



Article

Maize Grain Composition with Additions of NPK Briquette and Organically Enhanced N Fertilizer

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Abstract: NPK fertilizer briquettes (NPKBriq) and organically enhanced N fertilizer (OENF), as newly developed fertilizer products, are reported to increase maize (*Zea mays* L.) yield and N use efficiency, but their effects on maize grain composition are unknown. The objective of this study was to determine the effects of NPKBriq and OENF on the protein, oil, fiber, ash, and starch of maize grain. A field study was conducted at Jackson and Grand Junction, TN, during 2012 and 2013, with NPKBriq, OENF, ammonium sulfate ((NH₄)₂SO₄) (+P and K), and urea (+P and K) as the main treatments and 0, 85, 128, and 170 kg N ha⁻¹ as the sub treatments under a randomized complete block split plot design with four replicates. The fiber concentration was more responsive to the fertilizer source than the protein, oil, ash, and starch concentrations. OENF resulted in a higher fiber concentration than NPKBriq at 85 kg N ha⁻¹ in 2013, averaged over the two sites. Both OENF and NPKBriq had nearly no significant effects on the concentrations of the quality attributes compared with ammonium sulfate and urea. In conclusion, the nutrient-balanced NPKBriq exerts the same or greater effects on maize grain quality relative to the commonly used nutrient management practices of urea (+P and K) and ammonium sulfate (+P and K) under normal weather conditions. OENF is an alternate N source to urea and ammonium sulfate for similar to higher maize grain quality.

Keywords: protein; oil; fiber; ash; starch; NPK briquette; organically enhanced N fertilizer; nitrogen; *Zea mays* L.

1. Introduction

Maize (*Zea mays* L.) is one of the most important cereal crops in the human diet and an important feed source for livestock in large parts of the world, and global maize production exceeds 600 million metric tons per year [1]. Both maize grain and stalks can also be used as raw material to produce biofuel and biogas [2]. The United States of America produces 42% of maize yield and is the largest maize production country in the world [3].

The high yield potential of maize results in large requirements of nutrients, particularly for N. Nitrogen is often the most limiting factor in maize production. Appropriate N management (source, rate, timing, and placement) can improve maize yield. Abbasi et al. found that maize yield was significantly affected by the N fertilizer source [4]. Szulc et al. also reported that the N fertilizer source exerted significant effects on the maize yield [5]. Presently, urea and ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ are commonly used commercial N fertilizers, but their use efficiencies are low in maize production, resulting in a low yield and environmental pollution. Therefore, the development of innovative alternate N fertilizers with high use efficiency potentials is warranted for higher maize productivity, quality, and profitability and a healthier environment.

NPKBriq of large-sized super granules is an alternate N source, supplying N along with P and K with a goal of increasing the N, P, and K use efficiencies. NPKBriq is manufactured via the physical manipulation of the current commercially available prilled and granular N, P, and K fertilizers [6–13]. It is entirely mineral and supplies N, P, and K nutrients in a ratio that fits the targeted crop and soil [14]. This kind of NPKBriq fertilizer product, therefore, allows for nutrient-balanced site-specific fertilization in order to reduce nutrient, particularly N, losses and save labor because of its single application relative to the two to three split applications of commonly used prilled and granular fertilizers. NPKBriq possesses less surface area and thus dissolves slower, releasing nutrients at a more moderate pace for a longer time, which eventually reduces nutrient losses, particularly N, and consequently protects water and air quality compared with the prilled and granular fertilizers [15].

Agyin-Birikorang et al. reported that NPKBriq increased maize yield by 16% compared with ammonium sulfate (+P and K) and by 23% to 34% relative to urea (+P and K) under normal weather conditions [14]; NPKBriq also resulted in higher N, P, and K use efficiencies. Rice yields were increased by 25% to 50% with the application of the fertilizer briquette compared with commercial granular fertilizer in Vietnam and Cambodia [7–9]. In Bangladesh, the rice yield was enhanced by 25–35%, while expenditure on commercial fertilizer was decreased by 24–32% when the fertilizer briquette was used [16,17]. The increased N-use efficiency with the fertilizer briquette implies lower N losses to water bodies and the atmosphere through leaching and volatilization [18].

Another innovative N fertilizer source under development is organically enhanced N fertilizer (OENF). It is manufactured via a patented and proprietary process using sterilized and chemically converted organic materials extracted from municipal waste water biosolids [19]. In addition to its environmental benefits of recycling municipal and domestic wastes, this product has the potential to reduce N losses and thus lower N consumption and mitigate negative impacts on water and air compared with commonly used N fertilizers [19,20].

Singh et al. reported that the concentration of nitrate was lower in soils with OENF addition relative to urea in incubation studies due to the significantly longer lag phase duration, which could result in better matching between the soil N supply and the crop N demand, thus reducing nitrate N losses. Furthermore, NH_3 -N volatilization losses were significantly lowered with OENF application [20]. Winings et al. found in field studies that, although less P was applied to OENF, the maize yield was significantly greater from OENF than urea at 170 kg N ha^{-1} under normal weather conditions [21]. However, there was no documentation in the literature on the effects of the NPKBriq or OENF on the crop grain quality.

Evaluations of NPKBriq's and OENF's effects on both the grain yield and the quality of maize are needed for the appropriate use of these innovative N fertilizer products. Although initial studies have shown that NPKBriq and OENF increase the maize yield and N-use efficiency relative to commonly used commercial fertilizers, their effects on maize grain composition are unknown. Thus, a field study was carried out to examine the effects of four N fertilizers (nutrient-balanced NPKBriq, OENF (+P and K), urea (+P and K), and ammonium sulfate (+P and K)) under different N application rates on the concentrations and yields of protein, oil, fiber, ash, and starch in maize grain under different production and environmental conditions and determine the correlations among these maize grain quality attributes.

2. Materials and Methods

2.1. Experimental Site and Soil

A field experiment was conducted at the University of Tennessee's Research and Education Center located at Jackson and Grand Junction, TN, USA, from 2012 through to 2013. The soil was classified as a Memphis silt loam at Jackson and Lexington silt loam at Grand Junction. The land at the Jackson site was under no-till management, while the site at Grand Junction was under a conventional plowing system. The major soil properties prior to the experiment were presented as follows: organic matter 18 g kg⁻¹, pH 6.9, P 29 mg kg⁻¹, and K 98 mg kg⁻¹ at Jackson, and organic matter 14 g kg⁻¹, pH 6.9, P 12 mg kg⁻¹, and K 76 mg kg⁻¹ at Grand Junction. The soil available nutrients were extracted with Mehlich3 [22].

2.2. Experimental Design and Sample Analysis

In total, 16 treatments repeated four times were implemented in a randomized complete block split-plot design. The N fertilizers were the main plots, and the N application rates were the subplots. The N fertilizers used in this study included ammonium sulfate ((NH₄)₂SO₄, 21% N, 24% S), urea (46% N), NPKBriq (23.9% N, 19.2% P₂O₅, 19.1% K₂O, 0.9% Zn, and 2.5% S), and OENF (14.9% N, 4.3% P₂O₅, 18.1% S, 0.6% Fe, and approximately 8% organic C). The N application rates of 0, 85, 128, and 170 kg N ha⁻¹ were used at both sites in each year. The maize cultivar Dekalb 6483 was planted in 76.2 cm rows at a seeding rate of 79,000 plants ha⁻¹ at both sites each year. The Jackson trial was planted in eight-row plots, and the plots were 9.1 m in length and 6.1 m in width. The Grand Junction trial was planted in six-row plots, with a plot size of 9.1 m long by 4.6 m wide. At Jackson, the maize was planted on 18 April 2012 and 17 April 2013. At Grand Junction, the maize was seeded on 19 April in 2012 and 29 May in 2013.

A systems approach was used to compare the N fertilizers in this study. The entire NPKBriq, OENF, and ammonium sulfate were applied basally after maize planting but before the emergence of the seedlings. In the urea treatment, only one third of each N rate was applied basally; the other two thirds were applied as two equal splits at the six leaf-collar growth stage (V6) and tasseling (VT) to avoid excessive N losses. The basal application of ammonium sulfate and three split applications of urea mimicked the common N management practices used in many countries. All four N fertilizers were surface applied. Phosphorus, K, and Zn were all applied at the following uniform rates across all treatments: 45 kg P ha⁻¹, 85 kg K ha⁻¹, and 5 kg Zn ha⁻¹. The phosphorus was applied as triple super phosphate (TSP, 0–45–0). The OENF contained P (4.3% P₂O₅), so at the 85, 128, and 170 kg N ha⁻¹ rates, it supplied 23.8%, 35.8%, 47.6%, and 71.4% of the uniform P rate, respectively. Therefore, only the additional TSP to meet the uniform P rate was applied in these treatments. Potassium and Zn were applied as KCl (0–0–60) and ZnSO₄ (35.5% Zn, 17.5% S) for ammonium sulfate, urea, and OENF treatments. All the plots received a low amount of S application from the zinc fertilizer source (ZnSO₄) regardless of the N fertilizer source; however, since OENF and ammonium sulfate contained S (18% and 24%, respectively) while NPKBriq and urea did not contain any S, the plots under the OENF and ammonium sulfate treatments received a much higher S application in total at the same N rate, except for 0 kg N ha⁻¹. Overall, the actual treatment effects of the fertilizer source in this study included the effects of not only the N source but also the S nutrient and N application timing, etc. More details about the treatments are available in Agyin-Birikorang et al., Winings (2014), and Winings et al. (2017) [14,21,23].

The briquettes were unique in that they were manufactured from already commercially available fertilizers through a fertilizer briquetter machine developed by the International Fertilizer Development Center (IFDC). The briquetter machine allows the manufacturer to manipulate a fertilizer's guaranteed analysis to suit specific needs. In the case of this study, the briquettes were created by the IFDC and contained the appropriate mixture of nutrients so as to supply all the P, K, and Zn uniform rates while also applying the different N application rates according to the subplot treatment requirements. The S

rate supplied from the briquettes was $2.46 \text{ kg S ha}^{-1}$ at N rates above 0 kg N ha^{-1} . This occurred because the S in the briquettes was supplied by ZnSO_4 (17.5% S). The N, P, K, and Zn mineral sources used in the briquettes were urea, diammonium phosphate, potassium chloride, and zinc sulfate.

The protein, oil, fiber, ash, and starch concentrations in maize grain were determined with a near-infrared reflectance diode array feed analyzer (Pertec, Springfield, IL, USA), and the results were reported on the basis of the dry matter of grain, which was the constant dry weight at 65°C . The analytical methods used in this study were identical to those in Reddy et al. [24]. The yields of protein, oil, fiber, ash, and starch were calculated as the products of the grain yield multiplied by the concentrations of the protein, oil, fiber, ash, and starch in grain, respectively.

2.3. Statistical Analyses

An analysis of variance was conducted for each measurement combined across all the site-years with the Proc Mixed Model in SAS version 9.4 (SAS Institute, Cary, NC, USA). The two sites and two years (whole plot factors), four N fertilizers (sub-plot factor), four N application rates (sub-sub-plot factor), and all interactions were treated as fixed effects, while replicates within the site and year were treated as random factors in the model. The treatment means were separated with the Tukey test if the F test for the measurement was significant. The Pearson product-moment correlation coefficients were calculated among the concentrations of the grain quality attributes with the Proc CORR procedure of the SAS package. Probability values less than 0.05 for all analyses were designated as significant in this study.

3. Results and Discussions

We only present and discuss some important and significant effects of N fertilizer source and the significant interactions of the N fertilizer source with the N rate, site, and/or year because the emphasis of this study was on the performances of N fertilizers under different N rates, sites, and years, as stated in the objectives. In this way, the results and discussion are better condensed and focused.

3.1. Effects of N Fertilizer Source on Protein, Oil, Fiber, Ash, and Starch Concentrations

3.1.1. Protein

The interactions of year \times fertilizer source, site \times N rate \times fertilizer source, and year \times N rate \times fertilizer source were all significant in the protein concentration (Table 1). However, no significant difference in protein level was observed among the four fertilizers in the above-mentioned interactions according to the Tukey test.

3.1.2. Fiber

The interactive effect of N rate \times fertilizer source showed that the OENF resulted in a 21.6% higher fiber concentration than the NPKBriq at 85 kg N ha^{-1} , but no difference in fiber was observed among the four fertilizers at any other N rate, averaged over all the site-years (Figure 1). According to the interaction of site \times fertilizer source, the fiber level was 16.3% higher with the OENF than with the NPKBriq at Jackson, but it did not differ among the fertilizers at Grand Junction in the averages of the N rates and years (Figure 2). The interactive effect of year \times fertilizer source revealed that the fiber concentration did not differ among the fertilizers in 2012; while in 2013, the OENF resulted in a 15.1% higher fiber concentration than NPKBriq, averaged over the N rates and sites (Figure 3). The interactive effect of year \times N rate \times fertilizer source showed that the fiber concentration was not different among the four fertilizers at any N rate in 2012; however, it was 29.3% and 35.0% higher with the OENF than urea and NPKBriq, respectively, at 85 kg N ha^{-1} in 2013 (Table 2).

Overall, both the OENF and NPKBriq showed nearly no positive or negative effects on protein, oil, fiber, ash, or starch concentration compared with the commonly used commercial fertilizers, ammonium sulfate (+P and K) and urea (+P and K). The OENF and NPKBriq were generally comparable in terms

of the concentrations of the grain quality attributes, except that OENF sometimes was superior to NPKBriq in increasing the fiber concentration.

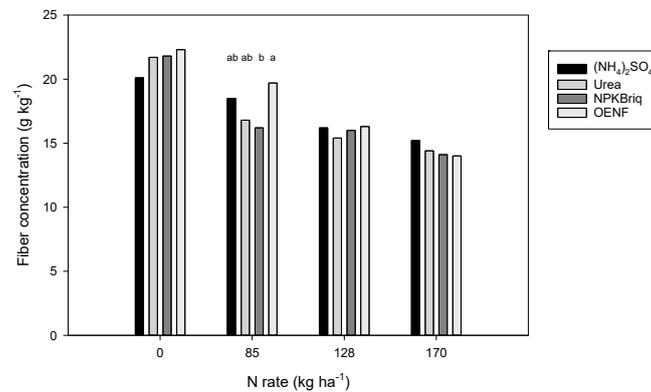


Figure 1. Fiber concentrations under different fertilizers and N rates averaged over the sites and years. NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values without any same letter among the fertilizers at the same N rate are significantly different at $p < 0.05$; values with no letter among the fertilizers at the same N rate indicate no significant difference at $p < 0.05$.

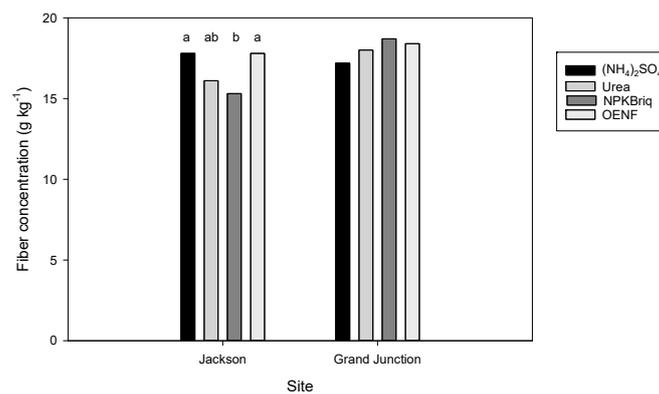


Figure 2. Fiber concentrations under different fertilizers and sites averaged over the N rates and years. NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values without any same letter among the fertilizers at the same site are significantly different at $p < 0.05$; values with no letter among the fertilizers at the same site indicate no significant difference at $p < 0.05$.

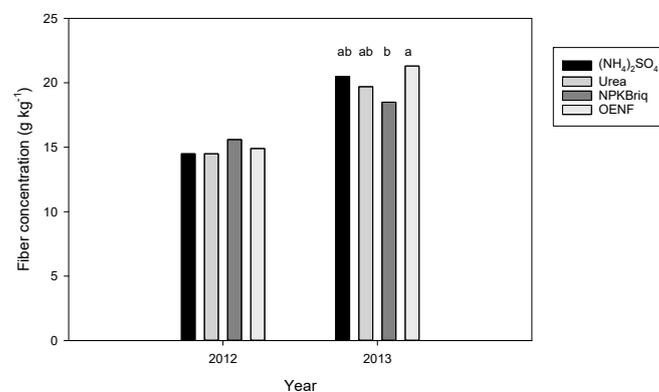


Figure 3. Fiber concentrations under different fertilizers and years averaged over the N rates and sites. NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values without any same letter among the fertilizers in the same year are significantly different at $p < 0.05$; values with no letter among the fertilizers in the same year indicate no significant difference at $p < 0.05$.

Table 1. Significance of the effects of the fertilizer source (F), N rate (N), site (St), year (Yr), and their interactions on the maize grain quality attributes.

Effect	DF	g kg ⁻¹				kg ha ⁻¹					
		Protein	Oil	Fiber	Ash	Starch	Protein	Oil	Fiber	Ash	Starch
St	1	***	*	**	ns	ns	*	ns	ns	ns	ns
Yr	1	***	ns	***	ns	***	***	***	***	***	***
St × Yr	1	***	ns	***	***	ns	ns	ns	**	ns	ns
F	3	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
St × F	3	ns	ns	**	ns	ns	ns	*	ns	ns	ns
Yr × F	3	**	ns	**	ns	ns	**	*	ns	*	*
St × Yr × F	3	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
N	3	***	ns	***	***	*	***	***	***	***	***
St × N	3	*	ns	***	***	***	**	*	***	***	***
Yr × N	3	***	ns	ns	**	***	***	***	***	***	***
St × Yr × N	3	ns	ns	***	ns	***	***	***	**	***	***
F × N	9	ns	ns	*	ns	ns	*	**	*	*	**
St × F × N	9	*	ns	*	ns	ns	ns	ns	***	ns	ns
Yr × F × N	9	***	ns	*	ns	ns	**	**	**	**	***
St × Yr × F × N	9	ns	ns	ns	ns	ns	ns	*	ns	ns	ns

DF, degree of freedom; *, significant at the 0.05 probability level; **, significant at the 0.01 probability level; ***, significant at the 0.001 probability level; ns, not significant at the 0.05 probability level.

Table 2. Fiber concentrations with different fertilizers, N rates, and years averaged over the sites.

Year	N Rate	(NH ₄) ₂ SO ₄	Urea	NPKBriq	OENF
2012	0	17.4a	19.4a	18.8a	19.8a
	85	15.3a	14.8a	14.4a	15.1a
	128	13.0a	12.6a	15.1a	13.0a
	170	12.3a	11.1a	14.0a	11.6a
2013	0	22.9a	24.0a	24.8a	24.8a
	85	21.8ab	18.8b	18.0b	24.3a
	128	19.4a	18.1a	16.9a	19.6a
	170	18.1a	17.8a	14.3a	16.4a

NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values without any same letter among the fertilizers at the same N rate in a year are significantly different at $p < 0.05$.

The higher fiber concentration with OENF than NPKBriq might have related to the following mechanism. Because OENF contained 18.1% S while there was no S in the NPKBriq product, the plots under OENF received much higher amounts of applied S than those with NPKBriq at the same N rate, except for 0 kg N ha⁻¹. Since the soils were tested low in available S (6.1 to 7.7 mg kg⁻¹) at both sites [23] and S is an essential component in enzyme synthesis, more enzymes that are responsible for fiber synthesis were synthesized under OENF than NPKBriq. Thus, a higher fiber concentration with OENF was observed.

The 2013 weather conditions were normal and favorable for maize production, with adequate rainfall during the growing season at both Jackson and Grand Junction (Figure 4, Supplemental Table S1). On the other hand, the weather conditions in the 2012 growing season were unfavorable for maize production, with two dry spells occurring. In our study, the protein concentration was higher but the fiber concentration lower in the dry year, 2012, than in the normal year, 2013, regardless of treatment at both sites. These results are in agreement with those of Zaidi et al., in that the protein concentration was higher under a drier climate [25].

There is controversy about the effect of the N fertilizer source on the maize grain quality. Some studies revealed that the N source had no marked effect on the protein, oil, or ash concentration of maize grain [26,27]. However, other investigations demonstrated that the N source significantly influenced the maize grain quality [28,29]. In this study, the effect of the N fertilizer source was significant on the fiber concentration only, and this effect was influenced by the N application rate, site, and year, which partially explained why the contradicting results were reported in the literature about the N source effect on maize grain quality. On the contrary, the protein, oil, ash, and starch

concentrations were not affected by the N fertilizer source, regardless of the N rate, site, and year. Our results suggest that fiber concentration is more responsive to the N fertilizer source than protein, oil, ash, and starch concentrations.

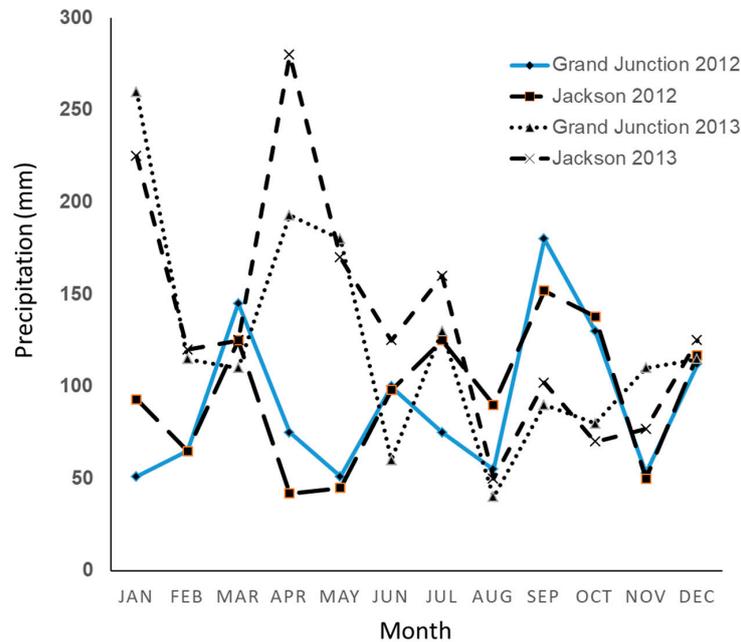


Figure 4. Average monthly precipitation at Jackson and Grand Junction during the growing season of 2012 and 2013.

3.2. Effects of N Fertilizer Source on Protein, Oil, Fiber, Ash, and Starch Yields

3.2.1. Protein

The interactive effect of year × N rate × fertilizer source revealed that protein yield was not different among the fertilizers at any N rate in 2012; however, the NPKBriq resulted in a higher protein yield than (NH₄)₂SO₄ and OENF at 85 kg N ha⁻¹ and urea at 170 kg N ha⁻¹ in 2013 (Table 3).

Table 3. Protein, oil, ash, and starch yields under different fertilizers, N rates, and years averaged over the sites.

Year	N Rate	Fertilizer	Protein kg ha ⁻¹	Oil kg ha ⁻¹	Ash kg ha ⁻¹	Starch kg ha ⁻¹
2012	0	(NH ₄) ₂ SO ₄	161.3a	79.7a	26.6a	1371.8a
		Urea	150.8a	75.1a	25.4a	1305.4a
		NPKBriq	135.5a	60.8a	21.1a	1077.5a
		OENF	136.4a	66.5a	23.4a	1200.2a
	85	(NH ₄) ₂ SO ₄	299.2a	130.7a	43.1a	2229.2a
		Urea	359.6a	158.9a	53.9a	2760.6a
		NPKBriq	339.7a	157.7a	50.9a	2651.7a
		OENF	373.3a	163.2a	55.8a	2958.8a
	128	(NH ₄) ₂ SO ₄	322.2a	141.1a	45.4a	2363.3a
		Urea	443.8a	184.9a	61.7a	3257.7a
		NPKBriq	364.1a	162.3a	54.5a	2878.2a
		OENF	395.3a	164.6a	54.3a	2932.9a
	170	(NH ₄) ₂ SO ₄	397.4a	145.5a	49.2a	2669.2a
		Urea	492.4a	198.5a	65.5a	3508.2a
		NPKBriq	449.1a	172.8a	60.1a	3280.2a
		OENF	428.0a	161.3a	55.2a	2953.7a

Table 3. Cont.

Year	N Rate	Fertilizer	Protein	Oil	Ash	Starch
2013	0	(NH ₄) ₂ SO ₄	149.4a	80.4a	26.4a	1432.1a
		Urea	170.4a	74.8a	27.2a	1483.3a
		NPKBriq	138.3a	74.4a	24.8a	1283.5a
		OENF	135.3a	70.4a	23.6a	1259.7a
	85	(NH ₄) ₂ SO ₄	405.6b	215.6b	75.5b	3982.0b
		Urea	433.7ab	245.7ab	80.9ab	4124.5b
		NPKBriq	584.8a	315.7a	101.1a	5340.1a
		OENF	428.2b	230.4b	78.8ab	4176.9ab
	128	(NH ₄) ₂ SO ₄	595.7a	288.3a	100.9a	5426.3a
		Urea	572.8a	306.9a	102.4a	5236.2a
		NPKBriq	697.7a	336.8a	116.3a	6076.1a
		OENF	587.5a	292.3a	102.7a	5628.7a
	170	(NH ₄) ₂ SO ₄	775.4ab	364.5ab	129.7a	6782.6a
		Urea	667.2b	296.9b	107.6a	5663.1a
		NPKBriq	838.9a	386.6a	132.1a	6814.0a
		OENF	771.5ab	371.9ab	128.2a	6801.5a

NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values in a column without any same letter among the fertilizers at the same N rate in a year are significantly different at $p < 0.05$.

3.2.2. Oil

The interaction of year \times N rate \times fertilizer source revealed that the oil yields were similar for the four fertilizers in 2012; however, the NPKBriq yielded a higher oil yield than (NH₄)₂SO₄ and OENF at 85 kg N ha⁻¹ and urea at 170 kg N ha⁻¹ in 2013 (Table 3).

3.2.3. Fiber

According to the interactive effect of site \times year \times N rate \times fertilizer source, the fiber yield did not differ among the N fertilizers at any N rate at Jackson in 2012 or at Grand Junction in either year; however, the NPKBriq produced less fiber than (NH₄)₂SO₄ and OENF at 170 kg N ha⁻¹ at Jackson in 2013 (Table 4).

Table 4. Fiber yield under different fertilizers, N rates, years, and sites.

Site	Year	N Rate	(NH ₄) ₂ SO ₄ Urea NPKBriq OENF			
			kg ha ⁻¹			
Jackson	2012	0	22.3a	20.6a	18.0a	22.0a
		85	62.9a	50.5a	43.2a	61.4a
		128	44.4a	66.4a	53.9a	49.5a
		170	50.6a	49.8a	51.2a	54.6a
	2013	0	63.9a	60.2a	53.2a	59.2a
		85	142.4a	116.2a	161.4a	139.4a
		128	192.9a	154.2a	160.0a	181.2a
		170	218.7a	157.9ab	142.1b	211.1a
Grand Junction	2012	0	56.4a	65.5a	46.5a	53.7a
		85	47.7a	79.3a	75.1a	78.4a
		128	50.3a	63.9a	89.0a	71.2a
		170	55.3a	75.6a	94.7a	55.6a
	2013	0	31.3a	43.8a	41.1a	33.5a
		85	125.8a	125.0a	142.2a	178.1a
		128	128.7a	138.0a	158.4a	160.0a
		170	161.6a	147.8a	160.5a	136.2a

NPKBriq, NPK fertilizer briquette; OENF, organically enhanced N fertilizer. Values without any same letter among the fertilizers at the same N rate in a year at a site are significantly different at $p < 0.05$.

3.2.4. Ash

According to the interactive effect of year \times N rate \times fertilizer source, ash yields were similar for the four fertilizers at each N rate in 2012; however, the NPKBriq produced more ash than $(\text{NH}_4)_2\text{SO}_4$ at 85 kg N ha⁻¹ in 2013 (Table 3).

3.2.5. Starch

The interactive effect of the year \times N rate \times fertilizer source showed that the four fertilizers produced similar starch yields at each N rate in 2012; however, the NPKBriq resulted in a higher starch yield than $(\text{NH}_4)_2\text{SO}_4$ and urea at 85 kg N ha⁻¹ in 2013 (Table 3).

Overall, the NPKBriq produced similar and sometimes higher protein, oil, ash, and starch yields compared with the commonly used commercial fertilizers, ammonium sulfate (+P and K) and urea (+P and K), depending on the N application rate and/or year in this study. This trend was mainly attributable to the fact that the NPKBriq produced a higher grain yield than the commonly used commercial fertilizers [14]. However, the fiber yield was mostly similar but occasionally lower at the highest N application rate with the NPKBriq relative to ammonium sulfate; this can likely be explained by the negative correlation between fiber and protein concentrations in maize grain [24].

The possible explanation for the higher oil, ash, and starch yields with the NPKBriq than urea in 2013 but not in 2012, averaged over the N rates and sites, was that the dry weather conditions in 2012 might have affected the dissolvment of the NPKBriq and thus its nutrient availability for plant uptake; in the 2013 growing season, there was plenty of rainfall for the NPKBriq to dissolve. Agyin-Birikorang et al. found that the NPKBriq increased maize yield by 16% compared with ammonium sulfate (+P and K) treatment and by 23% to 34% relative to urea (+P and K), and NPKBriq resulted in the highest fertilizer use efficiency in the 2013 growing season with normal weather conditions [14]. However, during the dry growing season of 2012, no significant difference was observed between the NPKBriq and the other N fertilizers in terms of the plant biomass, grain yield, or N-use efficiency. The results of Agyin-Birikorang et al. were obtained from the same field experiments where maize grain samples were collected for the analyses of quality attributes in this study [14]. Because the protein, oil, and starch concentrations did not respond to the N fertilizer source, the higher oil, ash, and starch yields with the NPKBriq than urea in 2013 resulted from the higher grain yield under the NPKBriq.

OENF mostly produced similar and occasionally higher protein, oil, fiber ash, and starch yields compared with the commonly used fertilizers ammonium sulfate (+P and K) and urea (+P and K) in this study, which coincided with the trends of grain yield. Winings et al. (2017) reported that the maize yield with OENF was similar to those using ammonium sulfate (+P and K) and urea (+P and K), at the N rate of 128 kg N ha⁻¹, but significantly greater than urea at 170 kg N ha⁻¹ in the 2013 growing season with normal weather conditions in the same experiments as we used for this study. However, the differences in grain yield were not significant between the OENF and ammonium sulfate and urea in 2012, a dry year. Obviously, our results confirmed that none of the protein, oil, fiber, ash, and starch yields were negatively influenced by the OENF, because neither the concentrations of these quality attributes nor the grain yield were negatively affected by the OENF relative to the commonly used commercial fertilizers.

As mentioned above, the OENF produced a similar and occasionally higher maize grain quality in terms of the concentrations and yields of the grain quality attributes relative to ammonium sulfate and urea. Furthermore, it decreased the soil N losses [20], reduced the P uses, recycled municipal and domestic waste, and increased the maize yield at an appropriate N level [21]. Therefore, OENF can be an effective alternate N source to ammonium sulfate and urea for upland maize production in the future in terms of crop productivity and environmental health.

3.3. Correlations Among Protein, Oil, Fiber, Ash, and Starch Concentrations

Protein concentration was significantly and negatively correlated with fiber, ash, and starch concentrations when the data were pooled over the site-years (Table 5). Oil was positively associated with ash, but negatively related to starch. Both fiber and ash had negative correlations with starch. Similarly, Chaudhary et al. reported a significant negative correlation between the crude protein and crude fiber concentrations in maize grain [30]. Our results suggest that the simultaneous production of maize grains with high protein and high fiber concentrations or high oil and high starch concentrations might unlikely be realized.

Table 5. Correlations (Pearson product-moment correlation coefficient and significance) between protein, oil, fiber, ash, and starch concentrations (g kg^{-1}) with the combined data from the sites and years.

Quality	Oil	Fiber	Ash	Starch
Protein	−0.02 ns	−0.67 ***	−0.18 **	−0.30 ***
Oil		−0.10 ns	0.31 ***	−0.55 ***
Fiber			0.10 ns	−0.13 *
Ash				−0.16 *

*, significant at the 0.05 probability level; **, significant at the 0.01 probability level; ***, significant at the 0.001 probability level; ns, not significant at the 0.05 probability level.

4. Conclusions

Fiber concentration was more responsive to the N fertilizer source than the protein, oil, ash and starch concentrations. Both the OENF and the NPKBriq had nearly no positive or negative effects on any quality attribute concentration compared with the commonly used commercial fertilizers, ammonium sulfate (+P and K) and urea (+P and K). The OENF and NPKBriq were generally comparable in terms of the concentrations of the grain quality attributes, except that OENF was superior to NPKBriq in increasing the fiber concentration, at 85 kg N ha^{-1} in 2013 averaged over the two sites. The higher fiber concentration with OENF than with NPKBriq might have been attributable to the fact that more enzymes responsible for fiber synthesis were synthesized with OENF than with NPKBriq, which was caused by the higher S application with OENF. NPKBriq produced similar to higher protein, oil, ash, and starch yields but similar to lower fiber yields relative to ammonium sulfate and urea. OENF produced similar to higher protein, oil, fiber, ash, and starch yields compared with the commonly used fertilizers. The higher yields of protein, oil, ash, and starch with NPKBriq and OENF were mainly the result of the higher grain yield. The impacts of the N fertilizer source on the concentration of fiber and yields of protein, oil, fiber, ash, and starch were more frequently affected by the N application rate and year but less often influenced by the site.

Based on the results of this study, we conclude that the nutrient-balanced NPKBriq could be the same as or more effective and efficient for maize grain quality relative to the commonly used nutrient management practices, urea (+P and K) and ammonium sulfate (+P and K), under normal weather conditions. The OENF could be an alternate N source to urea (+P and K) and ammonium sulfate (+P and K) for similar to higher maize grain quality; it also provides S, Fe, and some or all of the P requirements for crop production, and has additional environmental benefits such as recycling municipal and domestic waste.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/10/6/852/s1>, Table S1: Average monthly air temperature ($^{\circ}\text{C}$) at Jackson and Grand Junction during the growing season of 2012 and 2013.

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References

1. Tadesse, A.; Kim, H.K. Yield related traits and yield of quality protein maize (*Zea mays* L.) affected by nitrogen levels to achieve maximum yield in the central Rift Valley of Ethiopia. *J. Biol. Agric. Healthc.* **2015**, *5*, 2224–3208.
2. Zhong, W.; Zhang, Z.; Luo, Y.; Sun, S.; Qiao, W.; Xiao, M. Effect of biological pretreatments in enhancing corn straw biogas production. *Bioresour. Technol.* **2011**, *102*, 11177–11182. [[CrossRef](#)] [[PubMed](#)]
3. FAOSTAT (Food and Agriculture Organization of the United Nations). Statistics Division. Available online: <http://www.fao.org/faostat/en/#data/QC> (accessed on 13 May 2014).
4. Abbasi, M.K.; Tahir, M.M.; Rahim, N. Effect of N fertilizer source and timing on yield and N use efficiency of rainfed maize (*Zea mays* L.) in Kashmir–Pakistan. *Geoderma* **2013**, *195*, 87–93. [[CrossRef](#)]
5. Szulc, P.; Bocianowski, J.; Kruczek, A.; Szymanska, G.; Roszkiewicz, R. Response of two cultivar types of maize (*Zea mays* L.) expressed in protein content and its yield to varied soil resources of N and Mg and a form of nitrogen fertilizer. *Pol. J. Environ. Stud.* **2013**, *22*, 1845–1853.
6. Bautista, E.U.; Koike, M.; Suministrado, D.C. Mechanical deep placement of nitrogen in wetland rice. *J. Agric. Eng. Res.* **2001**, *78*, 333–346. [[CrossRef](#)]
7. IFDC (International Fertilizer Development Center) Fertilizer Deep Placement. *Mitigating Poverty and Environmental Degradation through Nutrient Management in South Asia*; IFDC: Muscle Shoals, AL, USA, March 2007.
8. IFDC (International Fertilizer Development Center) Fertilizer Deep Placement. *IFDC Solutions*; IFDC: Muscle Shoals, AL, USA. Available online: http://issuu.com/ifdcinfo/docs/fdp_8pg_final_web?e=1773260/1756718 (accessed on 22 May 2015).
9. IFDC (International Fertilizer Development Center). *IFDC Quarterly Magazine*; IFDC: Muscle Shoals, AL, USA. Available online: <http://ifdc.org/ifdc-magazine> (accessed on 15 March 2015).
10. Kapoor, V.; Singh, U.; Patil, S.K.; Magre, H.; Shrivastava, L.K.; Mishra, V.N.; Das, R.O.; Samadhiya, V.K.; Sanabria, J.; Diamond, R. Rice growth, grain yield and floodwater nutrient dynamics as affected by nutrient placement method and rate. *Agron. J.* **2008**, *100*, 526–536. [[CrossRef](#)]
11. Islam, M.S.; Rahman, F.; Hossain, A. Effects of NPK Briquette on Rice (*Oryza sativa*) in Tidal Flooded Ecosystem. *Agriculturalists* **2011**, *9*, 37–43. [[CrossRef](#)]
12. Bandaogo, A.; Fofana, B.; Youl, S.; Safo, E.; Abaidoo, R.C.; Andrews, O. Effect of fertilizer deep placement with urea supergranule on nitrogen use efficiency of irrigated rice in Sourou Valley (Burkina Faso). *Nutr. Cycl. Agroecosyst.* **2014**, *102*, 79–89. [[CrossRef](#)]
13. Miah, A.M.; Gaihre, Y.K.; Hunter, G.; Singh, U.; Hossain, S.A. Fertilizer Deep Placement Increases Rice Production: Evidence from Farmers' Fields in Southern Bangladesh. *Agron. J.* **2016**, *108*, 805–812. [[CrossRef](#)]
14. Agyin-Birikorang, S.; Winings, J.H.; Yin, X.H.; Singh, U.; Sanabria, J. Field evaluation of agronomic effectiveness of balanced-nutrient fertilizer briquettes for upland crop production. *Nutr. Cycl. Agroecosyst.* **2018**, *110*, 395–406. [[CrossRef](#)]
15. Savant, N.K.; Stangel, P.J. Deep placement of urea supergranules in transplanted rice: Principles and practices. *FeNutrti. Cycl. Agroecosyst.* **1990**, *25*, 1–83. [[CrossRef](#)]
16. Huda, A.; Gaihre, Y.K.; Islam, M.R.; Singh, U.; Islam, R.; Sanabria, J.; Satter, M.A.; Afroz, H.; Halder, A.; Jahiruddin, M. Floodwater ammonium, nitrogen use efficiency and rice yields with fertilizer deep placement and alternate wetting and drying under triple rice cropping systems. *Nutr. Cycl. Agroecosyst.* **2016**, *104*, 53–66. [[CrossRef](#)]
17. Gaihre, Y.K.; Singh, U.; Jahan, I.; Hunter, G. Improved nitrogen use efficiency in lowland rice fields for food security. *Fertil. Focus* **2017**, *4*, 48–51.

18. Gaihre, Y.K.; Singh, U.; Islam, S.M.; Huda, A.; Satter, M.A.; Sanabria, J.; Islam, R.; Shah, A. Impacts of urea deep placement on nitrous oxide and nitric oxide emissions from rice fields in Bangladesh. *Geoderma* **2015**, *6*, 370–379. [[CrossRef](#)]
19. NSF International. *NSF Protocol P353: Sewage Sludge Sterilization in Organically Enhanced Granular Fertilizer Production*; NSF International: Ann Arbor, MI, USA. Available online: www.nsf.org/business/engineering_and_research/protocols.asp?program=EngineeringSer (accessed on 30 August 2015).
20. Singh, U.; Sanabria, J.; Austin, E.R.; Agyin-Birikorang, S. Nitrogen transformation, ammonia volatilization loss, and nitrate leaching in organically enhanced nitrogen fertilizers relative to urea. *Soil Sci. Soc. Am. J.* **2012**, *76*, 1842–1854. [[CrossRef](#)]
21. Winings, J.H.; Yin, X.; Agyin-Birikorang, S.; Singh, U.; Sanabria, J.; Savoy, H.J.; Allen, F.L.; Saxton, A.M. Agronomic effectiveness of an organically enhanced nitrogen fertilizer. *Nutr. Cycl. Agroecosyst.* **2017**, *108*, 149–161. [[CrossRef](#)]
22. Mehlich, A. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [[CrossRef](#)]
23. Winings, J.H. Effects of Organically Enhanced Biofertilizer and Fertilizer Briquettes on Mineral Nutrition, Quality, and Yield of Corn and Soil Health. Master's Thesis, University of Tennessee, Knoxville, TN, USA, 2014.
24. Reddy, K.; Bellaloui, N.; Zablutowicz, R. Glyphosate Effect on Shikimate, Nitrate Reductase Activity, Yield, and Seed Composition in Corn. *J. Agric. Food Chem.* **2010**, *58*, 3646–3650. [[CrossRef](#)]
25. Zaidi, P.H.; Vasal, S.K.; Maniselvan, P.; Jha, G.C. Stability in performance of quality protein maize under abiotic stress. *Maydica* **2008**, *53*, 249–260.
26. Zhang, F.; Mackenzie, A.F.; Smith, D.L. Corn yield and shifts among corn quality constituents following applications of different nitrogen fertilizer sources at several times during corn development. *J. Plant Nutr.* **1993**, *16*, 1317–1337. [[CrossRef](#)]
27. Safdarian, M.; Razmjoo, J.; Dehnavi, M.M. Effect of nitrogen sources and rates on yield and quality of silage corn. *J. Plant Nutr.* **2014**, *37*, 611–617. [[CrossRef](#)]
28. Siam, H.S.; Mona, G.; Kader, A.E.; El-Alia, H.I. Yield and yield components of maize as affected by different sources and application rates of nitrogen fertilizer. *Res. J. Agric. Biol. Sci.* **2008**, *4*, 399–412.
29. Souza, J.A.; Buzetti, S.; Filho, M.C.M.T.; Moreira, A. Sources, Rates and Time of Nitrogen Application on Maize Crops under No-Tillage System. *Commun. Soil Sci. Plant Anal.* **2016**, *47*, 2200–2207. [[CrossRef](#)]
30. Chaudhary, D.P.; Kumar, A.; Kumar, R.; Singode, A.; Mukri, G.; Sah, R.P.; Tiwana, U.S.; Kumar, B. Evaluation of normal and specialty corn for fodder yield and quality traits. *Range Manag. Agrofor.* **2016**, *37*, 79–83.



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