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# Fertilizers Containing Balanced Proportions of $NH_4^+$-N and $NO_3^-$-N Enhance Maize (*Zea mays* L.) Yield Due to Improved Nitrogen Recovery Efficiency

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**Citation:** Masood, S.; Suleman, M.; Hussain, S.; Jamil, M.; Ashraf, M.; Siddiqui, M.H.; Nazar, R.; Khan, N.; Jehan, S.; Khan, K.S.; et al. Fertilizers Containing Balanced Proportions of $NH_4^+$-N and $NO_3^-$-N Enhance Maize (*Zea mays* L.) Yield Due to Improved Nitrogen Recovery Efficiency. *Sustainability* **2023**, *15*, 12547. https://doi.org/10.3390/su151612547

Academic Editors: Othmane Merah, Purushothaman Chirakkuzhyil Abhilash, Magdi T. Abdelhamid, Hailin Zhang and Bachar Zebib

Received: 22 June 2023
Revised: 8 August 2023
Accepted: 9 August 2023
Published: 18 August 2023



**Abstract:** The current study aimed to improve the nitrogen recovery efficiency (NRE) of maize under the application of balanced proportions of ammoniacal-nitrogen ($NH_4^+$-N) and nitrate-nitrogen ($NO_3^-$-N) (1:1), as well as to determine economic impacts of such fertilizers on maize productivity. A 3-year field study was carried out in Sahiwal, Punjab, Pakistan during the 2018–2020 growing seasons with autumn maize. In parallel, multi-location field experiments were conducted at farmer's fields in Sahiwal during the same growing seasons with autumn maize. The trials compared the effects of different fertilizers like urea, calcium ammonium nitrate (CAN), Sarsabz nitrophos (NP), nitrphos plus (NP Plus), and di-ammonium phosphate (DAP) on maize growth and yield, as well their economic efficiency. The results revealed that the application of Sarsabz NP and CAN increased the maize grain yield by 30%, 13%, 15%, 19%, 15%, and 9% as compared to the control, NP + urea, NP Plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN, respectively. In addition, the combined application of NP and CAN increased the total N and $NO_3^-$-N concentrations, whereas it decreased the $NH_4^+$-N concentrations in the soils. By contrast, NP + CAN increased the $NH_4^+$-N concentrations in maize leaves as compared to $NO_3^-$-N concentrations. Overall, the NRE of maize plants and the net return were higher under combined application of NP and CAN. In conclusion, CAN fertilizer increased the soil $NO_3^-$-N concentrations, which thus assimilated in the plants as $NH_4^+$ and improved the NRE of maize. Improved NRE thus enhanced maize yield and resulted in the maximum net return as compared to all other fertilizer combinations.

**Keywords:** economic efficiency; fertilizers; maize grain yield; nitrogen uptake; $NH_4^+$-N; $NO_3^-$-N; return on investment (ROI)

## 1. Introduction

Nitrogen (N) availability is a key factor that controls crop productivity throughout the world. In general, the soil surface layer (0–15 cm depth) contains 0.1–0.6% N [1] and plants mainly use inorganic forms of N like $NH_4^+$, $NO_3^-$, and nitrite ($NO_2^-$). In irrigated and aerated soils, $NO_3^-$ is the dominant form of N, whereas $NH_4^+$ can be dominant in acidic and/or anaerobic soils [2]. $NO_2^-$ concentrations in soils are typically lower than $NH_4^+$ concentrations; however, this is dependent on the balance of nitrification and denitrification [3]. Recent pieces of evidence suggest that plants also absorb the organic form of N from its sources—urea, amino acids, and peptides [4,5]—but organic N supplies are not comparable with inorganic N supplies, because $NH_4^+$-N and $NO_3^-$-N are often found in high amounts in soils than all the other forms [2]. Because of its diverse effects in plant nutrition and physiology, $NO_3^-$-N is regarded as a significant N source for all plants [6,7].

It is well known that N uptake by the plants is influenced by the presence of the N-form in the soil solution [8]. However, the soil reaction controls the nitrification and/or denitrification of N in soils [9,10]. Simek et al. [11] observed that the nitrification process accelerated when soil pH increased and vice versa. In Pakistan, soils are alkaline in nature (pH > 8.0) and contain low amounts of N. In this scenario, farmers are using nitrogenous fertilizers in the form of urea to meet the crop requirements [12]. In these soils, N losses from the urea are prevalent in the form of $NH_3$ volatilization [1] and/or $NH_4^+$ fixation as it has a higher potential for $NH_3$ volatilization with a lower susceptibility to $NO_3^-$ leaching and de-nitrification than nitrate-based fertilizers [13,14], such as CAN. It is projected that around 3.34 million tons of urea is wasted each year owing to volatilization, leaching, and de-nitrification, resulting in a USD 40.5 billion economic loss [15].

Under such conditions, N-fertilizer containing balanced proportions of $NH_4^+$-N and $NO_3^-$-N like CAN fertilizer could be used as an alternate source of fertilization. Because fertilizer CAN contains fast-acting $NO_3^-$-N and slow-release $NH_4^+$-N, volatilization losses are negligible [16]. Growing evidence exists that N is mainly transported by water; hence, soil water at the root interface exports N to the aerial parts of plants [17]. This implies that fast-acting $NO_3^-$-N is readily available to the plants through mass flow, whereas slow-release $NH_4^+$-N is available to the plants over time. Further, N uptake or utilization in plants is increased by 60% in the case of the ammonium nitrate (AN) source of N fertilization as compared to urea [16,18]. According to Sutton et al. [19], sub-optimal fertilizer management, including N fertilizers, may decrease nitrogen use efficiency (NUE) by 30–50%. Therefore, the right source of N fertilizer is the major management practice to improve NUE or NRE and crop production [20]. Therefore, increasing NRE is considered a major challenge in crop production.

Apart from the above, the assimilation of inorganic N greatly differs among crop species [21,22] as some plants prefer $NH_4^+$-N [23] while others prefer $NO_3^-$-N [24]. Nitrate is transformed into $NH_3$ by nitrate reductase (NR) and nitrite reductase (NiR) enzymes when it is taken up by the plants [25,26]. However, high concentrations of $NH_4^+$ in the plant tissues cause serious disorders [27,28], and reduce crop yield, especially under $NH_4^+$-N-containing inorganic N fertilization. Plants grow well when both types of inorganic N forms are supplied into the soils [29]. Plant growth and development were enhanced by the co-provision of both $NH_4^+$-N and $NO_3^-$-N inorganic forms more than by $NO_3^-$-N or $NH_4^+$-N alone [30].

Maize (*Zea mays* L.) is an essential crop around the world due to its usage as human food, animal (silage and grains), and poultry feed. Furthermore, it is a significant source of starch, dextrose, corn syrup, and corn flakes [31]. In Pakistan, it is considered one of the staple food crops after wheat and rice. Growing maize hybrids under the semiarid climates of Pakistan is advantageous over local cultivars because of their higher NRE and growers' income [32]. However, various genotypes respond differently to different sources and levels of N. Previous studies have examined the impact of different N sources (ammonia or nitrate), rates, and times of N fertilization on maize crops [32–35]. Furthermore, there are few studies that show that slow-release nitrogen fertilizers in field trials and co-provision of $NH_4^+$-N and $NO_3^-$-N in greenhouse conditions increased crop yield [20,30].

Multi-year and multi-location studies under field circumstances are required to undertake a comprehensive evaluation of the advantages of various N sources comprising a balanced amount of $NH_4^+$-N and $NO_3^-$-N. We hypothesized that the N sources containing balanced proportions of both N-forms improve the NRE of the crops, thereby increasing the net return when compared with $NH_4^+$-N or $NO_3^-$-N alone. The present study aimed to quantify the benefits of N sources under prevailing soil conditions of Pakistan and to determine the NRE of maize plants. Overall, the objective of the study was to evaluate the comparative effectiveness of the urea and CAN as N in terms of crop yield and growers' income.

## 2. Materials and Methods

### *2.1. Soil Sampling and Experimentation*

A 3-year field experiment with hybrid maize var. Syngenta 7720 was carried out in Sahiwal, Punjab, Pakistan (30°41′24′′ N, 73°1′48′′ E) during the maize growing season (August–November, 2018–2020). A total of 21 field blocks were prepared and each block had a length of 6.96 m and a width of 4.54 m. Before initiating fertilizer treatments, soil samples were collected from two depths—0–15 and 15–30 cm—air-dried, passed through a 2 mm sieve, and analyzed for soil physicochemical parameters (Table 1). Urea and CAN were used as the source of N, whereas di-ammonium phosphate (DAP), nitrophos (NP), and nitrophos plus (NP Plus) were applied as the P source of fertilization.

**Table 1.** Pre-soil analysis of samples collected from two different depths before sowing maize. All values are means ± S.E. of three replicates.

| Depth (cm) | Soil Texture | pH | EC (mS $cm^{-1}$) | meqNa 100 $g^{-1}$ Dry Soil | meq Ca + Mg100 $g^{-1}$ Dry Soil | SAR | SOM (%) | Total Soil N (mg $kg^{-1}$ Dry Soil) | mg $NH_4^+$ -N $kg^{-1}$ Dry Soil | mg $NO_3^-$-N $kg^{-1}$ Dry Soil | Available P (mg $kg^{-1}$ Dry Soil) | Extracatable K (mg $kg^{-1}$ Dry Soil) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0–15 | Loam | 8.18 ± 0.11 | 0.44 ± 0.03 | 9.19 ± 0.22 | 344 ± 11.21 | 0.77 ± 0.03 | 0.75 ± 0.03 | 573 ± 23.36 | 95 ± 4.17 | 197 ± 8.81 | 5.53 ± 0.16 | 107 ± 4.80 |
| 15–30 | Loam | 8.44 ± 0.03 | 0.47 ± 0.03 | 11.13 ± 0.36 | 356 ± 12.34 | 0.83 ± 0.04 | 0.53 ± 0.03 | 491 ± 21.77 | 78 ± 3.56 | 230 ± 10.63 | 5.15 ± 0.12 | 100 ± 4.03 |

Potassium (K) was used as sulphate of potash at a rate of 37 kg $K_2O$ $acre^{-1}$ in all blocks, whereas phosphorus (P) was given at a rate of 58 kg $P_2O_5$ $acre^{-1}$ from its sources: NP, NP Plus, and DAP during sowing. Nitrogen was sprayed at a rate of 110 kg N $acre^{-1}$ in three splits from two sources: CAN and urea. Although the composition of nutrients of the various fertilizers differed (Table S1), all fertilizers were applied at the same rate. The following seven fertilizer treatments were established: control (no N or P), NP + CAN, NP + urea, NP plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN. There were three replications for each treatment. Farmers' fields of different locations were used for reproducibility of the yield data during the years 2017–2018 and 2020–2021.

### *2.2. Plant Growth Conditions and Harvesting*

Plants received natural conditions with average day/night temperatures of 37/26 °C, a relative humidity of 30%, rainfall of 12 mm, and light duration of 14–15 h. A maximum rainfall of 30.08 mm was recorded in the month of September 2020. Plants were harvested upon completion of a life cycle or 100 days after sowing, and growth attributes like plant height, cob fresh and dry weights, cob length, no. of grain rows $cob^{-1}$, 1000-grain weight $plant^{-1}$, and total yield were monitored. Flag leaves were also collected for mineral analysis. Likewise, soil samples were also collected for post-harvest nutrient analysis.

### *2.3. Determination of Mineral N and Other N-Forms in Soils and Plant Tissues*

Total N concentrations were enumerated using Kjeldahl distillation apparatus (S3 Behr, Düsseldorf, Germany). $NH_4^+$-N concentrations in the soils were measured according to the methods described by Yuen and Pollard [36]. Briefly, 10 g of soil was extracted with 2 M KCl in a mechanical shaker at a speed of 200 rpm for 1 h. Soil suspension was filtered and collected filtrate was thus processed for steam distillation after adding 0.5 g of MgO. A 2% solution of boric acid containing a few drops of bromocresol green and methyl red indicators was used to collect ammonia ($NH_3$). After that, 0.01 N NaOH was titrated with the collected distillate until the pink end point. Likewise, $NO_3^-$-N concentrations in the soils were assessed, and Soltanpour and Workman's [37] techniques were used to measure them using a Spectrophotometer (UH 5300, Hitachi, Tokyo, Japan) at a wavelength of 540 nm. In a nutshell, 20 mL of AB-DTPA extraction solution was combined with 10 g of air-dry soil before being shaken at a speed of 180 rpm for 20 min and filtering through Whatman filter paper. The digestion flasks were filled with 1 mL of filtrate, 3 mL of 0.2 M $CuSO_4$, 2 mL of 0.01 M hydrazine sulfate, and 3 mL of 1.5 M NaOH, and heated for 20 min. After cooling, 3 mL of color development reagent was applied, and $NO_3^-$-N concentrations in soil samples were assessed.

Leaf samples were oven-dried at 65 °C until a constant dry weight was not achieved in order to determine total N, $NH_4^+$-N, and $NO_3^-$-N in plant tissues. After that, leaf samples were ground well and utilized to determine total N, $NH_4^+$-N, and $NO_3^-$-N using Kjeldahl distillation apparatus (S3 Behr, Düsseldorf, Germany) in accordance with AOAC methodologies [38] and Jackson [39] procedures. For that, a 0.1 g leaf sample was blended with 0.02 g of powdered pumice and 1.33 g of catalyst combination, and digested in 1.5 mL of $H_2SO_4$ at 200–240 °C for $NH_4^+$-N analysis. In addition, a few drops of 30% $H_2O_2$ were also mixed in order to enhance the digestion. The collected digests were thus diluted to 20 mL with distilled water and 5 mL of diluted digest was used for $NH_4^+$-N analysis. Likewise, a 0.1 g leaf material was treated with a salicylic acid–sulfuric acid mixture (1:30 g/v, 3 mL) and allowed to stand for 2 h for the determination of $NO_3^-$-N. Afterward, 0.5 g of $Na_2S_2O_3.5H_2O$ crystals, 0.02 g of powdered pumice, and 1.33 g of catalyst mixture were added and digested at 200–240 °C. A few drops of 30% $H_2O_2$ were also added in a similar way to the leaf N and $NH_4^+$-N analyses.

### 2.4. Determination of NRE in Maize

The NRE of maize plants was determined by computing the data of plant N and maize grain yield in an equation described by Lüder et al. [40]:

$$\text{NRE (kg kg}^{-1}\text{)} = \text{Uptake efficiency} \times \text{utilization efficiency}$$

where
Uptake efficiency = Nt/Ns;
Utilization efficiency = Gw/Nt;
Nt = Total N uptake by maize at harvesting (kg $acre^{-1}$);
Ns = Nitrogen supply rate (kg $acre^{-1}$);
Gw = Maize grain yield (kg $acre^{-1}$).

### 2.5. Determination of Available Soil Phosphorus (P) and Plant Total P Concentrations

Available soil phosphorus was measured with the help of a spectrophotometer (UH 5300, Hitachi, Tokyo, Japan) at a wavelength of 882 nm using 0.5 M $NaHCO_3$ (pH 8.5) as an extracting solution according to the published protocols of Olsen et al. [41].

Phosphorus concentrations in leaf tissues were determined spectrophotometrically (UH 5300, Hitachi, Japan) at a wavelength of 410 nm after digesting them in 5 mL of acid digestion mixture: $HNO_3$ and $HClO_4$ (4:1 *v*/*v*). Leaf digests were thus used for subsequent analysis using ammonium-vanadomolybdate as a color-developing reagent.

### 2.6. Determination of Potassium Concentrations in Soils and Leaf Tissues

Potassium concentrations in soil samples were measured using flame photometer (PFP 7, Jenway, London, UK) at a wavelength of 767 nm. For this purpose, 4 g of air-dried soil was mixed in 20 mL of 1 M ammonium acetate as an extracting solution according to the published protocols of Richards [42]. Likewise, K concentrations in acid digests ($HNO_3$:$HClO_4$) were determined with the help of a flame photometer at a wavelength of 767 nm.

### 2.7. Quantification of Net Return and Return on Investment (ROI)

Net return and ROI of maize grain yield were calculated on account of the fertilizer's cost, whereas other expenses incurred on management practices were considered constant. The following formulae were used to calculate *Net Return* and *ROI* [43]:

$$Net\ Return = Total\ Benifits - Total\ Cost\ of\ Fetilizers \tag{1}$$

$$ROI = \frac{Net\ Return}{Cost\ of\ Investment} \tag{2}$$

### 2.8. Experimental Design and Data Analysis

A randomized complete block design (RCBD) was used for the experiment. Treatment means and analysis of variance (ANOVA) were compared using Tukey's post hoc test ($p \leq 0.05$ level) of Sigma Stat (SPSS, Inc., Chicago, IL, USA). Sigma Stat (SPSS, Inc., Chicago, IL, USA) was used to perform an analysis of variance on the obtained data and compare treatment means using the Tukey's post hoc test ($p \leq 0.05$ level). To check the interdependency among the parameters, Pearson's correlation coefficients were calculated at $p \leq 0.05$, 0.01, and 0.001 levels.

## 3. Results

### 3.1. Plant Growth as Influenced by Inorganic Nitrogen Supplies

Plant growth attributes like shoot fresh and dry weights, plant height, cob fresh and dry weights, no. of grain rows cob$^{-1}$, and cob length improved by all kinds of fertilizer combinations when compared with the control (Figures 1 and 2). The application of NP + CAN increased the plant height by 21% as compared to the control. When comparing the various combinations of fertilizers, NP + CAN increased the plant height by 4% as compared to DAP + urea. By contrast, the combination of CAN and DAP remained insignificant for plant height when compared with the DAP + urea. Similarly, a maximum no. of grain rows cob$^{-1}$ was found in NP + CAN as compared to all the other fertilizer supplies and the control. When compared with the conventional fertilizer supplies, no. of grain rows cob$^{-1}$ was found significant in NP + CAN treatment. Furthermore, cob length was found significant in all the fertilizer applications when compared with the control.

Cob fresh (g plant$^{-1}$) was found to be substantial in all fertilizer combinations when compared with the control. In comparison to the control, NP + urea, NP Plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN, treatments like NP + CAN increased cob fresh weight by 55%, 14%, 16%, 17%, 18%, and 10%, respectively (Figure 2A). A maximum cob dry weight (g cob$^{-1}$) was observed in NP + CAN treatment, whereas all the other fertilizer combinations remained insignificant (Figure 2B). The increase in cob dry weight under NP + CAN application was comparable with conventional fertilization, i.e., DAP + urea.

### 3.2. Maize Grain Yield as Influenced by Inorganic Nitrogen Supplies

A significant ($p \leq 0.05$) effect of inorganic N supplies was observed on 1000-grain weight (g) and maize grain yield (kg acre$^{-1}$) when compared with the control (Figure 3A,B). Among the different fertilizer combinations, NP + CAN application resulted in a maximum grain yield. Overall, these results suggested that the application of the right sources of fertilizers, i.e., NP + CAN, improved the 1000-grain weight and maize grain yield (Figure 3).

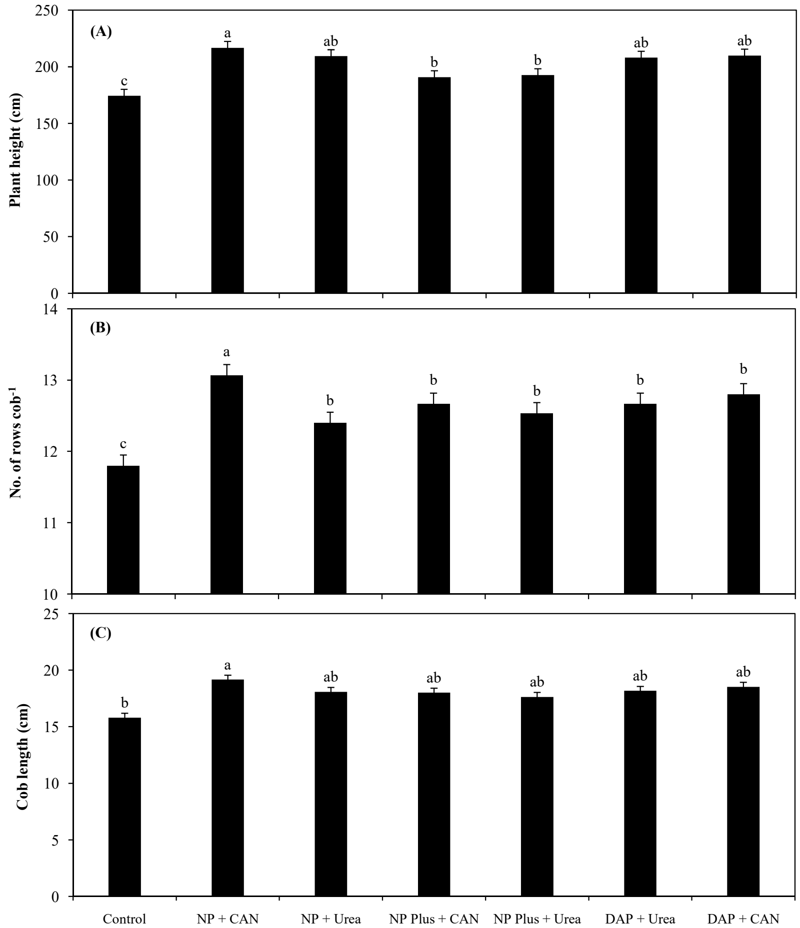


**Figure 1.** Plant growth attributes like plant height (**A**), no. of rows cob$^{-1}$ (**B**), and cob length (**C**) as influenced by N sources. All values are average of three years of experimental data ± S.E. of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level.

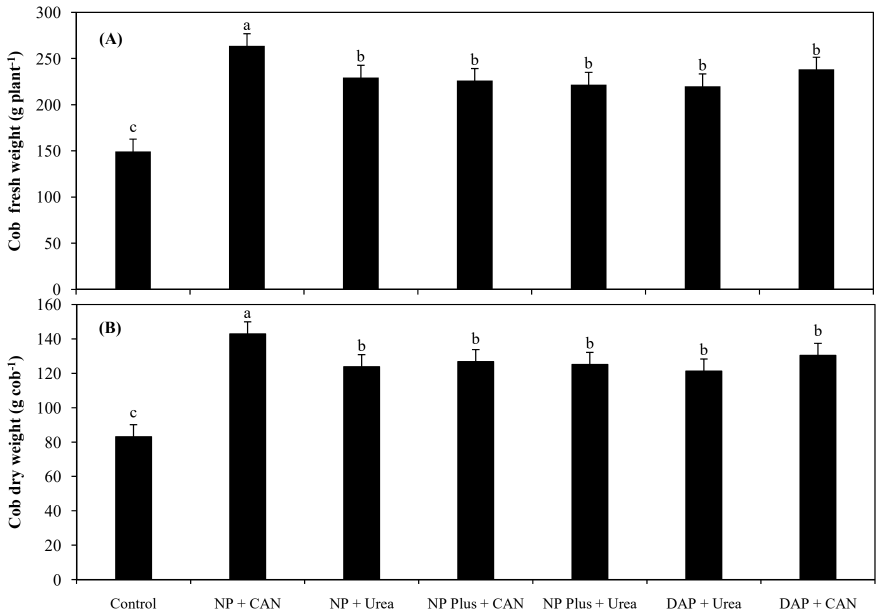


**Figure 2.** Cob fresh weigh (**A**) and cob dry weight (**B**) as influenced by N sources. All values are average of three years of experimental data ± S.E of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level.

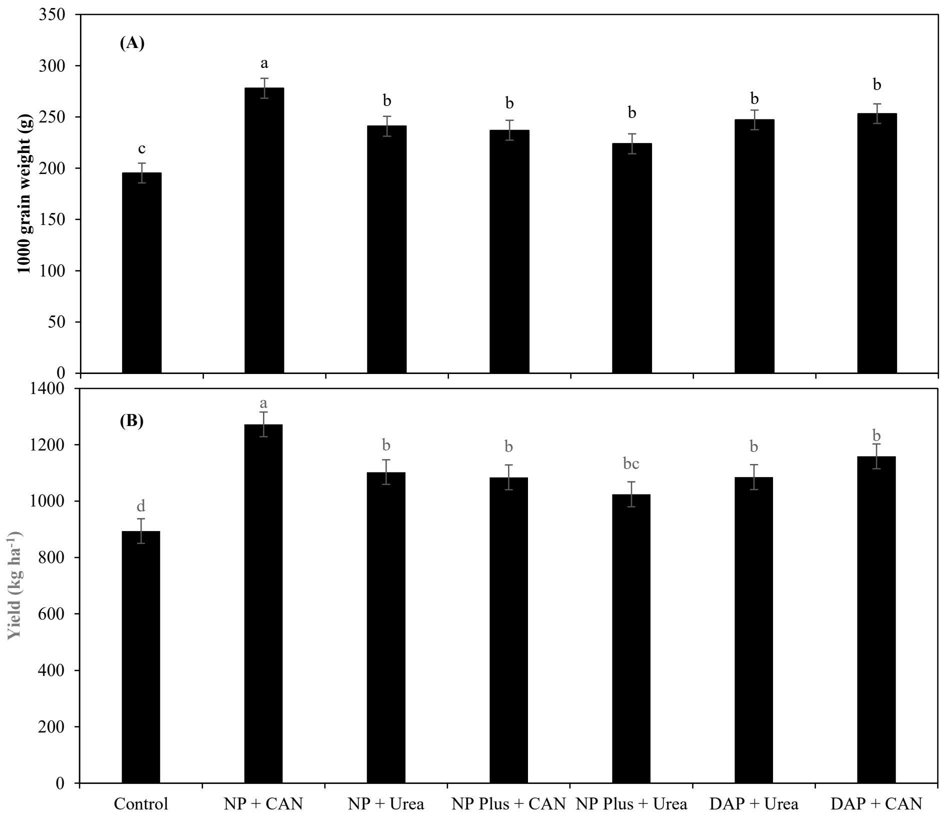


**Figure 3.** The 1000-grain weight (**A**) and maize grain yield (**B**) as influenced by N sources. All values are average of three years of experimental data ± S.E of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level.

### *3.3. Total N, $NH_4^+$-N, and $NO_3^-$-N Concentrations (mg $g^{-1}$ Dry Weight) and NRE of Maize as Influenced by Inorganic Nitrogen Supplies*

Under different inorganic N sources, maize leaves' total N, $NH_4^+$-N, and $NO_3^-$-N concentrations and NRE were considerably higher than they were under the control (Figures 4A–C and 5). Compared to the control, NP + urea, NP Plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN, the combined application of NP and CAN increased the leaf N by 66%, 10%, 18%, 19%, 17%, and 10%, respectively (Figure 4A). Similarly, NP and CAN supply enhanced the concentration of $NH_4^+$-N by 17% when compared with the control (Figure 4B). Furthermore, when compared with the NP Plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN, NP + CAN enhanced the $NH_4^+$-N content in maize leaves by 12%, 27%, 22%, 17%, and 11%, respectively (Figure 4A). In comparison to NP Plus + CAN, NP Plus + urea, DAP + urea, and DAP + CAN, combined application of NP and CAN raised the $NO_3^-$-N concentration in maize leaves by 19%, 33%, 47%, 45%, and 19%, respectively (Figure 4C).

The NRE of maize crop was influenced by different combinations of chemical fertilizers (Figure 5). Combined use of NP and CAN improved the NRE of maize by 28%, 13%, 15%, 19%, 15%, and 9% as compared to all other treatments, respectively.

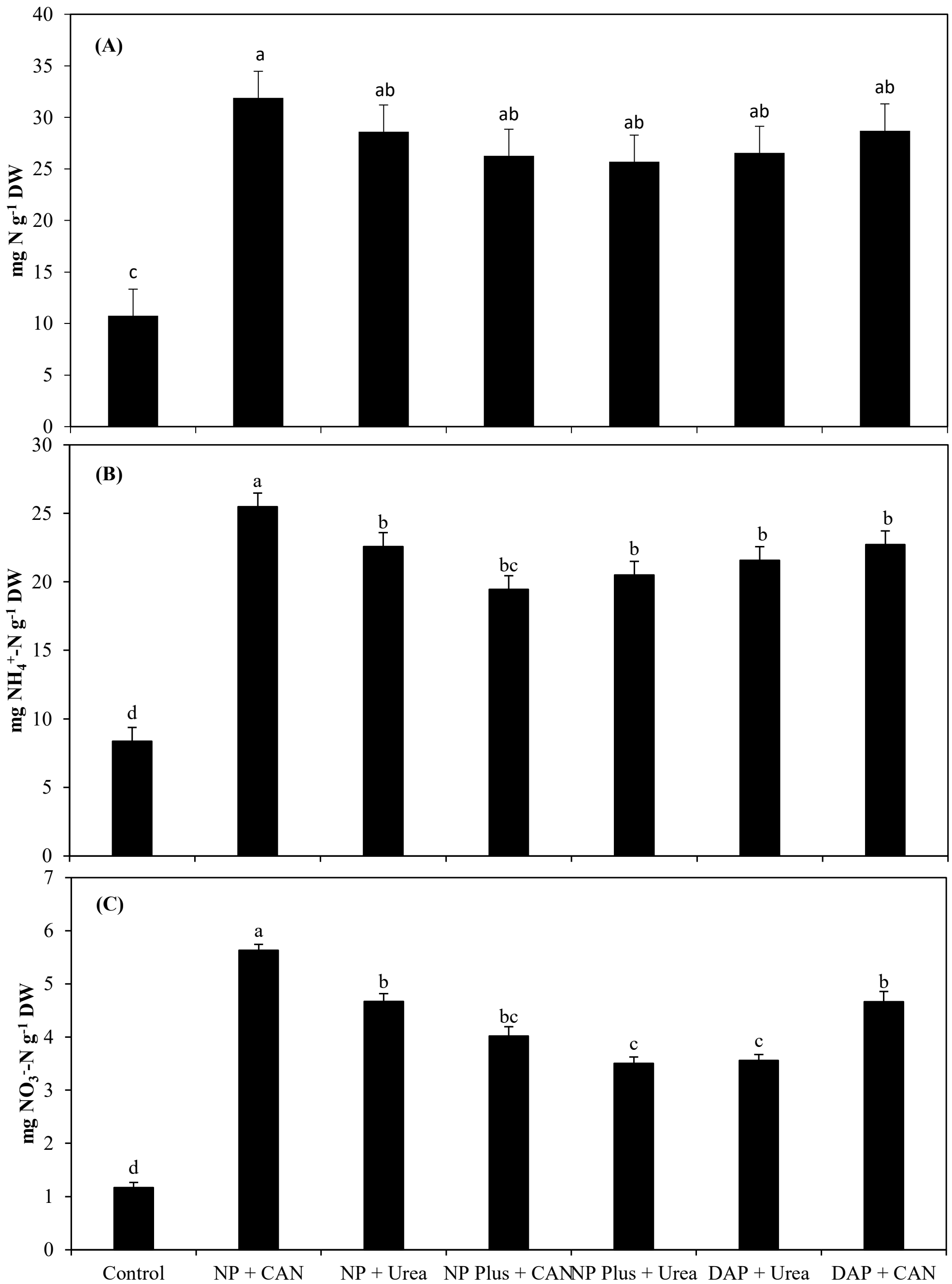


**Figure 4.** Total N (**A**), $NH_4^+$-N (**B**), and $NO_3^-$-N (**C**) concentrations (mg $g^{-1}$ dry weight) in maize leaves as influenced by N sources. All values are average of three years of experimental data ± S.E of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level.

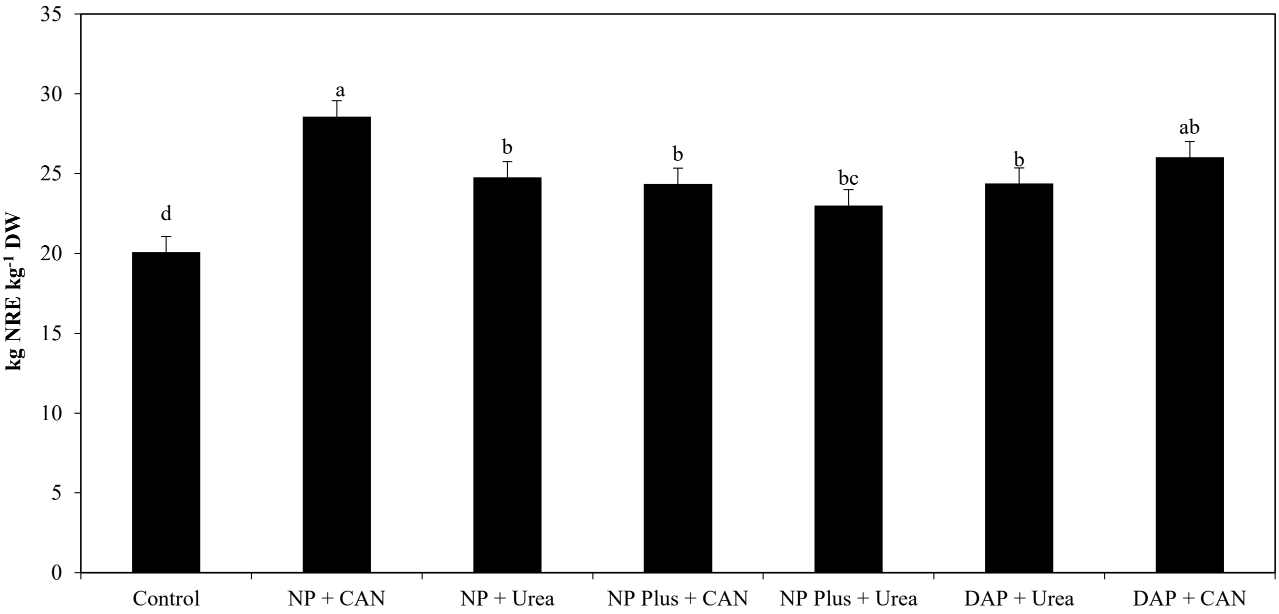


**Figure 5.** NRE (kg $kg^{-1}$ dry weight) of maize as influenced by N sources. All values are average of three years of experimental data ± S.E of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level.

### 3.4. Economic Analysis of Various Inorganic Fertilizers Supplies

Economic analyses in terms of the net return and ROI of hybrid maize under the influence of inorganic nitrogen and phosphorus supplies were assessed (Figure 6). Both net return and ROI were significant under all kinds of fertilizer supplies when compared with the control. These indicators were quantified on the basis of maize grain yield and cost of fertilizers. Maximum benefits were obtained in NP + CAN treatment, which were followed by NP + urea, DAP + urea, and DAP + CAN. Interestingly, ROI remained similar in all kinds of fertilizers combinations. This indicates that the additional cost of NP + CAN resulted in higher benefits in terms of maize yield.

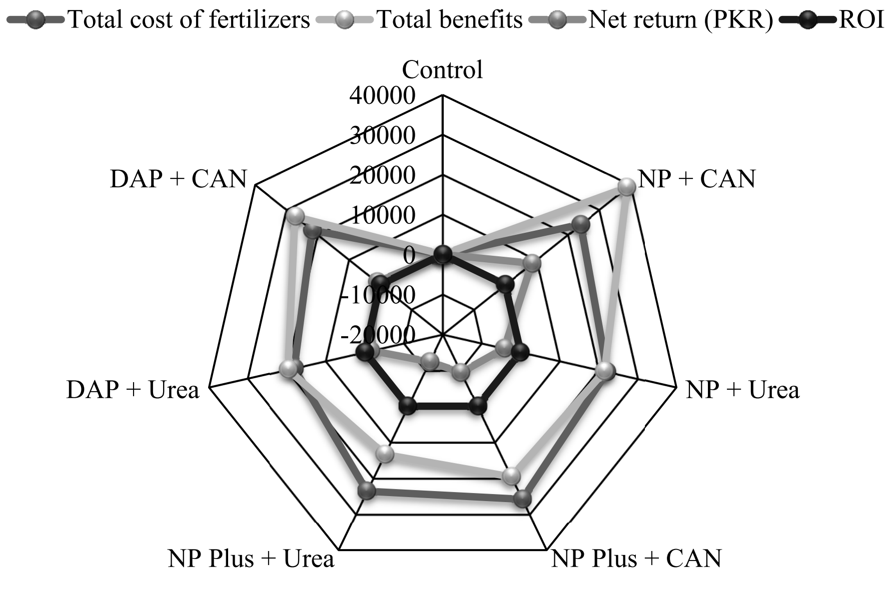


**Figure 6.** Quantitative analysis of different N sources with respect to additional cost of fertilizers, total benefits, net return, and ROI. All values are means of three replicates, whereas cost of fertilizer like SOP was subtracted from each treatment. Subsequently, net return of each treatment was calculated after obtaining the difference in control treatment.

### *3.5. Effect of Balance Application of $NH_4^+$-N and $NO_3^-$-N on Soil Physicochemical Properties and Mineral Nutrient Concentrations*

In the present study, NP fertilizer (pH 3.5) and CAN (pH 7.0) contained balanced proportions of $NH_4^+$-N and $NO_3^-$-N (Table S1). These balanced proportions in NP + CAN influenced the soil pH to some extent as compared to the control and all other fertilizer sources (Table 2). The change in the micro-environment of soil under the influence of NP + CAN influenced the physicochemical properties of the soil and nutrient availability, particularly mineral N and the other two inorganic N-forms. In comparison to all other fertilizer combinations, $NH_4^+$-N in the soils was much greater in the NP + CAN combination.

**Table 2.** Physicochemical properties of soils and mineral nutrient concentrations as influenced by N sources (post-harvest soil analysis). All values are average of three years of experimental data ± S.E of three replicates, whereas lower-case letters indicate significance among the treatments at $p \leq 0.05$ level. ns: not significant.

| Treatments | pH | EC (dSm$^{-1}$) | Sodium Adsorption Ratio | SOM (%) | Total Soil N (mg kg$^{-1}$ Dry Soil) | mg $NH_4^+$-N kg$^{-1}$ Dry Soil | mg $NO_3^-$-N kg$^{-1}$ Dry Soil | Available P (mg kg$^{-1}$ Dry Soil) | Extractable K (mg kg$^{-1}$ Dry Soil |
|---|---|---|---|---|---|---|---|---|---|
| Control | 8.38 ± 0.11 ns | 0.42 ± 0.06 $^{ab}$ | 0.6 ± 0.02 ns | 0.57 ± 0.05 $^{b}$ | 410.91 ± 17.22 $^{c}$ | 150.93 ± 7.08 $^{d}$ | 354.18 ± 10.29 $^{d}$ | 4.19 ± 0.18 $^{b}$ | 88.54 ± 3.29 $^{ab}$ |
| NP + CAN | 8.27 ± 0.10 ns | 0.51 ± 0.09 $^{a}$ | 0.7 ± 0.03 ns | 0.82 ± 0.05 $^{a}$ | 505.33 ± 18.17 $^{a}$ | 240.93 ± 6.50 $^{a}$ | 513.72 ± 14.78 $^{a}$ | 13.07 ± 0.28 $^{a}$ | 99.38 ± 5.03 $^{a}$ |
| NP + Urea | 8.26 ± 0.08 ns | 0.46 ± 0.07 $^{a}$ | 0.7 ± 0.08 ns | 0.87 ± 0.06 $^{a}$ | 420.76 ± 14.48 $^{c}$ | 206.77 ± 7.36 $^{b}$ | 471.04 ± 11.85 $^{ab}$ | 10.38 ± 0.37 $^{b}$ | 100.92 ± 4.85 $^{a}$ |
| NP plus + CAN | 8.28 ± 0.03 ns | 0.40 ± 0.02 $^{ab}$ | 0.7 ± 0.01 ns | 0.65 ± 0.05 $^{b}$ | 393.02 ± 12.76 $^{cd}$ | 176.19 ± 5.02 $^{c}$ | 430.12 ± 16.03 $^{c}$ | 10.50 ± 0.43 $^{b}$ | 102.47 ± 4.88 $^{a}$ |
| NP plus + Urea | 8.23 ± 0.10 ns | 0.50 ± 0.09 $^{a}$ | 0.7 ± 0.01 ns | 0.81 ± 0.03 $^{a}$ | 407.77 ± 14.17 $^{c}$ | 183.56 ± 4.98 $^{c}$ | 450.35 ± 17.11 $^{bc}$ | 11.43 ± 0.42 $^{ab}$ | 100.92 ± 3.31 $^{a}$ |
| DAP + Urea | 8.30 ± 0.06 ns | 0.55 ± 0.02 $^{a}$ | 0.6 ± 0.01 ns | 0.82 ± 0.07 $^{a}$ | 416.80 ± 7.37 $^{c}$ | 190.45 ± 4.38 $^{c}$ | 452.23 ± 14.36 $^{bc}$ | 10.38 ± 0.14 $^{b}$ | 94.73 ± 3.80 $^{ab}$ |
| DAP + CAN | 8.26 ± 0.06 ns | 0.40 ± 0.04 $^{ab}$ | 0.6 ± 0.01 ns | 0.80 ± 0.07 $^{a}$ | 446.39 ± 14.69 $^{b}$ | 209.54 ± 6.56 $^{b}$ | 477.79 ± 13.19 $^{ab}$ | 11.37 ± 0.54 $^{ab}$ | 90.09 ± 2.29 $^{ab}$ |

## 4. Discussion

### *4.1. The Improvement in Plant Growth and Grain Yield Was Attributed to Increased $NH_4^+$-N/$NO_3^-$-N Uptake as Well as NRE of Maize*

The aboveground biomass has a direct relationship with the availability of N [44]. The present study showed that the application of NP and CAN increased aboveground plant parts or growth attributes like plant height, cob fresh and dry weights, cob length, and no. of grain rows cob$^{-1}$ as compared to the conventional source of fertilization (urea and DAP). Furthermore, both NP and CAN fertilizers contain equivalent amounts of $NH_4^+$-N and $NO_3^-$-N, satiating plant needs through fast-acting $NO_3^-$-N and slow-release $NH_4^+$-N (Tables 2 and 3).

Nitrogen's primary role is to promote vegetative development, particularly plant height. This increase in maize plant height under varied N sources was attained by the increased N uptake that contributed to the plant development and increase in shoot and internode lengths and numbers, and thereby improved the growth and maize production [45,46]. According to Gasim [47], the increases in shoot length and no. of internodes are responsible for the increase in the number of leaves, which are the direct indicators of increased plant biomass. According to Asibi et al. [48], the growth of leaves under N application increased photosynthesis and the efficiency of biological processes including water and nutrient uptake. In the current study, co-application of both N-forms, viz., NP and CAN fertilizers, increased maize grain production in addition to enhancing plant development. Numerous studies [49,50] demonstrated that the co-provision of $NH_4^+$-N and $NO_3^-$-N increases plant nutrient availability that results in enhanced plant growth and development. Similar to plant growth, 1000-grain weight and maize yield were higher under CAN and NP application as compared to all the other treatments. An adequate supply of N is associated with aboveground biomass, which is a direct indicator of high maize yield [51,52]. Accordingly, the study of Eid et al. [53] reported that AN-based fertilizer improved the potato yield as compared to the urea. In the present study, CAN application improved the yield and its components (1000-grain weight) as compared to the urea and DAP or other combinations, which are correlated with high dry biomass production [32]. However, the response of yield and its components may vary under the acidic to alkaline strength of fertilizers.

**Table 3.** Pearson's correlation coefficients for interpretation of maize grain yield under the influence of fertilization. All the bold values represent significance among the attributes at $p \leq 0.01$ (**) and 0.05 (*) levels, respectively. ns: not significant.

| | Plant Height | Cob Length | No. of Rows Cob-1 | Cob FW | Cob DW | 1000-Grain wt. | Grain Yield | Leaf K | Leaf P | Total Leaf N | Leaf $NH_4^-$N | Leaf $NO_3^-$N | NUE | Soil pH | Soil EC | SAR | SOM | Soil P | Soil K | Total Soil N | Soil $NO_3^-$N | Soil $NH_4^-$N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant height | 1 | ** | * | ** | ** | ** | ** | ** | ** | ** | ** | ** | ** | ns | ns | ns | ** | ns | ns | ** | ** | ** |
| Cob length | **0.683** | 1 | ns | ** | ** | ** | ** | ** | ** | ** | ** | ** | ** | ns | ns | ns | * | ns | ns | ** | ** | ** |
| No. of rows $Cob^{-1}$ | **0.514** | 0.47 | 1 | ** | ** | ** | ** | ** | ** | ** | ** | ** | ** | ns | ns | ns | ns | ns | ns | ns | ** | ** |
| Cob FW | **0.745** | **0.846** | **0.638** | 1 | ** | ** | ** | ** | ** | ** | ** | ** | ** | * | ns | ns | * | * | ns | ** | ** | ** |
| Cob DW | **0.675** | **0.852** | **0.616** | **0.901** | 1 | ** | ** | ** | ** | ** | ** | ** | ** | ns | ns | ns | * | ns | ns | ** | ** | ** |
| 1000-grain wt. | **0.76** | **0.873** | **0.61** | **0.828** | **0.818** | 1 | ** | ** | ** | ** | ** | ** | ** | ns | ns | ns | * | ns | ns | ** | ** | ** |
| Grain yield | **0.865** | **0.754** | **0.806** | **0.911** | **0.878** | **0.843** | 1 | ** | ** | ** | ** | ** | ** | ns | ns | ns | * | ns | ns | ** | ** | ** |
| Leaf K | **0.634** | **0.732** | **0.563** | **0.798** | **0.837** | **0.676** | **0.704** | 1 | ** | ** | ** | ** | ** | * | ns | ns | ** | ns | ns | * | ** | ** |
| Leaf P | **0.751** | **0.786** | **0.637** | **0.881** | **0.901** | **0.865** | **0.834** | **0.878** | 1 | ** | ** | ** | ** | ns | ns | ns | ** | ns | ns | ** | ** | ** |
| Total leaf N | **0.697** | **0.805** | **0.605** | **0.906** | **0.928** | **0.863** | **0.772** | **0.905** | **0.978** | 1 | ** | ** | ** | * | ns | ns | ** | ** | ns | ** | ** | ** |
| Leaf $NH_4^-$N | **0.754** | **0.803** | **0.6** | **0.893** | **0.92** | **0.837** | **0.818** | **0.927** | **0.975** | **0.997** | 1 | ** | ** | * | ns | ns | ** | ns | ns | ** | ** | ** |
| Leaf $NO_3^-$N | **0.798** | **0.762** | **0.59** | **0.898** | **0.9** | **0.848** | **0.796** | **0.762** | **0.926** | **0.951** | **0.922** | 1 | ** | * | ns | ns | ** | ns | ns | ** | ** | ** |
| NUE | **0.754** | **0.826** | **0.599** | **0.866** | **0.852** | **0.992** | **0.891** | **0.668** | **0.861** | **0.863** | **0.841** | **0.895** | 1 | ns | ns | ns | ns | ** | ns | ** | ** | ** |
| Soil pH | −0.423 | −0.287 | −0.483 | **−0.524** | −0.39 | −0.369 | −0.41 | **−0.466** | −0.423 | **−0.46** | **−0.455** | **−0.447** | −0.42 | 1 | ns | ns | ns | ns | ns | ns | ns | ns |
| Soil EC | 0.167 | 0.136 | 0.204 | 0.185 | 0.152 | 0.194 | 0.203 | 0.22 | 0.229 | 0.229 | 0.241 | 0.168 | 0.141 | −0.17 | 1 | ns | ns | ns | ns | ns | ns | ns |
| SAR | 0.065 | 0.212 | 0.059 | 0.188 | 0.259 | 0.05 | 0.044 | 0.281 | 0.209 | 0.226 | 0.242 | 0.149 | 0.066 | 0.098 | 0.068 | 1 | ns | ns | ** | ns | ns | ns |
| SOM | **0.802** | **0.491** | 0.417 | **0.538** | **0.473** | **0.462** | **0.523** | **0.601** | **0.563** | **0.602** | **0.604** | **0.559** | 0.415 | −0.46 | 0.337 | 0.24 | 1 | ns | ns | * | * | ** |
| Soil P | 0.089 | 0.394 | 0.201 | **0.454** | 0.333 | 0.31 | 0.331 | 0.151 | 0.249 | 0.847 | 0.264 | 0.321 | **0.711** | 0.005 | 0.349 | 0.21 | 0.138 | 1 | ns | ** | * | * |
| Soil K | 0.045 | 0.085 | 0.358 | 0.229 | 0.292 | 0.086 | 0.092 | 0.285 | 0.27 | 0.282 | 0.291 | 0.229 | 0.133 | −0.16 | 0.267 | **0.61** | 0.093 | 0.140 | 1 | ns | ns | ns |
| Total soil N | **0.697** | **0.718** | 0.363 | **0.75** | **0.696** | **0.821** | **0.868** | **0.505** | **0.677** | **0.697** | **0.676** | **0.736** | **0.821** | −0.25 | 0.293 | 0.12 | **0.51** | **0.734** | 0.033 | 1 | ** | ** |
| Soil $NO_3^-$N | **0.711** | **0.764** | **0.607** | **0.851** | **0.857** | **0.849** | **0.798** | **0.763** | **0.883** | **0.896** | **0.89** | **0.865** | **0.857** | −0.28 | 0.331 | 0.21 | **0.518** | **0.522** | 0.183 | **0.813** | 1 | ** |
| Soil $NH_4^-$N | **0.775** | **0.727** | **0.64** | **0.82** | **0.765** | **0.876** | **0.807** | **0.629** | **0.835** | **0.832** | **0.806** | **0.881** | **0.901** | −0.4 | 0.34 | 0.08 | **0.573** | **0.456** | 0.258 | **0.839** | **0.865** | 1 |

Fertilizers with a pH of 3.5 and CAN of 7.0 may influence soil pH at the micro-environmental level and boost the availability of nutrients to plants. Because optimal soil pH varies from 6.5 to 7.5, the availability of N and P in Pakistani soils is an important constraint due to the high pH of the soils (8.0). Under such conditions, fertilizers having a neutral to alkaline pH may further reduce the nutrient availability to the plants after making insoluble complexes with Ca and Mg onto the soil surface [54]. Soil physicochemical research revealed that the application of CAN and NP fertilizers influenced soil pH more than other treatments, increasing nutrient availability in the soil and plant system. Furthermore, increasing nutrient availability from NP and CAN application promoted $NH_4^+$ absorption in plants and maize growth and production.

### *4.2. Fertilizers Containing Balanced Proportions of $NH_4^+$-N and $NO_3^-$-N Increase Soil N Mobility and thus NRE of Maize*

In the current investigation, soil $NO_3^-$-N concentrations were greater in the NP + CAN treatment than in the $NH_4^+$-N treatment. The application of nitrate-based fertilizers, as well as the oxidation of $NH_4^+$ to $NO_3^-$ under existing soil conditions, caused an increase in soil $NO_3^-$-N concentration. In addition, $NO_3^-$-N enters into the soil solution and becomes available to the plants after being repelled from negative sites of soil particles. It is evident from the literature that AN-based fertilizers resulted in an increase in the recovery of N to 95% as compared to the urea [55]. Further, N utilization has been reported higher in sugarcane under AN-based fertilizers (60%) as compared with the urea (45%) [18]. $NH_4^+$ is oxidized to $NO_3^-$ in warm, humid environments, which lowers the pH of the soil and makes $NH_4^+$ accessible to plants [56]. In general, mass flow and diffusion are the major methods used to deliver $NO_3^-$-N to the roots of plants. As a result, more $NO_3^-$-N will likely need to be present in the soil solution to support plant development [57,58]. Additionally, absorbed $NO_3^-$-N plays a crucial part in the process of filling grains and serves as a reservoir for N remobilization in situations of N deficit [59]. By contrast, $NO_3^-$-N absorption also occurs, which activates the reduction of $NO_3^-$ to $NH_4^+$ under the action of nitrate and nitrite reductase enzymes. The reduction of $NO_3^-$ to $NH_4^+$ is favored in $NH_4^+$ assimilation [60]. Consequently, plant growth and development are optimal when the plant receives N in both forms ($NH_4^+$ and $NO_3^-$) because of the sustaining of the constructive ionic balance inside the plant system [61,62]. Thus, fertilizers containing balanced proportions of $NH_4^+$ and $NO_3^-$ in the form of CAN and NP increase the N accumulation and NRE of plants (Table 2; Figure 5).

### *4.3. Net Return and Socioeconomic Impact of NP and CAN Fertilization*

Pakistan, being a developing country, requires assistance in addressing food security challenges. In this sense, chemical fertilizers are required for improving the country's agricultural crop yield. Excessive use of chemical fertilizers, on the other hand, not only reduces plant growth and productivity but also degrades soil health. As a result, it is critical to reduce the usage of extra fertilizers and other energy inputs by using the following strategies: the right source, right rate, and right timing [63]. In addition, economic analysis of the inputs is required to compare the effectiveness of different fertilizers in terms of net return. In the present study, the highest net return of the maize in NP + CAN is indicative of the right sources of fertilization. Moreover, both NP and CAN application did not affect ROI, which indicates that the end user earned a profit by using Sarsabz NP and CAN than all the other fertilizer sources. It has been suggested that farmers need to apply NP and CAN fertilizers in their soils instead of conventional fertilization.

To reveal the socioeconomic impact of NP and CAN fertilization on maize crop, Government of Punjab, Pakistan arranged a maize yield competition in 2018 where the autumn maize growers of the year of 2018 won the yield competition. Application of NP and CAN resulted in the highest maize yield in comparison to DAP and urea, and even the runners-up were NP and CAN users (Tables 4 and S2). Similarly, the technical team of the Fatima Group also conducted research trials to evaluate the effectiveness of NP and

CAN on maize yield in different districts of Punjab, Pakistan and a considerable no. of framers are now using NP and CAN sources of fertilization instead of DAP and urea as the increased net return has created awareness among the people during the years of 2018–2020. These results also strengthen the idea of the right proportion of $NH_4^+/NO_3^-$ in the form of CAN and NP fertilizer sources for increased maize yield.

**Table 4.** Approved data by Punjab Agriculture Department, Government of Punjab, Pakistan where combined application of NP and CAN resulted in highest yield in comparison to conventional fertilizers sources. Different farmers at different locations of Sahiwal Division also won maize yield competition by Government of Punjab, Pakistan.

| Sr. # | Farmer | Address with GPS Coordinates | Crop | Yield (kg Acre$^{-1}$) | Reference |
|---|---|---|---|---|---|
| 1 | Faisal Ali | 34/12 L Chichawatni Sahiwal, Punjab 30°28′48″ N, 72°43′11.9994″ E | Autumn Maize | 3840 | Maize Yield Competition [64], Government of Punjab, Pakistan |
| 2 | Ashfaq Ahmed Joyia | MouzaJoyia Tehsil Okara, Punjab 31°0′36″ N, 73°30′0″ E | Autumn Maize | 3680 | - |
| 3 | Malik Ali Gohar | Chak# 96/D Tehsil Pakpattan, Sahiwal, Punjab 30°28′11.9994″ N, 73°10′12″ E | Autumn Maize | 3280 | - |
| 4 | Ghulam Mujtaba | Chak# 50/SP Pakpattan, Arifwala, Sahiwal, Punjab 30°25′47.9994″ N, 73°10′12″ E | Autumn Maize | 3280 | - |
| 5 | Muhammad Sharif | 33/12 L Chichawatni Sahiwal, Punjab 30°27′36″ N, 72°42′35.9994″ E | Autumn Maize | 3160 | - |
| 6 | Abid Rasheed | Chak# 4/AL RenalaKhurd, Okara, Punjab 30°56′24″ N, 73°42′0″ E | Autumn Maize | 3280 | - |
| 7 | Masood Saeed | Chak# 56/5-L Tehsil Sahiwal, Punjab 30°42′36″ N, 73°15′36″ E | Autumn Maize | 3160 | - |
| 8 | Muhamamd Arshad | Tehsil Sahiwal, Punjab 30°38′24″ N, 73°8′24″ E | Autumn Maize | 3160 | - |
| 9 | Nawab Khan | Chak# 3/EB Jiwan Shan Pakpattan, Punjab 30°18′35.9994″ N, 73°12′0″ E | Autumn Maize | 3240 | - |
| 10 | Muhammad Asif | BalaraLakhoKa Tehsil Arifwala, Punjab 30°17′23.9994″ N, 73°4′11.9994″ E | Autumn Maize | 3200 | - |

Source: Maize Yield Competition [64], Government of Punjab, Commissioner's Office, Sahiwal, Punjab, Pakistan.

## 5. Conclusions and Recommendations

Our findings indicate that the fertilizers containing equal amounts of $NH_4^+$-N and $NO_3^-$-N (1:1) increased soil inorganic N forms, notably $NO_3^-$-N, which was absorbed by the plants as $NH_4^+$-N and improved maize grain production. It has been proposed that fertilizers containing balanced amounts of $NH_4^+$-N and $NO_3^-$-N (1:1) can be utilized instead of conventional fertilizer sources. The enhanced N uptake by maize further resulted in positive interactions with other nutrients like P and K. This study will provide a scientific basis to handle the high-pH soils in the future by following the 4R stewardship (right source, right rate, right time, and right place). It will also improve soil health, minimize environmental issues, and ultimately enhance yield. This study also recommends Government and other stakeholders to provide awareness on better nutrient management of agricultural crops.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/su151612547/s1, Table S1: Chemical reaction and nutrient content (%) of chemical fertilizers applied into the soils; Table S2: Highest maize grain yield obtained during [1] and 2020–2021 by the use of NP and CAN fertilizers. Reference [64] is cited in Supplementary Materials file.

**Author Contributions:** S.M., N.K., M.J. and R.N. designed the experiment, whereas S.M., M.J. and R.N. performed the experiment. M.S. and S.M. compiled the data and carried out lab analyses. S.M., M.H.S., M.A. and M.T. made a statistical evaluation of the data and interpretation, whereas S.M., M.S. and S.H. wrote the original draft. S.M., S.J., N.K. and K.S.K. critically improved the intellectual content of the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by Researchers Supporting Project number (RSP2023R347), King Saud University, Riyadh, Saudi Arabia.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data are available with a reasonable request to the corresponding author.

**Acknowledgments:** The authors would like to extend their sincere appreciation to the Researchers Supporting Project number (RSP2023R347), King Saud University, Riyadh, Saudi Arabia and Technical Services Department, Marketing Division, Fatima Fertilizer Company Limited for supporting this work. The authors also pay thanks to Shahid Iqbal for his help in data collection and lab analyses.

**Conflicts of Interest:** There are no conflict of interest among the authors.

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