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Value-Added Fertilizers Enhanced Growth, Yield and Nutrient Use Efficiency through Reduced Ammonia Volatilization Losses under Maize–Rice Cropping Cultivation

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Abstract: Plant nutrition is an essential element for crop production and enormous amounts of fertilizers are used in agricultural systems. However, these sources emit toxic gasses and compounds in the environment that not only deteriorate soil quality but also cause a reduction in the use efficiency of applied nutrients. Therefore, the value addition of these fertilizer sources by coating micronutrients, microbes, polymers or other organic and inorganic compounds have been advocated recently. The present study aimed to evaluate the effectiveness of value-added fertilizer sources for growth and yield improvement of *Zea mays* (Pioneer-30T60) and *Oryza sativa* (Super Basmati-515) with a reduction in ammonia volatilization and an improvement in nutrient recovery by crop grains. Different phosphorus (P), potassium (K) and nitrogen (N) fertilizer sources (Diammonium phosphate (DAP), polymer coated DAP, zarkhez plus NPK, urea, polymer-coated urea and zabardast urea) were used in different combinations keeping one control for N. The results revealed that maximum growth, yield and nutrient recovery was shown by polymer-coated urea and DAP followed by zarkhez plus NPK and zabardast urea. Moreover, a minimum ammonia emission was recorded by polymer-coated fertilizers, but other value-added fertilizers were found inefficient in reducing ammonia emission, though these sources improved all growth and yield attributes. Nutrient recovery efficiency was patterned as; polymer coated fertilizers > zarkhez plus NPK + zabardast urea > zarkhez plus NPK + urea > DAP + zabardast urea > DAP + urea > DAP. Thus, the use of polymer-coated fertilizers was beneficial for both the reduction in ammonia volatilization and for improving nutrient use efficiency with maximum crop benefits.

Keywords: nitrogen losses; ammonia emission; value-added fertilizers; polymer-coated fertilizers; *Zea mays*; *Oryza sativa*

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1. Introduction

Environmental problems are getting worse in the face of climate change. These problems are in the form of environmental degradation, environmental pollution, etc. Since it affects many forms of life, environmental pollution is easily the most difficult obstacle to overcome [1]. As the world's population rises, so does the pressure on farmers and food producers to keep up with rising demand [2]. To this end, the agricultural sector has used a massive amount of fertilizer to boost crop yields over the past few decades. There has been an annual increase in the need for nitrogen, phosphorus and potassium fertilizers of 1.9% since 2015 [3]. Nowadays, chemical fertilizers are used in all types of intensive farming [4,5], from field crops to vegetable gardens to ornamental and forestry nurseries. This is especially true in Pakistan, where the majority of crop production is dependent on chemical fertilizers.

N-containing fertilizers are the most widely used worldwide [6] due to nitrogen's crucial role in plant growth and development. The increasing use of fertilizers, however, has shown to have significant environmental consequences [7]. More than 40–70% of N fertilizers used are lost in the environment either through volatilization, denitrification or leaching of nitrates (NO_3^-), which further exacerbates groundwater contamination and the quality of surface water [8,9]. According to an estimate, the N consumed by the human body is only 14% in vegetarians and 4% in non-vegetarians right from the manufacturing of nitrogenous fertilizers (urea) to the food chain [10]. Low use efficiency and higher nutrient losses, especially N and P, lead to the overuse of N, P, and other fertilizers on agricultural lands to produce an optimum crop yield [11]. On the other hand, it results in significant losses of these elements due to runoff and the groundwater system. Eutrophication, a phenomenon known to have a detrimental influence on drinking water quality and treatment, animal and human health and the aquatic environment, is a consequence of this expansion of algae and aquatic plants in rivers and lakes, and is the outcome of overuse of fertilizers [12,13].

Over the past, slow-release fertilizers have been utilized to limit groundwater pollution, reduce GHGs emissions, and alleviate the consequences of climate change in a number of studies [14–16]. Most of these studies focus on fertilizer coatings made from materials that are costly and poisonous to soil microbes, such as sulphur, waxes, polyethylene, and synthetic polymers [17,18]. Plant polymers, on the other hand, have shown a more regulated release [17,19]. Using these polymers as a fertilizer coating is a better way to assure environmentally friendly agriculture [20]. In addition to ensuring better nutrient uptake by crops, value-added fertilizers also supply some essential nutrients, such as Zn and Fe. However, the findings concerning the application of value-added fertilizers and their pattern of release in soil are frequently ambiguous. For example, no environmental and agronomic benefits were achieved by fertilizer coating technologies for reducing nitrous oxide and ammonia emissions [21]. Moreover, coated fertilizers do not release nutrients according to the need of plants resulting in a stressful environment for plants [17].

Hence, there is an urgent need to examine the efficiency of these micronutrient rich fertilizers with polymer-coated fertilizers under different cropping conditions, as micronutrient efficiency could vary with a change in cultivation techniques [22]. To better use mineral nutrients and decrease N losses, this research aims to test a new generation of controlled-release fertilizers coated with novel biodegradable polymers. We took advantage by value adding different market-available N and P fertilizers and then comparing them with polymer-coated DAP and urea for growth improvement of cereal crops and reduction in ammonia volatilization. The specific objectives of this study were thus to (i) monitor the ammonia volatilization losses from polymer coated and other value-added fertilizers in rice and maize crops and (ii) check the impacts of these fertilizers on the crop growth, yield and nutrient-use efficiencies in rice and maize crops. We hypothesized that the application of value-added and polymer-coated fertilizers would result in a trade-off between nutrient use efficiencies and NH_3 volatilization, whereas their effects on crop performance may vary depending upon the type and release pattern of the applied fertilizers and soil condition.

2. Materials and Methods

2.1. Experimental Site and Layout

This research utilized two field experiments to assess the trade-off between crop yield and N losses, as well as the value-added effects of polymer and other coating materials on nutrient-use efficiencies in rice and maize crops. In the first trial, which started on 31 July 2021, rice was used as the test crop, and in the second trial, which started on 3 August 2021, maize was used as the test crop. Both experiments were conducted at the research area of the Institute of Soil and Environmental Sciences, University of Agriculture, Faisalabad, Punjab, Pakistan (situated at a latitude of 30°30′ and 32°0′ N and a longitude of 72°0′ and 73°45′ E) with the collaboration of Engro fertilizers (Pvt.) Ltd. The average temperatures during the crops' growth months of August, September, October and November were 35.6 °C, 35.2 °C, 32.6 °C and 26.6 °C, while the average precipitation was 115 mm, 65 mm, 16 mm and 8 mm, with a relative humidity of 65%, 59%, 50% and 50%, respectively. Fields were prepared with the help of a cultivator and a rotavator. Soil samples were taken from the field prior to the experiment using an auger at a depth of 12 inches for physiochemical analysis and analyzed for the following parameters. The soil texture was determined using the hydrometer method. The soil was sandy clay loam (plaggic), as it contained 49.03% sand, 27.40% silt, and 23.57% clay. The saturation percentage, organic matter contents, electrical conductivity of soil extract (ECe), hydrogen ion concentration of saturated soil paste (pHs) and cation exchange capacity (CEC) of this soil were 30%, 0.78%, 1.94 dS m^{-1}, 7.87 and 13.5 $cmol_c$ kg^{-1}, respectively. Meanwhile, the concentrations of Ca^{2+} + Mg^{2+}, SO_4^{2-}, Cl^{1-}, HCO_3^{1-}, CO_3^{2-}, and soluble Na^+ in the soil extract, which was obtained from saturated soil paste by using a suction pump, were 10.11 me L^{-1}, 9.86 me L^{-1}, 12.7 me L^{-1}, 2.49 me L^{-1}, 0.31 me L^{-1}, 16.86 me L^{-1}, respectively. Total N (Kjeldahl method), available P (Olsen method), and available K (Chapman and Parker method) were found to be 0.28%, 6.10 mg kg^{-1}, and 128 mg kg^{-1}, respectively.

The field experiments with rice and maize crops were arranged following a randomized complete block design (RCBD). There were a total of 18 plots for each experiment, conducted independently on a half-acre area with a size of 65 m^2 for each plot. The treatments described in (Table 1) were applied in three replications and compared for their effectiveness for both the crops. Seeds of the maize variety "Pioneer-30T60" were sown at the rate of 25 kg ha^{-1} on 3 August 2021, while seedlings of rice variety "Super Basmati-515" were transplanted to the study area on 31 July 2021. Rice seeds were sown for raising nursery at Rice Research Institute, Kala Shah Kaku using standard procedure, seedlings were brought to the study area for transplantation. Both the maize and rice trails were harvested in November of 2021. The maize trial was harvested on November 19th and the rice trial on 22 November.

Table 1. Treatment plan.

Treatment Code	Description	NPK Input
T1	Control (only DAP + MOP)	48 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}
T2	DAP + MOP + Urea	175 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}
T3	DAP + MOP + Zabardast urea	175 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}
T4	Zarkhez plus NPK + Urea	175 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}
T5	Zarkhez plus NPK + Zabardast urea	175 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}
* T6	Polymer coated DAP + Polymer-coated urea+ MOP	175 kg N ha^{-1}, 125 kg P_2O_5 ha^{-1}, 125 kg K_2O ha^{-1}

Here, * DAP, MOP and urea are conventional fertilizers; Zarkhez plus NPK, zabardast urea, polymer-coated urea and polymer-coated DAP are value-added fertilizers.

In both rice and maize fields, 600 mL/acre of Gengwei was applied as a pre-emergence herbicide. Carbofuran ($C_{12}H_{15}NO_3$), 3% G, 8 kg of Engro pesticide was used in combination with FMC Emamectin (200 mL/acre) and Jaffer Group of Companies Lufenuron (100 mL/acre) sprays to control insects; twice in the case of maize (for fall armyworm and shoot fly) and once in the case of rice to control stem borer and leaf miner during the whole growing season of both crops. The irrigation requirements of rice and maize were accomplished using canal water. Throughout the entire growing season, the rice crop received 16 irrigations and the maize crop received 12.

2.2. Ammonia Measurement

Static chambers were installed in the field to collect ammonia volatilized from the applied fertilizers. This collected ammonia was further trapped by 0.5 N sulfuric acid traps (5 mL placed in each chamber). Traps were changed regularly after 15 days and onward splits of N fertilizers were applied. The collected traps after 15 days were analyzed on Kjeldahl apparatus and titrated against 0.1 N sulfuric acid to get an estimate of ammonia volatilization. Ammonia emission was then measured through the following equation:

$$Ammonia\ (\%) = \frac{17 \times (Volume\ of\ acid\ used\ for\ sample - Volume\ of\ acid\ used\ for\ blank) * Normality\ of\ acid}{(Volume\ of\ sample\ used * 10)}$$

2.3. Chemical and Agronomic Analyses of Rice and Maize

Besides the measurement of ammonia emission, the growth and yield-related traits of both the crops were measured using standard procedures. In order to conduct the necessary chemical analysis (N, P, and K), after crop harvesting, root, shoot, and grain samples were collected, air-dried and ground. Following that, 54 pyriminx conical flasks of 100 mL were poured with 1 g of each plant part and wet-digested using the Wolf technique [23]. These digested samples were used to measure N, P and K using apparatus such as a Kjeldahl for N, a spectrophotometer for P, and a flame photometer for K analysis, in accordance with methods developed by [24–26], respectively. Agronomic and recovery N use efficiencies were calculated using equations used in [18].

$$Agronomic\ nitrogen\ use\ efficiency = \frac{Yield\ in\ N\ fertilized\ plot\ (kg\ ha^{-1}) - Yield\ in\ control\ plot\ (kg\ ha^{-1})}{Amount\ of\ N\ applied\ (kg\ N\ ha^{-1})}$$

$$Recovery\ nitrogen\ use\ efficiency = \frac{N\ uptake\ by\ fertilized\ grains - uptake\ by\ unfertilized\ grains}{Amount\ of\ N\ applied\ (kg\ N\ ha^{-1})}$$

$$N\ uptake\ by\ grains = \frac{N\ concentration\ in\ the\ grains \times Grain\ yield}{100}$$

2.4. Statistical Analysis

The collected data were analyzed using Statistics 8.1 software following Fisher's analysis of variance [27]. Treatment means were compared using the least significant difference (LSD) test. Correlation and principal component analysis (PCA) among treatments were drawn using R software. Excel and Prism were utilized for the regression analysis, and Prism was used for the plots of the agronomic, chemical, and physiological parameter values. Prism and Excel were used, respectively, to create graphs showing the agronomic N use efficiency and N recovery efficiency.

3. Results

3.1. Ammonia Volatilization from Value-Added and Conventional Fertilizers nder Maize and Rice

At the first interval, ammonia emission from DAP and zarkhez plus NPK was compared. It is clear from Figure 1A,B that ammonia emission was lower from zarkhez plus NPK treatments in comparison to the DAP treatments in both crops. From the second interval, ammonia emissions were representing emissions from urea and zabardast urea. While comparing value-added fertilizers with traditionally used DAP and urea, value-added fertilizers did not perform very efficiently in reducing ammonia losses except polymer-coated DAP and urea. In both the crops, polymer-coated fertilizers significantly reduced ammonia losses in comparison to all other amendments.

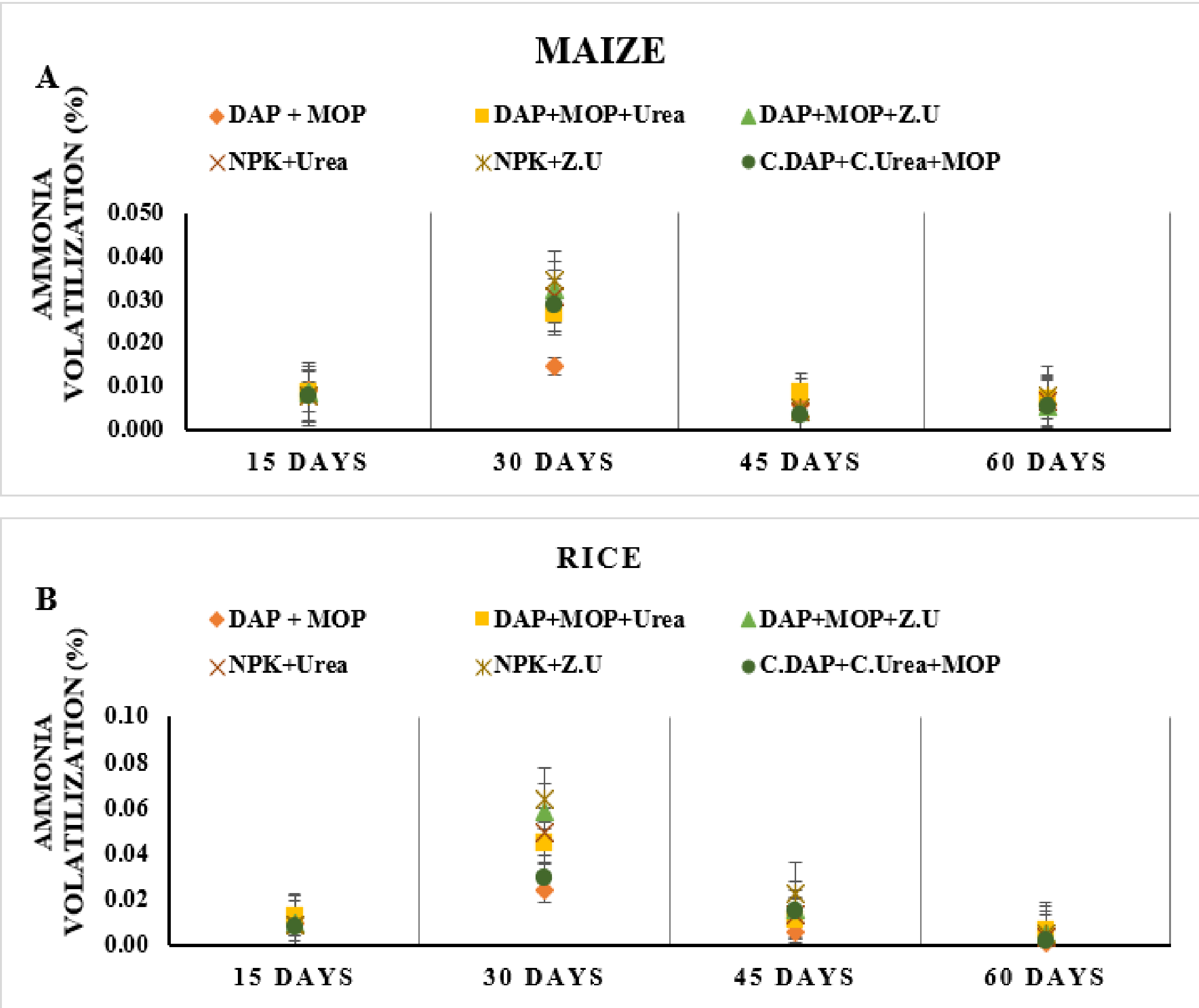

Figure 1. Ammonia volatilization from various value-added and conventional fertilizers under maize (**A**) and rice (**B**) at different intervals.

3.2. Morphological Traits of Maize and Rice

Polymer-coated urea and DAP outperformed all the treatments in both the crops for each morphological parameter (Table 2). The highest plant height was observed in the treatment where polymer-coated urea and DAP fertilizers were applied in both crops. The second-highest plant height in both crops was observed in the treatment where zarkhez plus NPK and zabardast urea fertilizers were applied in combination. The zabardast urea-treated plant also showed improvement in plant height when applied with DAP compared to urea when applied with DAP in both crops. While comparing the performance of zarkhez plus NPK and DAP, zarkhez plus NPK application gave better results. However, plant height was minimum where no urea or zabardast urea was applied (in control). In a similar manner, other morphological traits were also affected by the value-added fertilizers, as cob length, cob diameter and number of grains per cob in maize were improved with the use of zarkhez plus NPK in comparison to DAP; though the difference was small.

Table 2. Morphological traits of maize and rice under the influence of value-added and conventional fertilizers.

Treatment	Maize						Rice					
	Plant Height (cm)	Cob Length (cm)	Cob Diameter (cm)	Number of Grains per Cob	Root Weight (g)	Root Length (cm)	Plant Height (cm)	Panicle Length (cm)	Number of Panicles per Plant	Number of Grains per Panicle	Root Weight (g)	Root Length (cm)
DAP + MOP	148.7 c *	9.3 b	11.0 c	135 c	48.0 c	13.9 c	111.3 c	26.3 d	6.3 d	135.7 c	12.3 e	12.0 c
DAP + MOP + Urea	225.3 b	18.8 a	14.4 b	428 b	63.3 bc	24.2 b	124.3 b	28.0 c	10.7 c	156.0 bc	28.3 d	13.2 bc
DAP + MOP + Zabardast Urea	250.1 a	19.7 a	15.5 a	479 ab	63.3 bc	24.4 b	128.0 ab	28.7 bc	11.7 c	x156.3 bc	32.1 cd	13.7 bc
Zarkhez plus NPK + Urea	252.1 a	19.8 a	15.5 a	499 ab	110.0 ab	27.5 ab	133.7 a	29.3 b	12.7 bc	168.0 ab	37.0 bc	14.2 abc
Zarkhez plus NPK + Zabardast Urea	259.0 a	19.9 a	15.7 a	507 ab	126.7 a	27.5 ab	134.0 a	30.3 a	14.3 ab	179.7 ab	42.6 ab	15.0 ab
Coated DAP + Coated Urea + MOP	259.3 a	20.3 a	15.9 a	524 a	133.3 a	28.0 a	135.3 a	30.6 a	16.0 a	193.7 a	46.2 a	16.7 a

* Means sharing similar letter(s) do not differ significantly at a level of significance of $p < 5\%$.

Table 3. Yield parameters of maize and rice under the influence of value-added and conventional fertilizers.

Treatment	Maize				Rice			
	Biological Yield (kg ha^{-1})	Straw Yield (kg ha^{-1})	Grain Yield (kg ha^{-1})	1000-Grain Weight (g)	Biological Yield (kg ha^{-1})	Straw Yield(kg ha^{-1})	Grain Yield (kg ha^{-1})	1000-Grain Weight (g)
DAP + MOP	8006.2 d *	3657.2 d	3987.5 c	161.9 c	19,400.0 c	11,886.7 d	2696.4 d	12.6 c
DAP + MOP + Urea	14,936.1 c	7396.7 c	7431.7 b	232.7 b	24,833.3 bc	14,800.0 cd	3541.7 c	16.5 c
DAP + MOP + Zabardast Urea	19,702.5 b	9620.6 bc	8991.1 ab	233.3 b	25,900.0 abc	16,000.0 bcd	3720.2 bc	22.5 b
Zarkhez plus NPK + Urea	21,909.9 ab	11,712.8 ab	9032.4 ab	248.6 ab	27,580.0 ab	19,633.3 abc	4154.8 ab	24.1 ab
Zarkhez plus NPK + Zabardast Urea	22,404.2 ab	11,795.2 ab	9380.5 ab	253.2 ab	30,446.7 ab	21,300.0 ab	4297.6 a	25.8 ab
Coated DAP + Coated Urea + MOP	23,465.1 a	12,207.0 a	10,306.1 a	276.7 a	32,166.7 a	25,433.3 a	4452.4 a	26.5 a

* Means sharing similar letter(s) do not differ significantly at a level of significance of $p < 5\%$.

Similarly, the zabardast urea application improved cob length, cob diameter and number of grains per cob in comparison to urea in both the combinations. However, polymer-coated DAP and urea gave the highest cob length, cob diameter and number of grains per cob. An identical trend was seen for panicle length, number of panicles per plant and number of grains per panicle in case of rice. Root weight and root length were found minimum where no urea or zabardast urea was applied in both the crops. Urea improved root weight and root length significantly over control with both phosphatic fertilizer sources, but zarkhez plus NPK outperformed DAP. Zabardast urea further accelerated root weight and length over urea in both combinations, but the performance of polymer-coated urea and DAP again induced highest results.

3.3. Yield Attributes of Maize and Rice

In the control, where no additional N source was applied, the minimum biological yield, straw yield, grain yield, and 1000-grain weight were observed in the maize crop, demonstrating the significance of N (Table 3). Where N was applied along with DAP either as urea or zabardast urea, biological yield, straw yield, grain yield and 1000-grain weight of maize were significantly increased. Indeed, zabardast urea gave much better results than urea. Zarkhez plus NPK induced higher yield attributes than DAP with both N sources, however, zabardast urea outperformed urea. Moreover, polymer-coated urea and DAP gave highest biological yield, straw yield, grain yield and 1000-grain weight in maize.

Similar findings were seen in the case of rice, as the maximum biological yield, straw yield, grain yield and 1000-grain weight of rice were observed with polymer-coated DAP and urea. Zarkhez plus NPK with zabardast urea induced second-highest yield of rice. Urea applied with zarkhez plus NPK also gave higher yield attributes than DAP-treated plots. Among DAP-treated plots, the highest yield was observed where zabardast urea was applied followed by urea applied plots. However, the minimum biological yield, straw yield, grain yield and 1000-grain weight were observed where no urea or zabardast urea were applied.

3.4. Physiological Traits of Maize and Rice

As illustrated in (Figure 2A), the leaf area index of maize was abruptly increased with the application of N fertilizers over control. Moreover, the value-added N fertilizer (Zabardast urea and polymer coated urea) further enhanced the leaf area index. Zarkhez plus NPK as value-added P fertilizer also performed excellent over DAP with both urea and zabardast urea. However, Maximum leaf area index was produced by polymer-coated fertilizers. Chlorophyll contents (Figure 2B) also indicated the same influence for various fertilizers. The transpiration rate was not much affected by value-added fertilizers except for polymer-coated fertilizers, as polymer-coated fertilizers induced a significantly higher transpiration rate over all other treatments, but, all other treatments gave non-significant results among each other (Figure 2C). Figure 2D indicates that polymer-coated fertilizers induced a maximum photosynthesis rate in maize followed by zarkhez plus NPK along with zabardast urea. But in case of the DAP combination, a significantly lower photosynthesis rate was seen with zabardast urea over urea.

In case of rice, leaf area index and chlorophyll contents were affected by the value-added fertilizers in a just similar way by which influenced in case of maize (Figure 3A,B), as the minimum leaf area index and chlorophyll contents were observed in the control (where no urea or zabardast urea were applied), but with the application of N source, a significant improvement was witnessed. The value-added fertilizers such as zarkhez plus NPK and zabardast urea gave more promising results than the DAP and urea combination. However, the maximum leaf area index and chlorophyll contents were seen with polymer-coated fertilizers. In the case of transpiration rate (Figure 3C), zabardast urea does not perform very effectively, as it induced a lower transpiration rate than urea with both P sources. While zarkhez plus NPK significantly outperformed DAP, though polymer-coated DAP and urea gave a maximum transpiration rate. The photosynthesis rate was not much effected by value-added fertilizers, as only zarkhez plus NPK with zabardast urea and polymer-coated fertilizers induced a significantly higher photosynthesis rate than all other treatments. Other treatments gave non-significant results over each other except for control that induced minimum photosynthesis rate (Figure 3D).

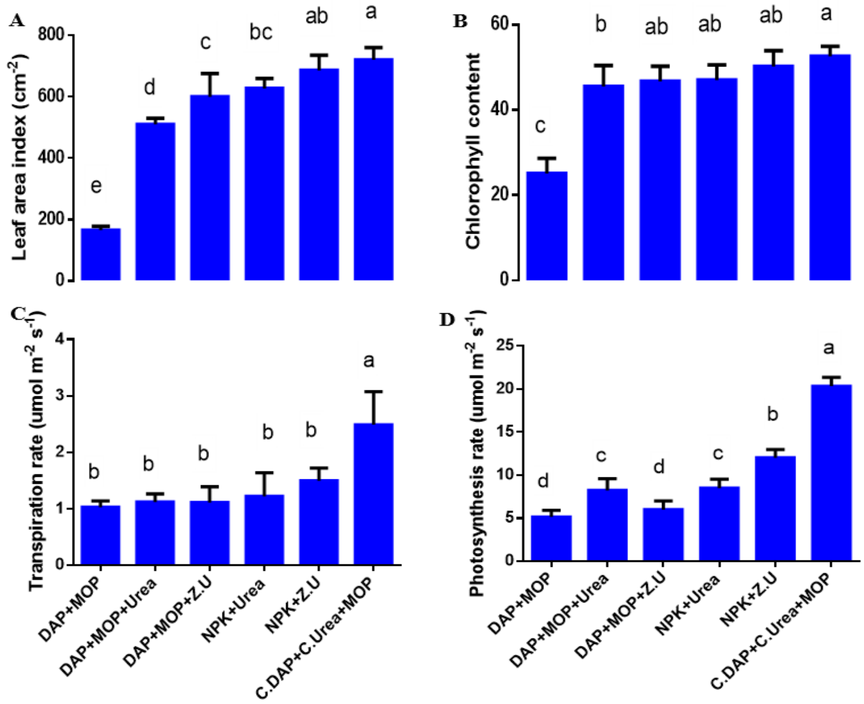

Figure 2. Impact of value-added and conventional fertilizers on physiological attributes ((**A**) Leaf area index, (**B**) Chlorophyll contents, (**C**) Transpiration rate, (**D**) Photosynthesis rate) of maize. Different letters indicate significant differences at a level of significance of $p < 5\%$.

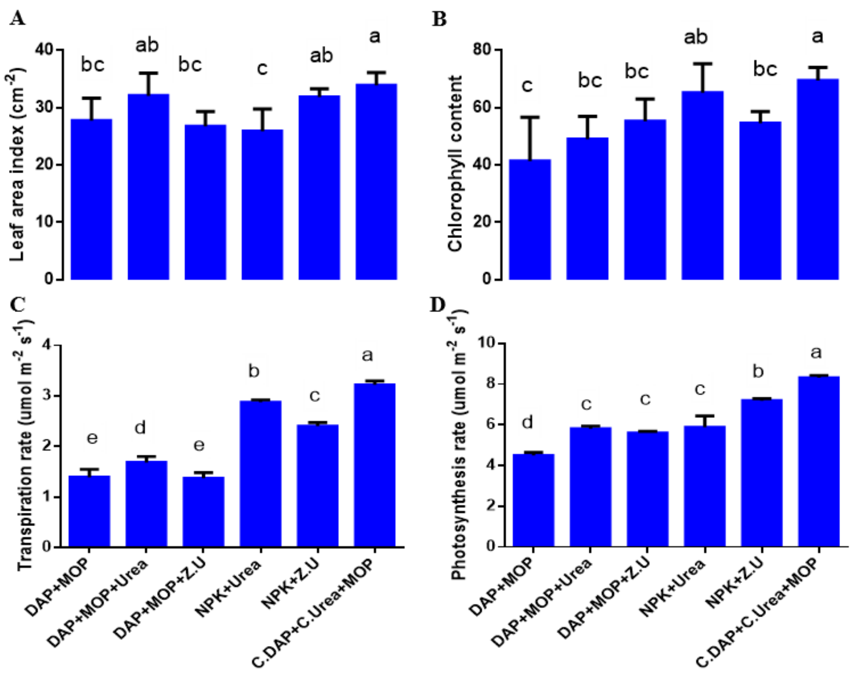

Figure 3. Impact of value-added and conventional fertilizers on physiological attributes ((**A**) Leaf area index, (**B**) Chlorophyll contents, (**C**) Transpiration rate, (**D**) Photosynthesis rate) of rice. Different letters indicate significant differences at a level of significance of $p < 5\%$.

3.5. N, P and K Concentrations in the Grains of Maize and Rice

Figure 4 illustrated the concentration of N, P and K in grains of both crops as influenced by value-added fertilizers. All three nutrients were found minimum in both crops treated with DAP and MOP only. However, with the addition of urea or zabardast urea in the combination, the concentration of N, P and K in grains of maize and rice were improved substantially. Zarkhez plus NPK also improved these concentrations in comparison with DAP, but the maximum improvement in primary macronutrient concentrations in maize and rice was seen with the use of polymer-coated DAP and urea. The N, P and K concentrations in maize grain are shown in Figure 4A–C, respectively, while the concentrations of N, P and K in rice grains were given in D, E and F parts of Figure 4, respectively.

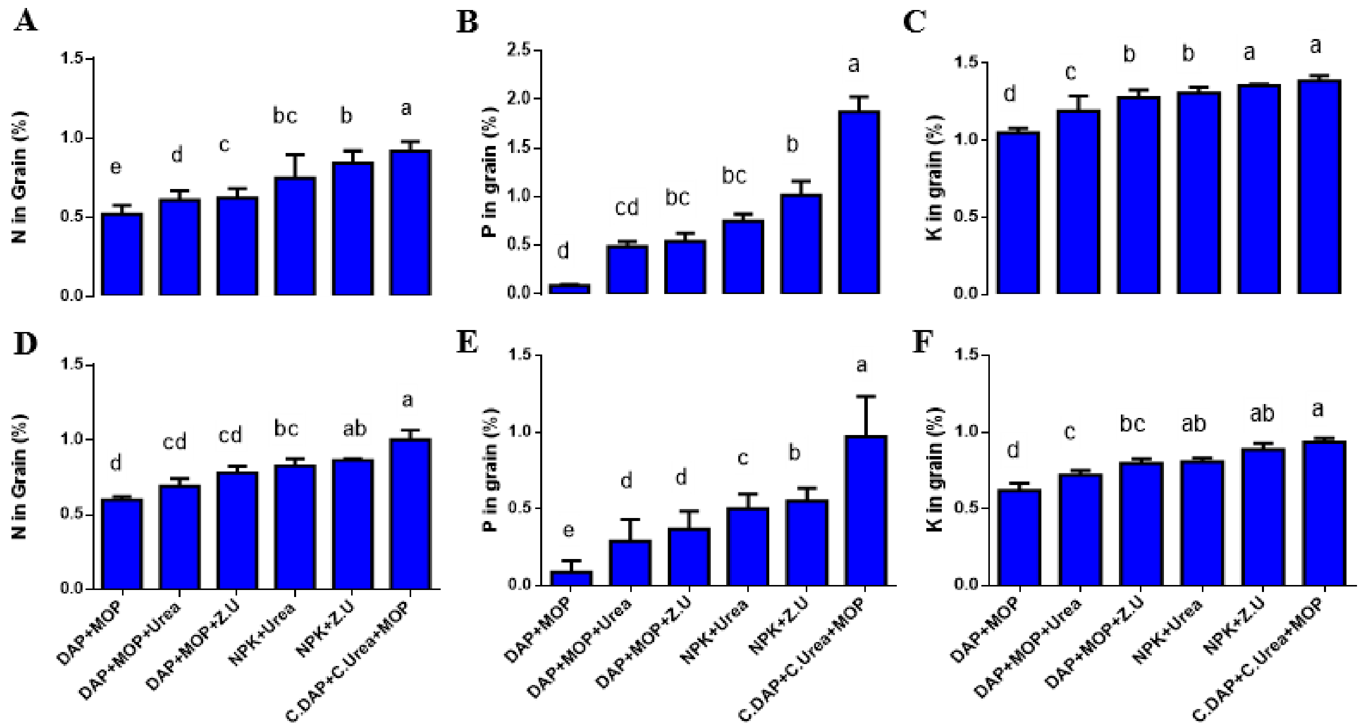

Figure 4. Impact of value-added and conventional fertilizers on N, P and K concentration in grains of maize and rice ((**A**) = N concentration in grains of maize, (**B**) = P concentration in grains of maize, (**C**) = K concentration in grains of maize, (**D**) = N concentration in grains of rice, (**E**) = P concentration in grains of rice, (**F**) = K concentration in grains of rice. Different letters indicate significant differences at a level of significance of $p < 5\%$.

3.6. N, P and K Concentrations in the Shoot Part of Maize and Rice

The N concentration in a shoot of maize was also altered with the application of value-added fertilizers in a similar manner to that of N concentration in the grains of maize (Figure 5A). Maximum N concentration in a shoot of maize was given by polymer-coated DAP and urea. P concentration in a shoot of maize was also maximum with polymer-coated DAP along with urea followed by zarkhez plus NPK along with zabardast urea (Figure 5B). Zarkhez plus NPK with zabardast urea also gave maximum K concentration in a shoot of maize in comparison to all other treatments except polymer coated DAP and urea (Figure 5C). In the case of rice, a similar trend was seen, as indicated in the D, E, and F sections of Figure 5 for N, P, and K concentrations in rice shoots, respectively.

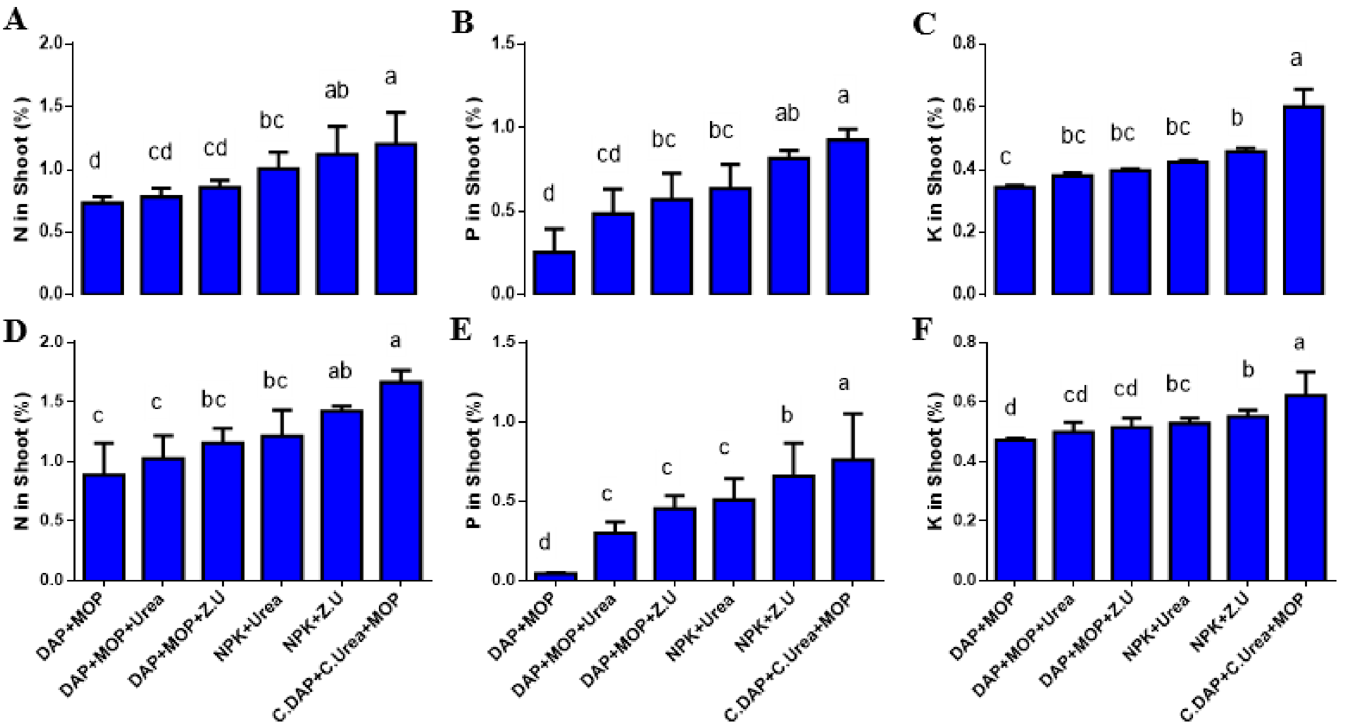

Figure 5. Impact of value-added and conventional fertilizers on N, P and K concentration in a shoot part of maize and rice ((**A**) = N concentration in shoot of maize, (**B**) = P concentration in shoot of maize, (**C**) = K concentration in shoot of maize, (**D**) = N concentration in shoot of rice, (**E**) = P concentration in shoot of rice, (**F**) = K concentration in shoot of rice). Different letters indicate significant differences at a level of significance of $p < 5\%$.

3.7. N, P and K Concentrations in the Root of Maize and Rice

Concentrations of N, P and K in roots of maize and rice were higher with the use of value-added fertilizers in comparison to DAP and urea. As zabardast urea induced more N, P and K concentration in a root of maize than urea (Figure 6A–C). Moreover, zarkhez plus NPK also improved the concentration of primary macronutrients in the root of maize in comparison to DAP. However maximum results were shown by polymer-coated DAP and urea. Similarly, the concentration of N, P and K in roots of rice were also lower with the use of DAP in comparison to zarkhez plus NPK and with the use of urea in comparison to zabardast urea. But all treatments gave lower N, P and K concentrations in roots of rice than that induced by polymer-coated DAP along with polymer coated urea (Figure 6D–F).

3.8. Agronomic Recovery and Nitrogen use Efficiency in Maize and Rice

Different sources of N showed strong influence on the agronomic N use efficiency in both the crops. Value-added fertilizers showed more efficiency over commonly-used urea along with DAP. Zabardast urea showed a significant increase in agronomic N use efficiency over urea in both combinations, though the response was more pronounced with zarkhez plus NPK. But polymer-coated urea along with polymer-coated DAP gave maximum agronomic N use efficiency in both crops (Figure 7). Similar to agronomic N use efficiency, polymer-coated urea along with polymer-coated DAP induced maximum recovery N use efficiency in both crops (Figure 8A,B). The second highest recovery was seen with the application of zabardast urea along with zarkhez plus NPK. However, minimum recovery was observed where urea along with DAP was applied.

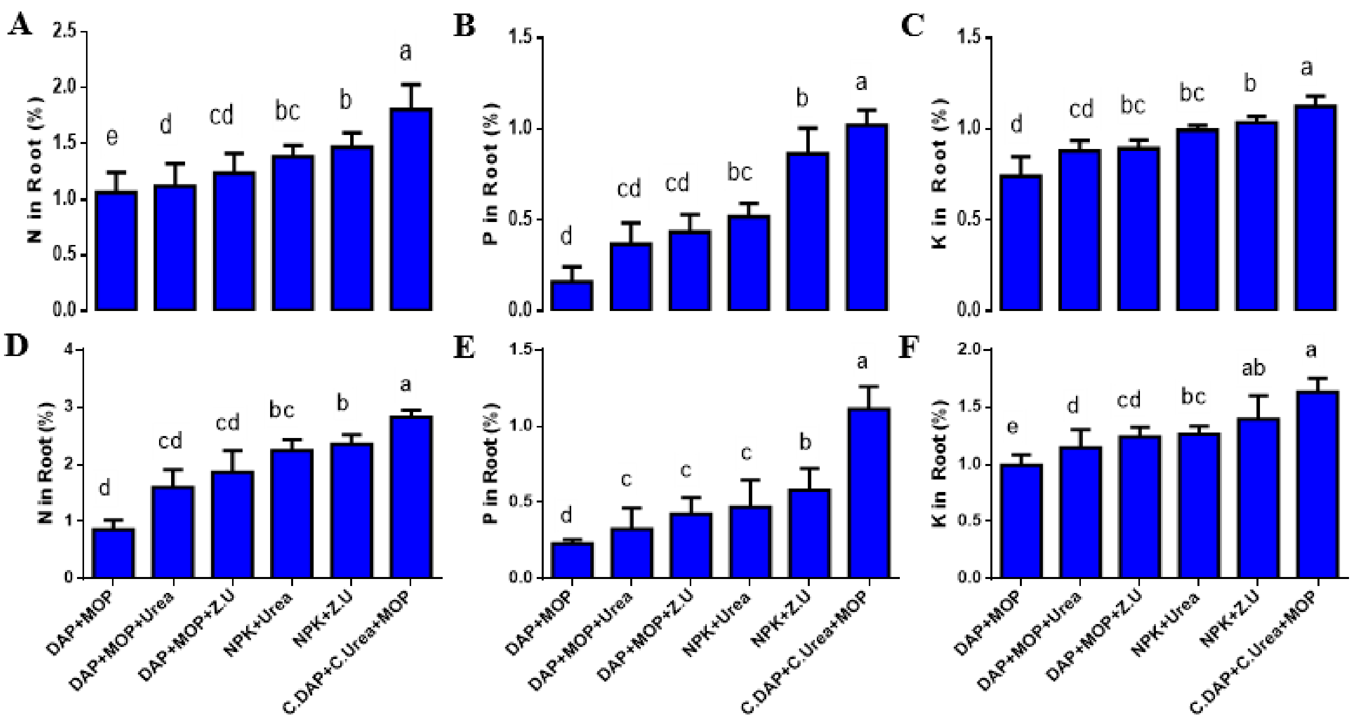

Figure 6. Impact of value-added and conventional fertilizers on N, P and K concentration in root of maize and rice ((**A**) = N concentration in root of maize, (**B**) = P concentration in root of maize, (**C**) = K concentration in root of maize, (**D**) = N concentration in root of rice, (**E**) = P concentration in root of rice, (**F**) = K concentration in root of rice). Different letters indicate significant differences at a level of significance of $p < 5\%$.

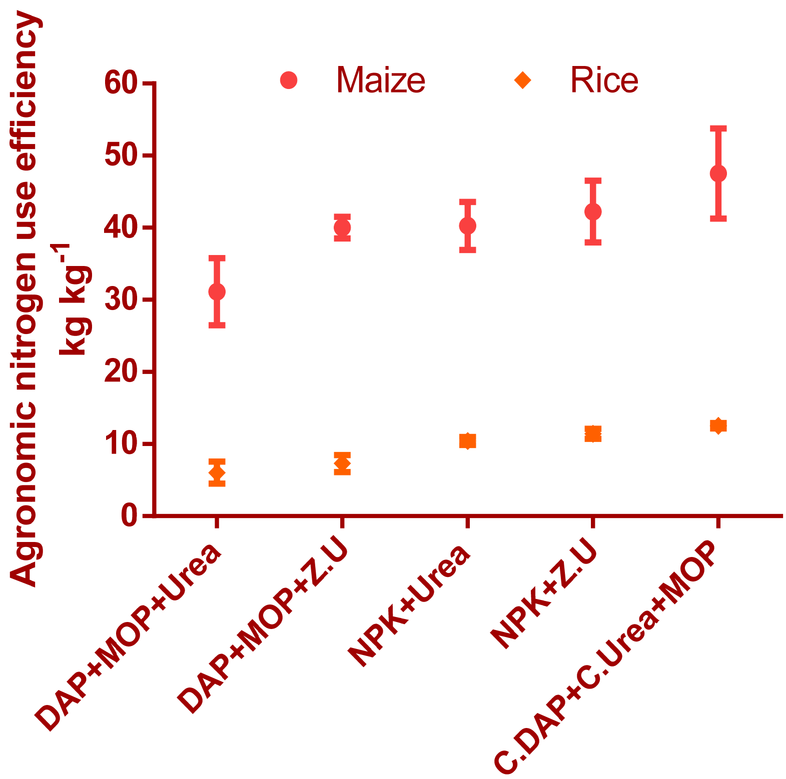

Figure 7. Impact of value-added and conventional fertilizers on agronomic nitrogen use efficiency of maize and rice.

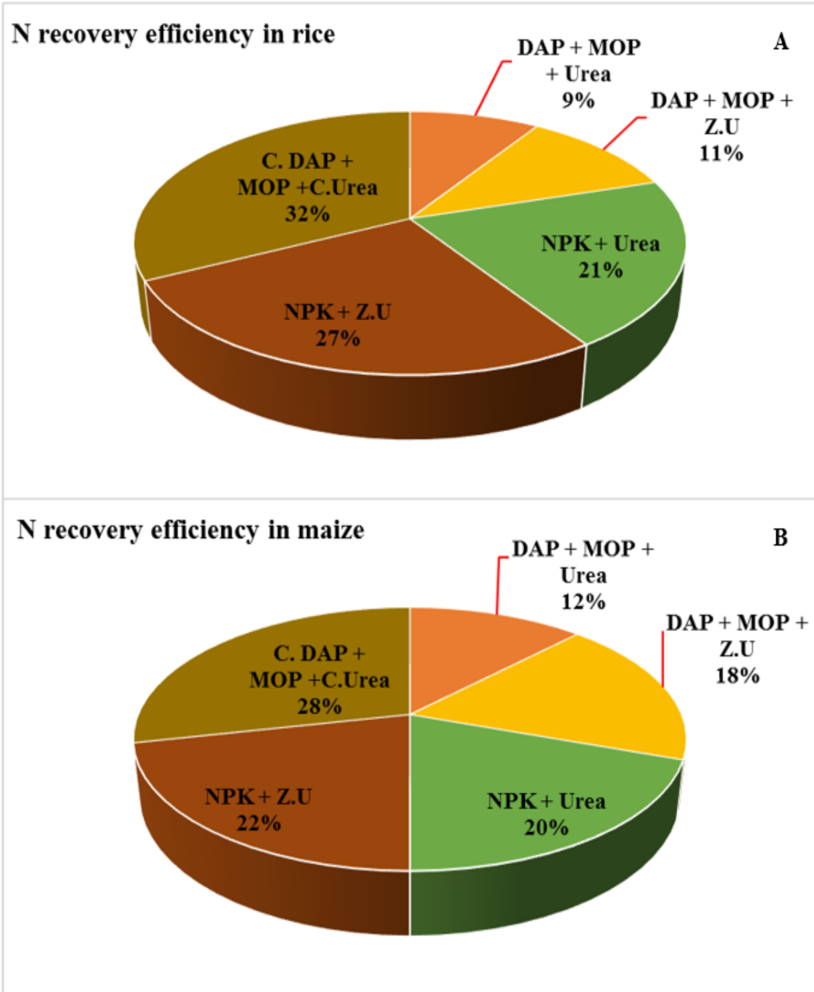

Figure 8. Impact of value-added and conventional fertilizers on nitrogen recovery efficiency of rice (**A**) and maize (**B**).

3.9. Results from Pearson Correlation and Principal Component Analysis

Significant positive and negative correlations were observed among plant growth (plant height, shoot dry weight, root dry weight, and grains weight) and physiological (internal carbon dioxide concentration, and SPAD index) parameters along with N, P and K contents of maize and rice in soil and plant tissues in plots treated with value-added fertilizers (Figure 9). The score and loading plots of a principal component analysis (PCA) are presented in Figure 10. Within the dataset, the first two components of PCA revealed maximum 96.21% (A) and 98.43% (B) variations among all the studied parameters, of which PC1 explained a 92.59% (A) and 87.87% (B) variation whereas PC2 explained 3.62% (A) and 10.55% (B) variation. Moreover, all of the applied treatments were successfully displaced with the first two components. This displacement of treatments provided a clear indication that the application of coated urea and coated DAP along with MOP had a significant ameliorative effect on all the studied attributes of maize and rice plants relative to the control. Here, PC1 was positively influenced by variables PCA (Figure 10) having parameters photosynthesis rate, P and K in root, N in shoot, N in root, dry biological yield, dry straw yield, leaf area, dry cob yield, grain yield, cob diameter, cob length, plant height and SPAD), whereas PC2 was positively influenced by observations PCA containing (DAP + MOP + urea, DAP + MOP + zabardast urea, NPK + urea, NPK + zabardast urea and coated DAP + coated urea + MOP). Figure 11 elaborated the relationship between N volatilization and N use efficiency for various value-added fertilizer combinations.

However, it is depicted that the maximum N use efficiency and minimum N volatilization were seen with polymer-coated fertilizers.

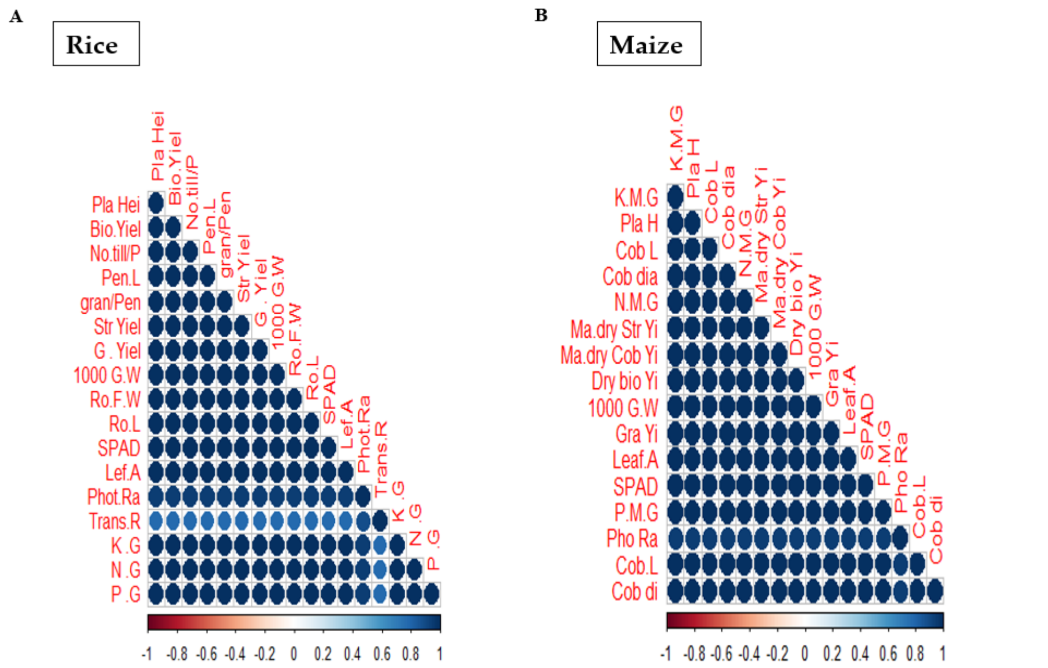

Figure 9. The agronomic, physiological and biochemical characteristics of rice (**A**) and maize (**B**), as well as maize grain N contents and rice grain N contents under the influence of applied value-added fertilizers, have a significant connection ($p = 0.05$).

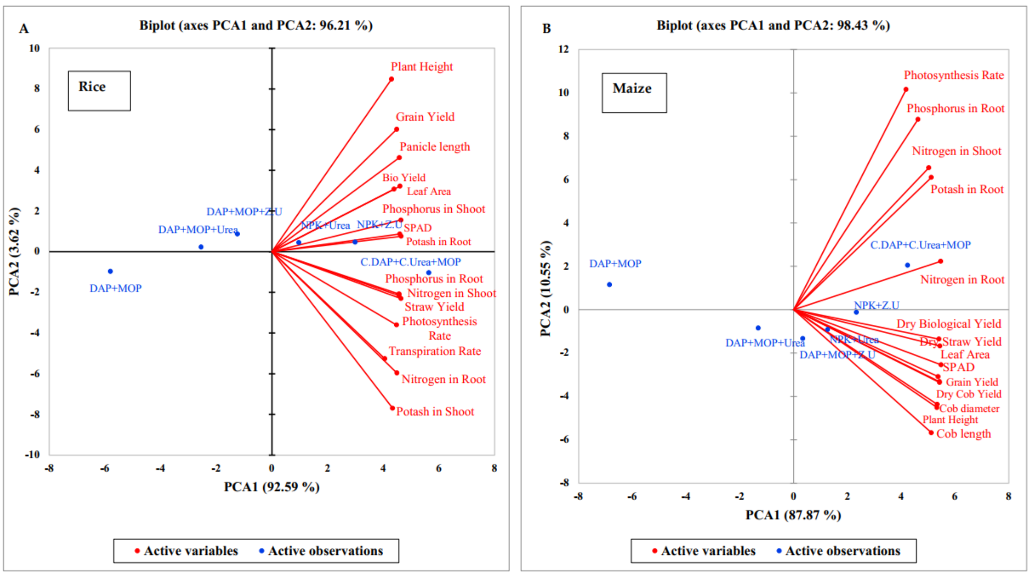

Figure 10. The first two components revealed 96.21% (**A**) and 98.43% (**B**) of the variability between the applied treatments and examined the parameters of maize and rice plants under value-added and conventional fertilizers in a principal component analysis of observations and variables. Observations are DAP + MOP: di-ammonium phosphate + muriate of potash; DAP + MOP + Urea: di-ammonium phosphate + muriate of potash + urea; DAP + MoP + Z.U: di-ammonium phosphate + muriate of potash + zabardast urea; NPK + Urea: zarkhez plus NPK + urea; NPK + Z.U: zarkhez plus NPK + zabardast urea and coated (DAP + Urea) + MOP: coated (di-ammonium phosphate + urea) + muriate of potash.

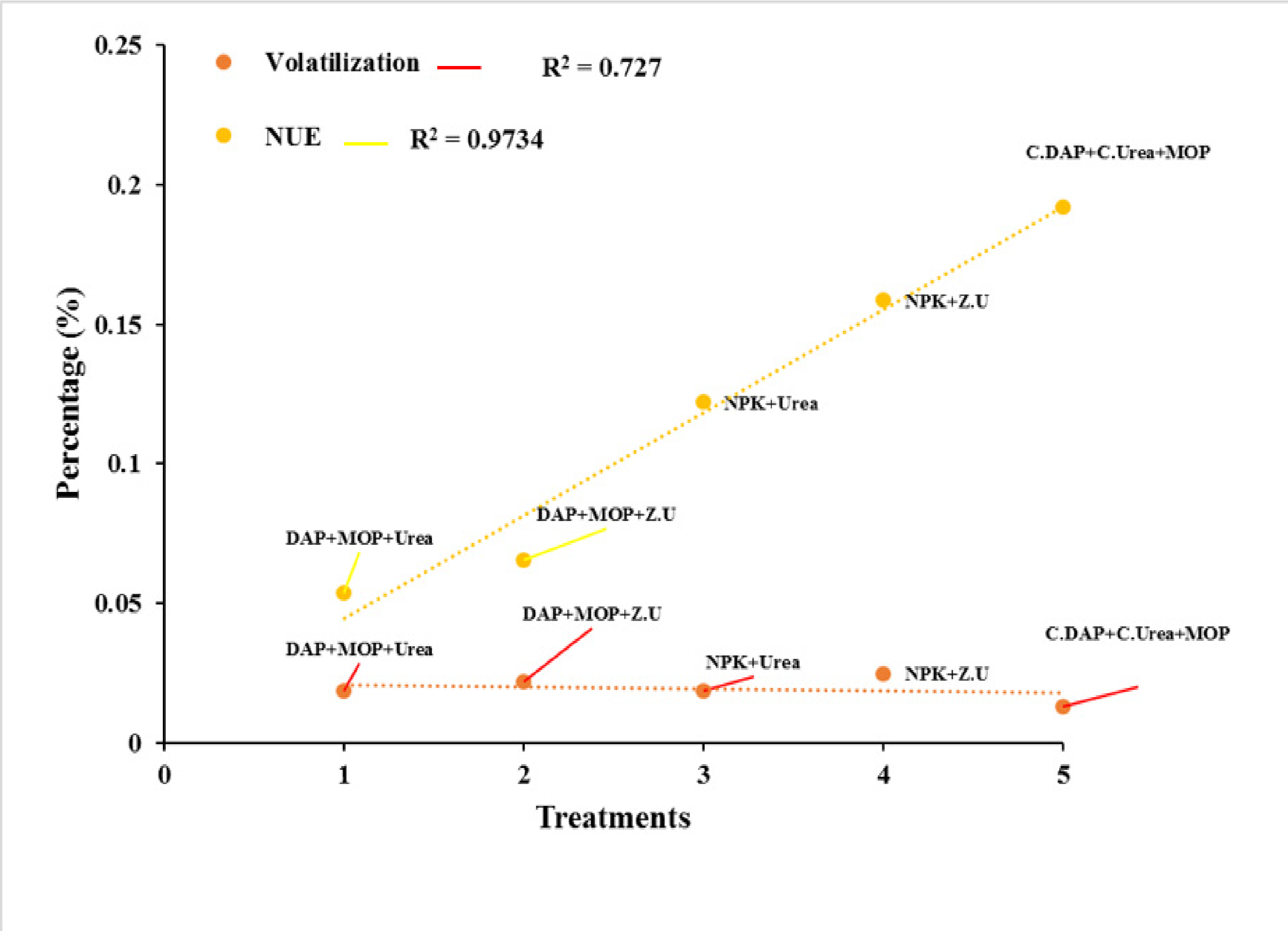

Figure 11. Relationship between N volatilization and N use efficiency (NUE) for value-added and conventional N fertilizers.

4. Discussion

Nitrogen loss as ammonia (NH_3) volatilization from applied fertilizers is estimated to be 20 to 30% and can be increased with the rise in soil pH and temperature [23]. The NH_3 volatilization generates reactive nitrogen species, which are responsible for environmental pollution. Due to NH_3 volatilization, applied fertilizer loses a significant amount of N, resulting in environmental pollution and decreased yields and crop nutrient utilization efficiency [28]. Nitrogen losses and efficiency of fertilizer usage have previously been addressed using a variety of ways. For minimizing N losses and boosting N use efficiency, the value addition of conventional N fertilizers is one of the most successful approaches [29]. The addition of micronutrients and beneficial microbial strains to major nutrient sources could accelerate the crop performance due to their interaction with major nutrients and improvement in soil health [30]. It has been shown that biodegradable polymer-coated N fertilizers can reduce losses of ammonia and leaching during periods of heavy rain [31].

We found that NH_3 emissions were substantially decreased by applying coated fertilizers in comparison to the traditional fertilizer application approach and other value-added fertilizers in both the crops (Figure 8). This might be due to the lower exposure of ammoniacal N to the atmosphere for a further reaction [32]. Once applied, N fertilizer yields ammonium, which is taken up by plants, nitrified into nitrate, fixed in soil colloids, leached and or volatilized as ammonia [33]. However, ammonia emission from zabardast urea was relatively higher than polymer-coated urea and even common urea. It might be a consequence of poor coating in case of zabardast urea on the fertilizer granule that ruptured quickly, particularly in standing water of rice crop. Moreover, when agricultural plants are able to fully utilize the fertilizer that has been supplied, there is a little risk of undesired outcomes. This maximum consumption of N may result in the least ammonia emissions, as we found in our study that applied polymer-coated N fertilizer had a greater recovery/use efficiency than those found by other value-added fertilizers (Figure 7). Coating the N fertilizer lowered ammonia emissions greatly because it maximized the use of the applied N [34,35], as was also revealed by higher N use efficiency and recovery efficiency in the present study (Figures 7 and 8).

Polymer-coated fertilizers were more effective than a standard surface application of uncoated N fertilizer in considerably enhancing plant growth parameters of both the crops (Table 2). Optimal N availability boosts the production of carbohydrates, which can be used to develop the top portion of the plants if N is available to plants for an extended period. Therefore, the coated N fertilizer may be the primary explanation for the long-term availability of N to crop plants, resulting in increased growth performance. In a similar way, a larger number of tillers and subsequent yield of wheat were reported by [36], who used the controlled release of N fertilizer to achieve these findings. Other value-added fertilizers like zabardast urea and zarkhez plus NPK, when applied in combination, produced encouraging results, which may be an attribute for the reduced contact of released nutrients with the atmosphere. Plant growth and biomass have been reported to be boosted by deep placement of N fertilizer by other studies [37–39].

Value-added fertilizer treatments resulted in higher chlorophyll content in rice and maize leaves at physiological maturity than uncoated urea and DAP treatment (Figures 2 and 3). A steady supply of N is required for the improved chlorophyll molecules, because N is a structural component of the molecule. According to the results of this study, the synthesis of chlorophyll in rice and maize may have been affected by the controlled release of N by value-added N fertilizers (polymer-coated urea and zabardast urea). The chlorophyll contents of wheat and fine rice were increased by using coated N fertilizers and the deep placement of N fertilizer [40,41].

Zabardast urea outperformed standard urea in increasing rice and maize yields across the board, including grain yield, straw yield, and biological output (Table 3). Zinc as a micronutrient have interaction with other plant nutrients like N and P. Zabardast urea have an additive effect for zinc coating that may have synergistic interactions with other nutrients, especially N and P, that accounted for better crop yields. Nitrogen contributes directly to increased crop yields, but its synergistic interactions with other nutrients magnify its impact. Zarkhez plus NPK also gave better crop yields than DAP that could be attributable to increased P availability in zarkhez plus NPK that contains a coating surface of some microbial inoculum. Similarly, rice yield increased due to the deeper placement of N fertilizer, which reduced gaseous emissions from the fertilizer [42]. Polymer-coated N fertilizer was found to increase crop yields in this study, probably due to the minimal damage that N fertilizer grain can do to seedlings, as described by [18] and [17], as toxic levels of a vital nutrient near the seedling's roots might damage its growth, resulting in a lower crop yield. Increased nutrient concentrations in soil can stunt plant growth if roots are exposed to it directly without the covering layer protecting them. Therefore, it is possible that coated N fertilizer is responsible for the increased production. Coated N fertilizers were found to greatly increase maize yields when compared to uncoated N fertilizers [43].

When coated fertilizers were used, the plant's ability to absorb nutrients was improved, so N, P, and K concentrations were higher in different plant sections of maize and rice in coated treatments than in uncoated ones (Figures 5–7). Nitrogen uptake is directly influenced by the application of value-added N fertilizers, as demonstrated in this study. Uncoated urea showed the lowest concentration of N in all plant sections examined, whereas coated urea showed a higher concentration. This could be due to increased N availability in the root zone soil, as well as low N losses to the environment. An increase in N fertilizer uptake by field crops was reported by [44]. Deep N fertilizer placement also increased rice crop N uptake [45]. Another intriguing finding was the influence of value-added fertilizer application on the concentrations of P and K in plant parts, with the maximum concentrations in plant parts being seen with polymer-coated fertilizers followed by zarkhez plus NPK and zabardast urea treatment (Table 3). This may be due to the effect of the interactive effect of nutrients in the soil, which alters the soil microenvironment. A cationic form of N known as ammonium can be used by plants to mobilize P from organic sources and fixed P complexes [46]. Because of the exchange mechanism that occurs when plants take in cationic form, the soil rhizosphere becomes acidic. In addition, urea to ammonium conversion results in acidic soil conditions [47]. Consequently, the plant parts may have a larger concentration of P due to the solubilization of the fixed P in the soil. Because of urea and ammonium nitrate fertilizer, soil pH has fallen [48]. Similarly, a decrease in soil pH has a significant effect on plant nutrition [49]. Increasing the concentration of K in plant parts may be a result of this interaction between N and K, as N plays a function in the acquisition of K in higher plants [50] and [51] found that N and K interact synergistically in rice, wheat and other field crops.

Polymer-coated fertilizers have shown the highest agronomic and recovery N usage efficiency in this study (Figures 7 and 8), which may be related to the minimal N losses and maximal consumption of N released from fertilizer granule. Increased crop N absorption is a result of increased soil N availability, which has a direct impact on plant physiological and metabolic processes. An increase in yield can be achieved by cultivating plants that have more metabolic and physiological activity. When more N is ingested, the efficiency of reusing N is increased [37]. Slow-release N fertilizer enhanced sunflower N utilization efficiency in a study [52]. The activation of indigenous P and K solubilizing bacteria in the soil may have influenced the efficiency of P and K consumption in the study, as zarkhez plus NPK contains plant growth promoting rhizobacterial strain in the coating material that boosts microbial activity in the soil. P and K fixation with counter ions and clay colloids can be minimized by microbial activities in the soil. Zabardast urea might be due to the zinc coating performed better than standard urea in improving N use efficiency. In a similar study, [53] proved that the simultaneous application of plant nutrients resulted in higher nutrient use efficiencies.

In both the experiments, polymer-coated fertilizers outperformed other fertilizer sources in terms of performance. Moreover, water and counter ion react with the covering substance, preventing the internal contents from being exposed to these ions or water molecules. Therefore, it is possible that coated fertilizers enhanced growth, yield and nutrient use efficiency with lower ammonia emissions due to the coating layer's ability to protect nutrients. Using polymer-coated fertilizers, wheat and other field crops were able to use their N more efficiently because of the slower release of N [44,54]. It was found that zarkhez plus NPK with zabardast urea was superior to DAP with standard urea in terms of plant growth, yield and nutrient usage efficiency. This might be due to the better lower nutrient exposure to the atmosphere, as both these fertilizers were coated. A reduction in N gaseous loss and an increase in rice biomass and yield were both achieved by applying N fertilizer deeply [55–57]. However, all value-added fertilizers performed better in comparison to the standard fertilizer sources, while polymer-coated fertilizers ideally improved growth, yield, and nutrient utilization efficiency with a considerable decrease in ammonia volatilization. As a result of the current approach, farmers' income and food quality can be improved, and the environment can be protected from dangerous gas emissions like ammonia from the use of N fertilizers.

5. Conclusions

Value-added fertilizers have a strong impact on the growth and yield of maize and rice crops; these fertilizers improve the nutrition of crops very effectively. We found that polymer-coated N fertilizers were more efficient in reducing volatilization losses in comparison to the commercially available sources like zabardast urea. Moreover, polymer-coated fertilizers were very effective in improving fertilizer use efficiency in addition to the reduction in N losses. We thus concluded that the utilization of controlled-release (polymer-coated) fertilizers in maize–rice extensive cropping systems not only improves crop production via increased nutrient use efficiencies but is also environmentally friendly, owing to their biodegradability and reduced ammonia losses. Additional studies are necessarily required to compare the efficacy of coated fertilizers with those of commercially available fertilizers to perform a precise cost–benefit evaluation on long-term field trials.

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Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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