lyase (PAL) enzyme, a key enzyme in the synthesis of phenolic compounds. A decrease in the PAL activity due to the administration of high N rates was also documented [51]. Furthermore, it was established that increased N rates could result in a lower accumulation of total tocopherols [52] and oil [20], which is in agreement with results obtained in this study.

4.4. Interaction of Factors Affecting Maize Yield and Qualitative Parameters and the Correlation among Studied Parameters

The interaction of the soil tillage system and the N rate with the year of investigation very significantly influenced all observed parameters, while the interaction of soil tillage and the N rate was significant for majority of the tested parameters, but not for the GSH, phenols and Phy content. Results obtained by Wasaya et al. [46], proved that interactions between deeper soil tillage and a higher N level did not significantly affect either yield or the contents of oil, protein and starch in maize grain. In this research, it was demonstrated that lower N inputs and lesser intensive tillage (T1 and T2) were more important for the accumulation of starch, oil, and P_i in grain. Wasaya et al. [46] also reported that the higher N uptake and protein accumulation in maize grain were recorded with the N rate increase of up to 200 kg N ha^{-1}, while the contents of starch and oil had an opposite trend: they were higher with a lower N supply (100 kg N ha^{-1}). Nevertheless, the content of phytate, GSH and carotenoids increased with soil tillage intensification and the application of higher N rates. Considering GSH and carotenoids as important nutrients, it is desirable to produce maize grain with the higher concentration of carotenoids, especially β-carotene-pro-vitamin A, as well as GSH [26,53]. Irrespective of the fact that phytic acid is generally considered an anti-nutrient, it also has an important role as an antioxidant and could serve in the prevention and treatment of some chronic diseases [54], thus its moderate level could be important from a nutritional standpoint.

5. Conclusions

According to the obtained results, deep soil tillage and the increased N rate can contribute to the higher maize GY, especially in seasons with favourable growing conditions. The highest GY was established in the conventional system of tillage at all three levels of N application—8.67, 9.34 and 9.57 t ha^{-1}. The interaction of these two factors is especially significant for the increased content of proteins, starch and total carotenoids, which are very important nutritional components. High levels of oil, tocopherols, and phenols are inversely proportional to GY, which means that even in stressful agro-meteorological conditions and reduced yields, high nutritional quality, from the perspective of total tocopherol and oil, could be achieved. According to the PCA analysis, the content of proteins, carotenoids, GSH and Phy were positively and significantly correlated with GY in all tested tillage systems and N rates. The medium and high supply of soil with macronutrients, together with conventional tillage, is the optimal strategy for the achievement of high and nutritionally valuable maize yield on arable areas in Serbia and South East Europe, thus contributing to the increase in maize production usability.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4395/10/7/976/s1, Table S1: Correlation coefficients for interaction between GY and quality parameters of maize grown in different tillage systems and fertilizer regimes, Table S3: The average GY and quality parameters of maize grain in different

years and soil tillage systems, Table S4: The average GY and quality parameters of maize grain in different years and fertilizer rates.

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