Nepheline Syenite and Phonolite as Alternative Potassium Sources for Maize

Thiago Assis Rodrigues Nogueira 1,2,*, Bruno Gasparoti Miranda 1,2, Arshad Jalal 2,*, Luis Gustavo Frediani Lessa 3, Marcelo Carvalho Minhoto Teixeira Filho 2,*, Nericlenes Chaves Marcante 4, Cassio Hamilton Abreu-Junior 5, Arun Dilipkumar Jani 6,*, Gian Franco Capra 7,*, Adônis Moreira 8 and Éder de Souza Martins 9,*

Abstract: Some silicate rocks are a rich source of potassium (K), with the possibility for use in agriculture. The present study aimed to evaluate the agronomic efficiency index (AEI) of nepheline syenite (NS) and phonolite (PN) rocks in comparison with potassium chloride (KCl) as a K source in maize production. An experiment was conducted in a greenhouse in Ilha Solteira, São Paulo, Brazil. A maize hybrid was grown in 8 L pots filled with 6 kg of soil with a low K concentration and contrasting physical attributes (medium and sandy texture). A completely randomized design in a 3 × 6 factorial scheme was used, consisting of three K sources (NS, PN, and KCl) and six rates (0, 50, 100, 150, 200, and 400 mg kg⁻¹) with four replications. All plants were harvested 45 days after emergence to evaluate biomass production, macronutrient (N, P, K, Ca, Mg, and S) concentration and uptake, stem diameter, and leaf chlorophyll index. After crop harvest, soil was collected for further chemical evaluation, which included organic matter (OM), pH, cation exchange capacity (CEC), H⁺Al, Al, sum of bases (SB), base saturation (BS), P, K, Ca, Mg, and S, in both soils. The increase in NS and PN rates provided linear growth of shoot dry matter. Leaf macronutrient concentrations were similar for NS and PN compared to KCl. All three K sources (NS, PN, and KCl) increased K accumulation in maize plants. Maize treated with KCl had the largest AEI, followed by PN and NS. However, the results indicated similar AEI with both rocks as a K source for maize, especially with application of the highest K rates. This research demonstrated the efficiency of NS and PN as alternative K sources for maize.

Keywords: Zea mays L.; rock powder; igneous rock; agronomic efficiency index

1. Introduction

Brazilian agriculture has experienced great progress in recent years, stemming from technological innovations that are the result of extensive and widespread research efforts.
One of the most important components in achieving a high yield has been the use of fertilizers that aim to correct soil chemical attributes and increase the productive potential of crops through the supply of nutrients for crop development [1,2].

Among these nutrients, potassium (K) is generally applied through K fertilizers with potassium chloride (KCl) being the most used source due to its high concentration (60% K2O) [3,4]. However, the accentuated use of this fertilizer can cause severe adverse environmental impacts, since about half the amount applied may be lost through leaching, resulting in the contamination of rivers and groundwater [2,5]. The risk of K losses by leaching may be even greater in sandy soils, since the soil colloidal fraction may not retain large K concentrations [6].

In addition, excessive application of K salts increases cell external osmotic pressure, which may hinder absorption of water by seeds and radicles [7] thereby causing a reduction in seed germination. Another cause for concern is that Brazilian agricultural production is highly dependent on the import of K fertilizer, which compromises Brazil’s food security. National fertilizer production in 2018 was around 8.2 million tons and imports amounted to 27.4 million tons [8], of which 10.5 million tons were KCl [9].

Brazil is abundant in several silicate rocks, which can possibly be used as sources of K in a ground-up form [10]. These rocks weather very slowly in their aggregate form. However, when applied to soils rich in organic matter, high biological activity, and large edaphic faunal populations, these rock minerals may break down relatively fast with nutrients such as K, making plants more available [11].

The use of these silicate agrominerals (soil remineralizers) is intended to reduce the dependence on the use of imported fertilizers [12,13]. In recent years, this practice has been investigated for its agronomic potential, especially in the supply of K in several regions of Brazil [12,14,15] and the results have demonstrated the benefits of using rocks as sources of nutrients, leading to a good agronomic efficiency index (AEI) for crops [11,12,16,17].

Several studies were conducted with these materials as a source of K in the cultivation of maize (Zea mays L.) with promising results [18–21]. Maize is one of the most widely cultivated cereals globally, and K is the second most required nutrient [22]. Therefore, K fertilization is essential to produce acceptable yields.

Igneous rocks like nepheline syenite and phonolite contain considerable amounts of K2O, which can be considered an alternative source of K in fertilizer markets. However, there are few studies evaluating the potential use of these two K sources in agricultural soils. Thus, the objective of this study was to evaluate the agronomic efficiency of nepheline syenite and phonolite in comparison to KCl as sources of K for maize on two soils with different chemical and physical attributes.

2. Materials and Methods

2.1. Pot Experiment

The experiment was conducted under greenhouse conditions at the School of Engineering of Sao Paulo State University (UNESP), Ilha Solteira, State of Sao Paulo, Brazil. Pots with 8 L soil capacity were used and filled with a Typic Quartzipsamment (TQ) and Rhodic Hapludox (RH) [23] collected in the 0 to 20 cm deep layer in the municipality of Selvícia, State of Mato Grosso do Sul, Brazil. The chemical and physical attributes of these soils are described in Table 1.

Lime was applied as CaCO3 and MgCO3 30 days before planting to maintain the Ca:Mg ratio of 3:1, thereby increasing base saturation up to 70% [24]. In the same period, sources of K (nepheline syenite: total phosphorus (P2O5) < 1% and K2O = 8.0%; phonolite: total phosphorus (P2O5) < 1% and K2O = 9.1%; and potassium chloride (KCl) = 60% K2O) were applied. Nepheline syenite and phonolite are used as finely ground soil remineralizers (granulometry < 0.3 mm) and were obtained in Lavrinhas-SP and Poços de Caldas-MG, Brazil, respectively. Subsequently, the soil samples were homogenized, packed in plastic bags, and incubated for 30 days with moisture concentration maintained at 60% of the
water holding capacity. After the period of incubation, soil samples were collected from each pot to determine the pH.

The experiment was set up using a completely randomized design with four replications. The treatments were arranged in a $3 \times 6$ factorial scheme, consisting of three K sources (nepheline syenite, phonolite, and KCl) which were applied at six rates (0, 50, 100, 150, 200, and 400 mg kg$^{-1}$). The pots received 100 mg kg$^{-1}$ of N as ammonium sulfate (AS, 20% N) and 200 mg kg$^{-1}$ of P via monoammonium phosphate (MAP, 52% of P$_2$O$_5$) as recommended by Malavolta [25] before planting.

Table 1. Chemical and physical attributes $^1$ of soil samples used in the experiment (Mean ± standard deviation; $n = 3$).

| Attributes | Units | Soils $^2$ |
|------------|-------|------------|
| pH (CaCl$_2$) | - | TQ | RH |
| | | 5.1 ± 0.15 | 4.3 ± 0.06 |
| SOM | g dm$^{-3}$ | 13 ± 0.58 | 21 ± 2.31 |
| P | mg dm$^{-3}$ | 2 ± 0.58 | 7 ± 0.58 |
| K$^+$ | mmol dm$^{-3}$ | 0.3 ± 0.06 | 0.7 ± 0.15 |
| Ca$^{2+}$ | mmol dm$^{-3}$ | 7 ± 0.00 | 9 ± 2.65 |
| Mg$^{2+}$ | mmol dm$^{-3}$ | 7 ± 0.58 | 6 ± 1.15 |
| S-SO$_4$ | mg dm$^{-3}$ | 4 ± 1.73 | 6 ± 0.58 |
| Al$^{3+}$ | mmol dm$^{-3}$ | 0.33 ± 0.47 | 9 ± 4.62 |
| H+Al | mmol dm$^{-3}$ | 15 ± 0.58 | 45 ± 5.77 |
| SB | mmol dm$^{-3}$ | 14.0 ± 0.61 | 16.0 ± 3.92 |
| BS % | | 48 ± 2.00 | 26 ± 7.23 |
| CEC | mmol dm$^{-3}$ | 29.3 ± 0.52 | 61.3 ± 1.93 |
| B | mg dm$^{-3}$ | 0.05 ± 0.02 | 0.20 ± 0.02 |
| Cu (DTPA) | mg dm$^{-3}$ | 0.7 ± 0.06 | 2.5 ± 0.10 |
| Fe (DTPA) | mg dm$^{-3}$ | 17 ± 0.00 | 24.5 ± 2.52 |
| Mn (DTPA) | mg dm$^{-3}$ | 5.4 ± 0.31 | 30.0 ± 3.01 |
| Zn (DTPA) | mg dm$^{-3}$ | 0.2 ± 0.06 | 0.7 ± 0.06 |
| Sand (>0.002 and <0.05 mm) | g kg$^{-1}$ | 869 ± 2.52 | 544 ± 4.51 |
| Silt (>0.002 and <0.05 mm) | g kg$^{-1}$ | 33 ± 6.03 | 116 ± 3.61 |
| Clay (<0.002 mm) | g kg$^{-1}$ | 96 ± 3.51 | 340 ± 4.36 |

$^1$Analyses performed in accordance with official procedures [26,27]. $^2$Values on an air-dried basis. TQ = Typic Quartzipsamment. RH = Rhodic Hapludox. SOM = soil organic matter; CEC = cation-exchange capacity; SB = sum of bases; BS = base saturation.

Six seeds of maize hybrid (DOW 2B 710 PW®) were sown per pot and after nine days of seedling emergence (DSE), thinning was performed, leaving two plants per pot. A solution containing micronutrients (1.0 mg kg$^{-1}$ of B as boric acid, 2.0 mg kg$^{-1}$ of Cu as copper sulphate, 5.0 mg kg$^{-1}$ of Zn as zinc sulphate and 3.0 mg kg$^{-1}$ of Mn as manganese sulphate) was applied 10 DSE. A cover fertilization was performed by applying 100 mg kg$^{-1}$ of N via ammonium sulfate. These applications were made in all treatments.

2.2. Leaf Chlorophyll Index, Plant Height, and Stem Diameter

Leaf chlorophyll index (LCI) was evaluated in the middle third fully expended leaves of two plants per pot at 45 DSE, using portable ClorofiLOG equipment (model CFL 1030, Falkor). Plant height (cm) and stem diameter (mm) were obtained at 10 cm from ground level.

2.3. Chemical Analysis

2.3.1. Plant Analysis

Shoots were cut close to the ground 45 days after the emergence of maize (BBCH growth stage 3: stem elongation), washed in tap water, packed in paper bags, and placed in an air-forced oven at 60 °C for 72 h. After drying, the material of each treatment was
weighed to obtain plant dry matter (DM) and then ground in a Wiley mill to determine concentration of N, P, K, Ca, Mg, and S [28]. The concentration of N was determined by steam distillation in the sulfuric digestion extract. The concentrations of K, Ca, and Mg were determined by atomic absorption spectrophotometry (model: Perkin-Elmer, AAS-700, Norwalk, CT, USA), P by colorimetry, and S by turbidimetry. The accumulation of K (mg per plant) was calculated based on the shoot K concentration (g kg\(^{-1}\)) and shoot dry matter (g per plant) of each treatment.

2.3.2. Soil Analysis

After harvesting plants, soil samples were collected to assess soil chemical attributes according to the methods described by Raij et al. [26] The soil pH values were determined potentiometrically in air-dried thin soil (ADTS) suspensions in a 0.01 mol L\(^{-1}\) CaCl\(_2\) solution in a 1:2.5 soil-solution ratio. The organic matter was determined after oxidation with K\(_2\)Cr\(_2\)O\(_7\) in the presence of H\(_2\)SO\(_4\) and titration of excess dichromate with 0.4 mol L\(^{-1}\) of Fe (NH\(_4\))\(_2\) (SO\(_4\))\(_2\)-6H\(_2\)O. Exchangeable aluminum (Al\(^{3+}\)) was extracted with 1 mol L\(^{-1}\) and then titrated with 0.025 mol L\(^{-1}\) of NaOH. Exchangeable calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) were extracted with ion exchange resin and quantified by atomic absorption spectrophotometry (AAS). Exchangeable potassium (K\(^{+}\)) and phosphorus (P) were also extracted by resin, K\(^{+}\) being determined by flame photometry and P by colorimetry. Potential acidity (H\(^{+}\)Al\(^{3+}\)) was estimated by a pH SMP method. Sulfur was extracted by 0.01 mol L\(^{-1}\) solution of Ca(H\(_2\)PO\(_4\))\(_2\) and subsequent measurement of turbidity formed by the precipitation of sulfate by barium chloride in colorimetry. These results were used to calculate the cation exchange capacity (CEC) at pH 7.0, sum of bases (SB), and base saturation (BS%).

2.4. Agronomic Efficiency Index

The agronomic efficiency index (AEI) of K sources was calculated according to the equation described by Goedert et al. [29]:

\[
\text{AEI} (%) = \frac{\text{SDM ASP} - \text{SDM CT}}{\text{SDM SAF} - \text{SDM CT}} \times 100
\]

where SDM ASP = shoot dry matter of alternative source of potassium, SDM CT = shoot dry matter of control treatment, and SDM SAF = shoot dry matter with standard applied fertilizer.

2.5. Statistical Analysis

The results were subjected to a normal data distribution test and then to the analysis of variance (ANOVA), F test, and subsequent polynomial regression studies for significant interactions and/or effect of K rates between variables evaluated in the soil and plants [30].

3. Results and Discussion

The pH values were changed after the period of 30 days of incubation of limestone and K sources in soils (Table 2). The pH values prior to incubation were 5.1 and 4.3 for Typic Quartzipsamment (TQ) and Rhodic Hapludox (RH), respectively (Table 1), and after the incubation period increased to 5.5 and 5.6 (Table 2). Thus, it was noted that there was an effective correction of the soil pH within the 5.5 to 6.5 range as indicated, suitable for the cultivation of maize [31]. After maize cultivation, there were interactions between K sources and rates for the values of H\(^{+}\)Al\(^{3+}\), and CEC in TQ and pH in the RH (Table 3). The pH, H\(^{+}\)Al\(^{3+}\), and Al\(^{3+}\) differed between the K sources in TQ, while in the RH soil, a difference was noted only for the pH and H\(^{+}\)Al\(^{3+}\), which demonstrates a similarity between nepheline syenite and phonolite sources for the chemical attributes in two investigated pedotypes.
Table 2. pH values (CaCl2) obtained after 30 days of incubation and before sowing the maize crop according to the treatments studied.

| Treatments                          | Typic Quartzipsamment | Rhodic Hapludox |
|-------------------------------------|-----------------------|-----------------|
|                                     | Sandy Texture         | Medium Texture  |
| Source (F)                          |                       |                 |
| Nepheline syenite                   | 5.5                   | 5.5             |
| Phonolite                           | 5.4                   | 5.4             |
| KCl                                 | 5.5                   | 5.5             |
| F-test                              | **1.52 NS**           | NS              |
| K rates (DK)                        |                       |                 |
| 0 (mg kg\(^{-1}\))                 | 5.5                   | 5.6             |
| 50 (mg kg\(^{-1}\))                | 5.5                   | 5.5             |
| 100 (mg kg\(^{-1}\))               | 5.5                   | 5.6             |
| 150 (mg kg\(^{-1}\))               | 5.5                   | 5.6             |
| 200 (mg kg\(^{-1}\))               | 5.4                   | 5.5             |
| 400 (mg kg\(^{-1}\))               | 5.4                   | 5.5             |
| F-test                              | **5.25 **             | 1.87 NS         |
| F-test (P) × (DK)                   | **2.06 **             | 1.42 NS         |
| Means                               | 5.5                   | 5.6             |
| CV (%)                              | 1.3                   | 1.6             |

**, * and NS—Significant at 1 and 5% probability and not significant, respectively.

Regarding the pH values, there was no difference between nepheline syenite and phonolite with both of the soils being higher than with application of KCl. This fact may be related to a greater absorption of K and other exchangeable bases (Ca and Mg) with greater release of H\(^+\) ions by plants to the soil solution [12]. There were differences between two soils with KCl application. The effect was only detected on pH in the TQ and may have been due to higher concentrations of Al\(^{3+}\) (1.9 mmol c dm\(^{-3}\)), while the absence of an effect in the RH might be explained by the pH values being above 5.2 (Table 3), with Al\(^{3+}\) precipitated in soil [32]. The rates of K had a significant effect on pH, H+Al, Al\(^{3+}\) and CEC (Table 4). The increasing rates in phonolite increased pH values with a variation of 4.9 to 5.3 in the TQ and from 5.3 to 5.6 in the RH (Table 4). These values are classified as high to medium acidity for TQ and average to low acidity in RH [33]. The rates of KCl were effective only in TQ, with a linear increase for H+Al and CEC and a quadratic effect for Al\(^{3+}\) with a maximum point in the rates of 260 and 290 mg kg\(^{-1}\) respectively (Table 5).

There was an interaction between sources and rates of K for the concentrations of K, Ca, Mg, and S in the TQ, whereas it was with K and S in RH (Table 6). With the exception of P and Mg concentrations in the TQ and Mg concentrations in the RH, there was variations in macronutrient concentrations for the investigated K sources.
Table 3. Effects of treatments on some chemical attributes of the soil after maize cultivation in Typic Quartzipsamment, and in Rhodic Hapludox, depending on the application of sources and rates of K.

| Treatments                        | Typic Quartzipsamment | Rhodic Hapludox |
|-----------------------------------|------------------------|-----------------|
|                                   | OM pH H+Al Al SB CEC BS| OM pH H+Al Al SB CEC BS |
| Source (F) g dm⁻³ CaCl₂ mmol dm⁻³ | % g dm⁻³ CaCl₂ mmol dm⁻³ | % |
| Nepheline syenite                 | 11.8 4.9 a 18.7 a 1.0 b 17.3 ab 36.1 48.1 ab 17.6 b 5.3 a| 27.2 b 0 51.5 78.7 65.4 a |
| Phonolite                         | 11.8 5.0 a 17.0 b 0.2 c 17.6 a 35.1 50.6 a 18.2 a 5.3 a| 27.7 b 0 52.6 80.3 65.4 a |
| KCl                               | 11.7 4.6 b 19.1 a 1.9 a 15.9 b 34.6 45.2 b 18.6 b 5.2 b| 30.3 a 0 50.1 80.4 62.1 b |
| F-test                            | 0.11 NS 26.40 ** 5.59 ** 21.5 ** 3.97 * 1.47 NS 8.33 ** 10.99 ** 10.45 **| 6.47 ** 0.00 NS 1.60 NS 0.67 NS 7.36 ** |
| K rates (DK) (mg kg⁻¹)            |                          |                 |
| 0                                 | 11.5 4.8 18.4 1.0 15.0 33.9 45.1 18.0 5.3| 28.0 0 52.7 80.7 65.4 |
| 50                                | 11.9 4.8 18.6 0.9 15.7 34.3 45.5 18.0 5.2| 29.0 0 50.5 79.5 63.5 |
| 100                               | 11.8 4.8 18.2 1.3 16.6 34.9 47.6 18.1 5.3| 28.5 0 49.2 77.7 63.2 |
| 150                               | 12.0 4.9 17.6 0.9 17.5 35.2 49.5 18.0 5.3| 27.0 0 51.6 78.6 65.6 |
| 200                               | 11.7 4.8 18.0 1.2 18.0 36.8 51.0 18.2 5.3| 29.4 0 49.2 79.1 62.8 |
| 400                               | 11.9 4.9 19.0 0.9 18.8 37.0 49.0 18.5 5.3| 28.7 0 49.7 83.2 65.3 |
| F-test                            | 0.73 NS 0.70 NS 0.52 NS 0.56 NS 5.25 ** 2.65 * 3.09 * 1.03 NS 0.75 NS 0.86 NS 0.00 NS 1.96 NS 1.41 NS 1.65 NS |
| F-test (F) × (DK)                  | 7.03 ** 1.51 NS 2.86 ** 2.09 * 3.28 ** 4.92 ** 1.47 NS 1.42 NS 4.66 ** 1.72 NS 0.00 NS 1.60 NS 0.84 NS 2.48 * |
| Means                             | 11.8 4.8 18.3 1.0 16.9 35.3 48.0 18.1 5.3| 28.4 0 51.4 79.8 64.3 |
| CV (%)                            | 5.0 4.6 12.4 80.4 12.7 8.3 9.5 4.1 2.1| 11.2 0 9.4 7.0 5.2 |

**, *, and NS—Significant at 1 and 5% probability and not significant, respectively. Means followed by the same letter do not differ by Tukey’s test at 5% probability. OM = organic matter; CEC = cation-exchange capacity; SB = sum of bases; BS = base saturation.
Table 4. Chemical attributes of a Typic Quartzipsamment and a Rhodic Hapludox after maize cultivation, depending on the rates and sources of K.

| K Rates | Typic Quartzipsamment | Rhodic Hapludox | F-test |
|---------|-----------------------|----------------|--------|
|         | OM | pH | H+Al | Al | SB | CEC | BS | OM | pH | H+Al | Al | SB | CEC | BS |
| mg kg⁻¹ | g dm⁻³ | CaCl₂ | mmol dm⁻³ |      |      |      | % | g dm⁻³ | CaCl₂ | mmol dm⁻³ | % |
| 0      | 12.50 | 4.80 | 22.50 | 1.50 | 16.45 | 38.95 | 42.15 | 16.75 | 5.27 | 27.25 | 0.00 | 51.47 | 78.72 | 65.42 |
| 50     | 12.25 | 4.92 | 19.00 | 0.50 | 16.55 | 35.55 | 46.57 | 17.75 | 5.40 | 27.25 | 0.00 | 50.97 | 78.22 | 65.22 |
| 100    | 11.75 | 4.80 | 19.50 | 1.75 | 17.67 | 37.17 | 47.45 | 18.00 | 5.45 | 27.25 | 0.00 | 47.72 | 74.97 | 63.67 |
| 150    | 11.25 | 5.00 | 16.75 | 1.00 | 17.20 | 33.95 | 50.70 | 17.50 | 5.45 | 26.50 | 0.00 | 55.20 | 81.70 | 67.57 |
| 200    | 11.50 | 5.02 | 16.75 | 0.75 | 17.67 | 34.42 | 51.35 | 17.75 | 5.40 | 27.57 | 0.00 | 52.65 | 78.40 | 67.05 |
| 400    | 12.00 | 5.05 | 18.00 | 0.50 | 18.72 | 36.72 | 50.85 | 18.00 | 5.22 | 29.50 | 0.00 | 51.15 | 80.65 | 63.47 |

**F-test**

|         | 1.39 NS | 2.87 NS | 6.39 NS | 2.16 NS | 2.66 NS | 0.57 NS | 4.52 * | 2.83 NS | 9.56 ** | 0.94 NS | 0.00 NS | 0.80 NS | 0.65 NS | 0.31 NS |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 0      | 11.25 | 4.97 | 15.75 | 0.75 | 15.17 | 30.92 | 49.02 | 18.75 | 5.32 | 29.50 | 0.00 | 52.90 | 82.40 | 64.25 |
| 50     | 12.50 | 4.87 | 18.50 | 0.75 | 17.17 | 35.67 | 48.10 | 17.50 | 5.27 | 28.00 | 0.00 | 52.40 | 80.40 | 65.20 |
| 100    | 12.25 | 5.05 | 17.00 | 0.25 | 17.20 | 34.20 | 50.22 | 18.00 | 5.32 | 28.00 | 0.00 | 52.40 | 80.40 | 65.15 |
| 150    | 11.50 | 5.12 | 16.75 | 0.00 | 20.92 | 37.67 | 55.47 | 18.25 | 5.27 | 27.25 | 0.00 | 48.90 | 76.15 | 64.27 |
| 200    | 11.25 | 5.10 | 17.25 | 0.00 | 17.17 | 34.20 | 49.92 | 18.25 | 5.40 | 28.75 | 0.00 | 52.65 | 81.40 | 64.67 |
| 400    | 12.25 | 5.30 | 17.25 | 0.00 | 18.00 | 35.25 | 51.12 | 19.00 | 5.60 | 25.00 | 0.00 | 56.40 | 81.40 | 68.95 |

**F-test**

|         | 0.62 NS | 6.73 * | 0.10 NS | 2.16 NS | 2.17 NS | 1.74 NS | 0.68 NS | 2.83 NS | 17.66 ** | 3.46 NS | 0.00 NS | 1.49 NS | 0.00 NS | 3.92 NS |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 0      | 11.00 | 4.75 | 17.00 | 1.00 | 13.65 | 30.65 | 44.27 | 18.75 | 5.40 | 27.25 | 0.00 | 53.90 | 81.15 | 66.52 |
| 50     | 11.00 | 4.65 | 18.50 | 1.50 | 13.45 | 31.95 | 41.97 | 18.75 | 5.17 | 31.75 | 0.00 | 48.40 | 80.15 | 60.20 |
| 100    | 11.50 | 4.67 | 18.25 | 2.00 | 15.10 | 33.35 | 45.37 | 18.50 | 5.22 | 30.25 | 0.00 | 47.57 | 77.82 | 61.05 |
| 150    | 13.25 | 4.62 | 19.50 | 2.75 | 14.50 | 34.00 | 42.57 | 18.25 | 5.22 | 27.25 | 0.00 | 50.97 | 78.22 | 64.97 |
| 200    | 12.50 | 4.40 | 20.00 | 3.00 | 21.80 | 41.80 | 51.95 | 18.75 | 5.10 | 33.75 | 0.00 | 44.00 | 77.75 | 56.70 |
| 400    | 11.50 | 4.52 | 21.75 | 2.25 | 17.37 | 39.12 | 45.20 | 18.75 | 5.27 | 31.75 | 0.00 | 55.80 | 87.55 | 63.60 |

**F-test**

|         | 3.37 NS | 2.75 NS | 9.71 ** | 4.44 * | 8.06 ** | 26.47 ** | 1.18 NS | 0.01 NS | 0.66 NS | 2.84 NS | 0.00 NS | 1.22 NS | 3.67 NS | 0.35 NS |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|

**NS—Significant at 1 and 5% probability and not significant, respectively. OM = organic matter; CEC = cation-exchange capacity; SB = sum of bases; BS = base saturation.**
Table 5. Determination coefficients \( (R^2) \) and regression equations that best fit the relationships between the chemical attributes of soils after maize cultivation as a function of potassium sources.

| Variable (y) | Typic Quartzipsamment | Rhodic Hapludox |   |
|-------------|------------------------|-----------------|---|
|             | Equation               | \( R^2 \)       | Equation | \( R^2 \)       |
| OM          | \( y = 11.87 \)        | 0.11 \( \text{NS} \) | \( y = 17.62 \) | 0.36 \( \text{NS} \) |
| pH          | \( y = 4.93 \)         | 0.60 \( \text{NS} \) | \( y = 5.30 + 0.001x - 0.000004x^2 \) | 0.89 ** |
| H+Al        | \( y = 18.75 \)        | 0.35 \( \text{NS} \) | \( y = 27.25 \) | 0.30 \( \text{NS} \) |
| Al          | \( y = 1.00 \)         | 0.29 \( \text{NS} \) | \( y = 0.00 \) | 0.27 \( \text{NS} \) |
| SB          | \( y = 17.97 \)        | 0.87 \( \text{NS} \) | \( y = 51.52 \) | 0.01 \( \text{NS} \) |
| CEC         | \( y = 36.12 \)        | 0.07 \( \text{NS} \) | \( y = 78.77 \) | 0.18 \( \text{NS} \) |
| BS          | \( y = 42.50 + 0.069x - 0.0001x^2 \) | 0.97 * | \( y = 65.40 \) | 0.06 \( \text{NS} \) |
|             | \( \text{Nepheline syenite} \) |             |           |                     |
| OM          | \( y = 11.83 \)        | 0.03 \( \text{NS} \) | \( y = 18.29 \) | 0.28 \( \text{NS} \) |
| pH          | \( y = 4.93 + 0.009x \) | 0.84 * | \( y = 5.25 + 0.0007x \) | 0.79 ** |
| H+Al        | \( y = 17.08 \)        | 0.03 \( \text{NS} \) | \( y = 27.75 \) | 0.73 \( \text{NS} \) |
| Al          | \( y = 0.29 \)         | 0.59 \( \text{NS} \) | \( y = 0.00 \) | 0.00 \( \text{NS} \) |
| SB          | \( y = 17.60 \)        | 0.14 \( \text{NS} \) | \( y = 52.60 \) | 0.31 \( \text{NS} \) |
| CEC         | \( y = 34.69 \)        | 0.15 \( \text{NS} \) | \( y = 80.35 \) | 0.00 \( \text{NS} \) |
| BS          | \( y = 50.64 \)        | 0.10 \( \text{NS} \) | \( y = 65.41 \) | 0.70 \( \text{NS} \) |
|             | \( \text{Phonolite} \) |             |           |                     |
| OM          | \( y = 11.79 \)        | 0.07 \( \text{NS} \) | \( y = 18.65 \) | 0.00 \( \text{NS} \) |
| pH          | \( y = 4.66 \)         | 0.46 \( \text{NS} \) | \( y = 5.23 \) | 0.04 \( \text{NS} \) |
| H+Al        | \( y = 17.47 + 0.011x \) | 0.94 ** | \( y = 30.33 \) | 0.20 \( \text{NS} \) |
| Al          | \( y = 0.93 + 0.012x - 0.000002x^2 \) | 0.77 * | \( y = 0.00 \) | 0.00 \( \text{NS} \) |
| SB          | \( y = 12.29 + 0.044x - 0.00007x^2 \) | 0.51 ** | \( y = 50.10 \) | 0.07 \( \text{NS} \) |
| CEC         | \( y = 31.52 + 0.024x \) | 0.61 ** | \( y = 80.44 \) | 0.41 \( \text{NS} \) |
| BS          | \( y = 45.22 \)        | 0.09 \( \text{NS} \) | \( y = 62.17 \) | 0.01 \( \text{NS} \) |

** *, * and \( \text{NS} \)—Significant at 1 and 5% probability and not significant, respectively. OM = organic matter; CEC = cation-exchange capacity; SB = sum of bases; BS = base saturation.

Table 6. Effect of treatments on macronutrient concentrations after maize cultivation in the Typic Quartzipsamment, and in the Rhodic Hapludox, depending on the application of potassium sources and rates.

| Treatments | Typic Quartzipsamment | Rhodic Hapludox |   |
|------------|-----------------------|-----------------|---|
|            | P mg dm\(^{-3}\) K mmol dm\(^{-1}\) Ca mg dm\(^{-3}\) Mg mg dm\(^{-3}\) S-SO\(_4\) mg dm\(^{-3}\) | P mg dm\(^{-3}\) K mmol dm\(^{-1}\) Ca mg dm\(^{-3}\) Mg mg dm\(^{-3}\) S-SO\(_4\) mg dm\(^{-3}\) |
| Source (F) |                       |                 |   |
| Nepheline syenite | 57.6 0.46 b 11.2 a 5.6 | 51.5 a 54.0 b 31.5 ab 19.5 | 72.8 a |
| Phonolite | 55.7 0.44 b 11.7 a 5.4 | 45.6 ab 66.8 a | 20.0 | 67.2 a |
| KCl | 55.7 0.60 a 9.9 b 5.4 | 35.5 b 65.7 a | 19.6 | 57.2 b |
| F-test | 0.83 NS 28.19 ** 11.93 ** 0.42 NS | 3.36 * 18.88 ** 133.06 ** 4.49 * 0.31 NS | 14.94 ** |
| K rates (DK) |                       |                 |   |
| 0 (mg kg\(^{-1}\)) | 55.3 0.42 9.1 5.5 | 40.1 58.5 | 32.0 | 20.3 | 77.8 |
| 50 (mg kg\(^{-1}\)) | 56.0 0.47 10.0 5.1 | 39.3 63.5 | 32.1 | 18.9 | 66.0 |
| 100 (mg kg\(^{-1}\)) | 54.7 0.49 10.5 5.5 | 41.1 63.0 | 29.7 | 19.0 | 59.9 |
| 150 (mg kg\(^{-1}\)) | 53.8 0.45 11.8 5.2 | 41.5 62.5 | 31.5 | 19.7 | 62.5 |
| 200 (mg kg\(^{-1}\)) | 56.6 0.46 12.4 6.0 | 61.8 58.1 | 30.5 | 18.8 | 60.9 |
| 400 (mg kg\(^{-1}\)) | 61.5 0.70 11.7 5.5 | 43.3 67.4 | 32.3 | 21.5 | 58.5 |
| F-test | 2.64 * 17.71 ** 10.14 ** 1.01 NS | 1.69 NS 2.22 NS 50.04 ** | 1.52 NS 2.12 NS 3.53 ** |
| F-test (F) × (DK) | 1.24 NS 13.14 ** 3.94 ** 3.92 ** | 2.22 * 0.71 NS 67.37 ** | 1.64 NS 1.39 NS 2.12 * |
| Overall average | 56.3 0.5 10.9 5.5 | 44.5 62.2 | 31.2 | 19.7 | 64.2 |
| CV (%) | 10.3 16.2 12.2 18.4 | 51.1 12.8 | 7.7 | 8.6 | 12.6 |

**, *, and NS—Significant at 1 and 5% probability and not significant, respectively. Averages followed by the same letter do not differ by Tukey’s test at 5% probability.
Regarding the comparison of K sources, KCl provided the highest K concentration in both soils (Table 6). Except for Mg concentration, there was an increasing linear adjustment for Ca concentration in the TQ, while a linear increase in K concentration in RH occurred with increasing rates of agromineral nepheline syenite (Table 7). The application of phonolite resulted in a linear increase in P concentration and a quadratic adjustment for TQ Ca and S concentrations at K rates of 278 and 225 mg kg\(^{-1}\), respectively, resulting in the highest concentrations of these elements. A linear decrease was observed in S concentration in RH soil. The concentration of Ca showed a quadratic adjustment with increasing rates of KCl in TQ, with the highest concentrations obtained at a rate of 238 mg kg\(^{-1}\) of K. A linear increase in K concentrations was observed with increasing rates of KCl.

Table 7. Macronutrient concentrations after maize cultivation in the Typic Quartzipsamment, and in the Rhodic Hapludox, depending on the rates and sources of K.

| K Rates | Typic Quartzipsamment | Rhodic Hapludox |
|---------|------------------------|------------------|
|         | P  | K  | Ca  | Mg  | S-SO\(_4\)  | P  | K  | Ca  | Mg  | S-SO\(_4\)  |
| mg kg\(^{-1}\) |  | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) |
| 0 | 59.00 | 0.45 | 10.00 | 6.00 | 48.50 | 55.25 | 0.40 | 30.50 | 20.50 | 83.25 |
| 50 | 59.50 | 0.55 | 10.25 | 5.75 | 39.75 | 55.50 | 0.40 | 32.00 | 18.50 | 64.25 |
| 100 | 57.50 | 0.43 | 11.50 | 5.75 | 55.50 | 54.00 | 0.40 | 29.00 | 17.75 | 65.75 |
| 150 | 55.75 | 0.45 | 11.25 | 5.50 | 48.25 | 53.75 | 0.45 | 34.00 | 20.75 | 76.25 |
| 200 | 56.75 | 0.43 | 11.50 | 5.75 | 52.25 | 45.75 | 0.48 | 32.25 | 20.00 | 61.75 |
| 400 | 57.25 | 0.48 | 13.00 | 5.25 | 44.75 | 60.00 | 0.48 | 31.25 | 19.50 | 85.75 |
| F-test | 0.32 NS | 0.08 NS | 11.63 ** | 1.02 NS | 0.01 NS | 0.35 NS | 15.14 ** | 0.17 NS | 0.03 NS | 1.25 NS |

|         | P  | K  | Ca  | Mg  | S-SO\(_4\)  | P  | K  | Ca  | Mg  | S-SO\(_4\)  |
|---------|  | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) |
| 0 | 51.50 | 0.43 | 9.25 | 5.50 | 22.50 | 63.75 | 0.40 | 32.75 | 19.75 | 84.50 |
| 50 | 55.75 | 0.43 | 11.00 | 5.75 | 52.00 | 66.50 | 0.40 | 32.25 | 19.75 | 72.75 |
| 100 | 52.50 | 0.43 | 11.00 | 5.75 | 43.00 | 68.50 | 0.40 | 31.75 | 20.25 | 68.75 |
| 150 | 51.25 | 0.45 | 14.50 | 6.00 | 58.25 | 69.00 | 0.40 | 30.25 | 18.25 | 60.25 |
| 200 | 57.00 | 0.43 | 12.00 | 4.75 | 57.25 | 64.75 | 0.40 | 32.25 | 20.00 | 67.25 |
| 400 | 66.75 | 0.50 | 12.75 | 4.75 | 41.00 | 68.50 | 0.40 | 33.75 | 22.25 | 50.00 |
| F-test | 15.32 ** | 11.84 ** | 10.49 ** | 2.66 NS | 6.91 * | 0.33 NS | 15.14 ** | 0.17 NS | 0.03 NS | 1.25 NS |

|         | P  | K  | Ca  | Mg  | S-SO\(_4\)  | P  | K  | Ca  | Mg  | S-SO\(_4\)  |
|---------|  | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mmol dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) | mg dm\(^{-3}\) |
| 0 | 55.50 | 0.40 | 8.25 | 5.00 | 23.50 | 56.75 | 0.40 | 32.75 | 20.75 | 65.75 |
| 50 | 53.00 | 0.45 | 9.00 | 4.00 | 26.25 | 68.75 | 0.40 | 29.50 | 18.50 | 61.00 |
| 100 | 54.25 | 0.60 | 9.25 | 5.25 | 25.00 | 66.75 | 0.58 | 29.00 | 20.00 | 51.00 |
| 150 | 54.50 | 0.50 | 9.75 | 4.25 | 18.25 | 64.75 | 0.48 | 30.25 | 20.25 | 51.00 |
| 200 | 56.25 | 0.55 | 13.75 | 7.50 | 76.00 | 64.00 | 0.50 | 27.00 | 16.50 | 53.75 |
| 400 | 60.75 | 1.13 | 9.50 | 6.75 | 44.25 | 73.75 | 1.05 | 32.00 | 22.75 | 39.75 |
| F-test | 3.25 NS | 181.43 ** | 18.97 ** | 16.30 NS | 6.18 NS | 5.29 * | 753.89 ** | 0.04 NS | 2.32 NS | 7.27 ** |

** *, and NS—Significant at 1 and 5% probability and not significant, respectively.

The application of KCl resulted in an increase in P and K concentrations and a reduction in S concentration in RH soil (Table 8). The P and K concentrations in soils as a function of applied rates and sources were close and were being verified with P concentrations ranging from 45.8 to 73.8 mg dm\(^{-3}\) and K concentrations ranging from 0.4 to 1.1 mmol\(_{c}\) dm\(^{-3}\) (Table 7). According to Raij et al. [33], these values are considered high for P (41 to 80 mg dm\(^{-3}\)) and very low and low (0.0 to 1.5 mmol\(_{c}\) dm\(^{-3}\)) for K. The correction of soil acidity causes an increase in OH\(^{-}\) ions from corrective material and may have desorption of phosphate ions, which increase their availability in soil [34]. The low K concentration with nepheline syenite application and phonolite are possibly related to the lower solubility of these sources and the duration of the experiment, which may directly affect the rapid release of this element in soil [10]. For KCl, the results corroborate findings by Castro et al. [12] In that study, Brazilian rocks had low K concentrations in TQ. Santos [3] also reported that less soluble K sources lost less K when compared to KCl in sandy soil.
Table 8. Coefficients of determination (R²) and regression equations that best fit the relationships between macronutrient levels in soils after maize cultivation as a function of K sources.

| Variable (y) | Tylic Quartzipsamment | Rhodic Hapludox |
|--------------|------------------------|-----------------|
|              | Equation             | R²  | Equation | R²  |
| P            | y = 57.62             | 0.28 NS | y = 54.04 | 0.05 NS |
| K            | y = 0.46              | 0.01 NS | y = 0.47 + 0.0002x | 0.74 ** |
| Ca           | y = 10.16 + 0.007x    | 0.91 ** | y = 31.58 | 0.02 NS |
| Mg           | y = 5.66              | 0.79 NS | y = 19.50 | 0.00 NS |
| S-SO₄        | y = 48.16             | 0.00 NS | y = 72.83 | 0.10 NS |
|              |                        |      | Phonomite |    |
| P            | y = 50.37 + 0.036x    | 0.76 ** | y = 66.83 | 0.21 NS |
| K            | y = 0.44              | 0.66 NS | y = 0.40  | 0.00 NS |
| Ca           | y = 9.38 + 0.030x – 0.00005x² | 0.64 ** | y = 32.16 | 0.15 NS |
| Mg           | y = 5.41              | 0.47 NS | y = 20.04 | 0.45 NS |
| S-SO₄        | y = 27.88 + 0.281x – 0.0006x² | 0.75 *  | y = 78.53 – 0.075x | 0.83 ** |
|              |                        |      | KCl       |    |
| P            | y = 55.70             | 0.75 NS | y = 61.42 + 0.029x | 0.53 * |
| K            | y = 0.34 + 0.001x     | 0.86 ** | y = 0.32 + 0.001x | 0.83 ** |
| Ca           | y = 7.55 + 0.034x – 0.00007x² | 0.56 ** | y = 29.91 | 0.00 NS |
| Mg           | y = 5.45              | 0.43 NS | y = 19.62 | 0.15 NS |
| S-SO₄        | y = 35.54             | 0.23 NS | y = 61.15 – 0.056x | 0.67 ** |

**, * and NS—Significant at 1 and 5% probability and not significant, respectively.

The concentrations of Ca²⁺, Mg²⁺ and S-SO₄²⁻ after maize cultivation varied in both soils, ranging from 8.3 to 34.0 mmol c⁻³, 4.0 to 22.8 mmol c⁻³ and 18.3 to 85.8 mmol c⁻³ respectively, depending on applied K rates and sources (Table 7). These concentrations are considered high (>7 mmol c⁻³) for Ca²⁺, low (<4.0 mmol c⁻³) and high (>8.0 mmol c⁻³) for Mg²⁺ and high for S-SO₄²⁻ (>10.0 mg dm⁻³) [32]. The lowest concentrations of Ca²⁺ and Mg²⁺ were verified in TQ due to lower application of limestone, which significantly contributed to the differences of these elements in this soil.

Regarding the macronutrient concentrations in maize DM, there was an interaction found between K sources and rates for N, P, K, and Mg concentrations in the TQ and for K and Mg concentrations in RH (Table 9). It was observed that macronutrient concentrations varied significantly according to the sources applied. Except for K concentrations, the other macronutrients were higher with application of nepheline syenite and phonolite when compared to KCl. This fact must be related to the effect of the concentration of these elements on the plant tissue [35], since it is usual to find less plant growth in the soils that received less soluble sources.

Among the comparison of soil types, shoot K concentration in maize ranged from 3.86 to 8.50 g kg⁻¹ in TQ and from 5.0 to 11.5 g kg⁻¹ in RH (Table 9). The values observed in this study were similar to those obtained by Castro et al. [12] Regarding K sources (nepheline syenite and phonolite), the K concentration in plants did not differ from each other. Additionally, an increase in K rates promoted a linear decrease in shoot nutrient concentrations when maize plants were grown in both soils and an increase in shoot K concentration in maize plants grown in RH (Tables 10 and 11). The reductions in macronutrient concentrations must be related to the dilution effects [35] and inhibition, as described by Malavolta et al. [28].
Table 9. Effects of treatments on macronutrient concentrations in the shoot of maize plants grown in the Typic Quartzipsamment and in the Rhodic Hapludox, depending on the application of sources and rates of potassium.

| Treatments | Typic Quartzipsamment | Rhodic Hapludox |
|------------|------------------------|-----------------|
|            | N  | P  | K | Ca | Mg | S   | N  | P  | K | Ca | Mg | S   |
| Source (F) |    |    |   |    |    |    |    |    |   |    |    |    |
| Nepheline syenite | 16.0 a | 4.4 a | 3.93 b | 5.4 a | 5.7 a | 2.3 a | 15.3 a | 2.6 a | 5.0 b | 5.4 a | 6.0 a | 1.8 a |
| Phonolite | 13.9 b | 4.4 a | 3.86 b | 5.3 a | 5.6 a | 2.2 a | 13.9 a | 2.5 a | 5.5 b | 5.6 a | 6.0 a | 1.7 a |
| KCl | 9.0 c | 3.2 b | 8.50 a | 4.3 b | 3.3 b | 1.6 b | 11.3 b | 2.0 b | 11.5 a | 4.9 b | 4.9 b | 1.6 b |
| F-test | 36.33 ** | 10.01 ** | 193.29 ** | 12.27 ** | 159.66 ** | 19.92 ** | 23.49 ** | 16.18 ** | 175.49 ** | 8.32 ** | 53.58 ** | 6.98 ** |
| K rates (DK) |    |    |   |    |    |    |    |    |   |    |    |    |
| 0 (mg kg\(^{-1}\)) | 23.6 | 6.9 | 4.11 | 6.7 | 5.9 | 2.8 | 16.8 | 3.1 | 4.7 | 5.6 | 6.0 | 1.9 |
| 50 (mg kg\(^{-1}\)) | 15.3 | 5.1 | 4.35 | 5.6 | 5.3 | 2.3 | 13.6 | 2.4 | 5.6 | 5.4 | 6.0 | 1.7 |
| 100 (mg kg\(^{-1}\)) | 10.8 | 3.4 | 5.15 | 4.8 | 5.1 | 1.9 | 13.1 | 2.1 | 6.1 | 5.3 | 5.7 | 1.6 |
| 150 (mg kg\(^{-1}\)) | 11.5 | 3.2 | 5.58 | 4.5 | 4.7 | 1.8 | 11.5 | 2.1 | 6.7 | 4.9 | 5.4 | 1.6 |
| 200 (mg kg\(^{-1}\)) | 8.9 | 3.0 | 5.91 | 4.3 | 4.2 | 1.6 | 11.5 | 2.1 | 6.7 | 4.9 | 5.4 | 1.6 |
| 400 (mg kg\(^{-1}\)) | 7.9 | 2.6 | 7.47 | 4.0 | 4.0 | 1.7 | 13.8 | 2.4 | 9.3 | 5.5 | 5.7 | 1.7 |
| F-test | 47.39 ** | 29.52 ** | 20.20 ** | 16.89 ** | 24.83 ** | 11.94 ** | 9.80 ** | 10.66 ** | 45.67 ** | 2.23 NS | 9.31 ** | 3.12 * |
| F-test (F) × (DK) | 4.53 ** | 3.15 ** | 30.91 ** | 0.33 NS | 7.58 ** | 1.07 NS | 1.46 NS | 0.88 NS | 26.13 ** | 0.99 NS | 8.56 ** | 1.31 NS |
| Overall average | 13.0 | 4.0 | 5.43 | 5.0 | 4.9 | 2.0 | 13.5 | 2.4 | 7.4 | 5.3 | 5.6 | 1.7 |
| CV (%) | 22.3 | 25.8 | 17.2 | 16.3 | 10.4 | 21.7 | 15.3 | 17.5 | 18.1 | 12.0 | 7.5 | 11.4 |

**, *, and NS—Significant at 1 and 5% probability and not significant, respectively. Averages followed by the same letter do not differ by Tukey’s test at 5% probability.

Table 10. Concentration of macronutrients in the shoots of maize plants grown in the Typic Quartzipsamment and in the Rhodic Hapludox, depending on the rates and sources of K.

| K Rates | Typic Quartzipsamment | Rhodic Hapludox |
|---------|------------------------|-----------------|
| mg kg\(^{-1}\) | N  | P  | K | Ca | Mg | S   | N  | P  | K | Ca | Mg | S   |
| 0 | 23.95 | 6.05 | 4.27 | 6.82 | 5.97 | 3.05 | 17.25 | 3.25 | 4.03 | 5.35 | 5.83 | 2.10 |
| 50 | 23.20 | 7.47 | 3.92 | 7.08 | 6.20 | 2.72 | 16.58 | 2.28 | 5.45 | 6.05 | 6.23 | 1.85 |
| 100 | 18.57 | 5.77 | 4.00 | 5.78 | 5.85 | 2.62 | 14.03 | 2.68 | 4.95 | 5.68 | 6.13 | 1.83 |
| 150 | 11.95 | 3.67 | 4.20 | 5.18 | 5.72 | 2.17 | 13.43 | 2.23 | 5.00 | 5.48 | 5.83 | 1.65 |
| 200 | 9.57 | 3.40 | 4.52 | 5.56 | 5.62 | 2.02 | 11.88 | 2.23 | 4.58 | 5.38 | 6.13 | 1.75 |
| 400 | 6.10 | 3.17 | 4.77 | 5.27 | 5.10 | 1.92 | 13.68 | 2.15 | 6.58 | 5.20 | 6.03 | 1.85 |
| F-test | 60.27 ** | 32.04 ** | 15.18 ** | 5.08 * | 9.56 ** | 5.86 * | 11.00 ** | 5.07 * | 0.13 NS | 0.02 NS | 14.88 ** |
| F-test (F) × (DK) | 45.33 ** | 31.55 ** | 30.91 ** | 0.33 NS | 7.58 ** | 1.07 NS | 1.46 NS | 0.88 NS | 26.13 ** | 0.99 NS | 8.56 ** | 1.31 NS |
| Overall average | 22.3 | 25.8 | 17.2 | 16.3 | 10.4 | 21.7 | 15.3 | 17.5 | 18.1 | 12.0 | 7.5 | 11.4 |
| CV (%) | 22.3 | 25.8 | 17.2 | 16.3 | 10.4 | 21.7 | 15.3 | 17.5 | 18.1 | 12.0 | 7.5 | 11.4 |

**, *, and NS—Significant at 1 and 5% probability and not significant, respectively.

Agronomy 2021, 11, 1385
11 of 19
Table 11. Determination coefficients ($R^2$) and regression equations that best fit the relationships between the macronutrient concentration in the shoot of maize plants as a function of the K sources, in the different types of soil.

| Variable (y) | Typic Quartzipsamment | Rhodic Hapludox |  |
|--------------|------------------------|----------------|---|
|              | Nepheline syenite       | Phonolite      | KCl |
| N            | $y = 21.45 - 0.035x$    | $y = 19.12 - 0.034x$ | $y = 9.08$ |
|              | $R^2 = 0.74^{**}$      | $R^2 = 0.70^{**}$ | $R^2 = 0.25^{NS}$ |
| P            | $y = 5.90 - 0.009x$    | $y = 5.81 - 0.009x$ | $y = 3.28$ |
|              | $R^2 = 0.64^{**}$      | $R^2 = 0.52^{**}$ | $R^2 = 0.38^{NS}$ |
| K            | $y = 3.93$             | $y = 3.86$     | $y = 5.36 - 0.006x$ |
|              | $R^2 = 0.44^{NS}$      | $R^2 = 0.48^{NS}$ | $R^2 = 0.97^{**}$ |
| Ca           | $y = 6.17 - 0.005x$    | $y = 6.09 - 0.005x$ | $y = 4.10 + 0.029x$ |
|              | $R^2 = 0.64^{**}$      | $R^2 = 0.56^{**}$ | $R^2 = 0.97^{**}$ |
| Mg           | $y = 5.99 - 0.001x$    | $y = 6.02 - 0.002x$ | $y = 4.85 - 0.009x$ |
|              | $R^2 = 0.45^{*}$       | $R^2 = 0.87^{**}$ | $R^2 = 0.82^{**}$ |
| S            | $y = 2.72 - 0.002x$    | $y = 2.55 - 0.002x$ | $y = 2.09 - 0.003x$ |
|              | $R^2 = 0.53^{**}$      | $R^2 = 0.68^{*}$ | $R^2 = 0.45^{**}$ |

** and NS—Significant at 1 and 5% probability and not significant, respectively.

The K sources with low water solubility (nepheline syenite and phonolite) influenced shoot K accumulation in maize plants grown in both soils, with a linear increase in the accumulated amounts (Figure 1a,b). Increasing KCl (K source with high water solubility) rates led to a linear increase in shoot K accumulation by maize plants in both soils, and it was noted that this source was responsible for significantly increasing the amount of K accumulated, characterizing luxury consumption by the crop. This fact is due to the greater availability of the nutrient in the soil, which is reflected in greater exports of the crop [10], even if it is not used in biomass production. For millet (Pennisetum glaucum), there have also been observations of an increase in K accumulation through the application of KCl and phonolite. However, there was no effect of nepheline syenite on the accumulation of K in this crop at the end of two 30-day cultivations [3].

There was positive interaction between sources and rates of K for plant height, shoot dry matter (SDM), stem diameter and leaf chlorophyll index (LCI) except for plant height in RH (Table 12). The application of KCl in both soils produced taller plants (135.2 in RH and 115.0 cm in TQ). The less soluble sources of K showed no differences in plant height in RH soil, while rates of K increased plant height in TQ (Table 12). The K rates applied via nepheline syenite led to a linear increase in plant height in both soils (Figures 2a and 3a). Conversely, there were quadratic adjustments in plant height when phonolite and KCl were used in both soils. The highest plant height values in TQ (121.8 and 145.6 cm) were found through the rates of 329.1 and 289.4 mg kg$^{-1}$, respectively (Figure 2c,e). Plant height in RH had a quadratic adjustment through the application of phonolite and KCl, with application of estimated rates of 259.6 and 303.1 mg kg$^{-1}$, respectively, promoting the highest values (phonolite = 128.5 cm and KCl = 153.8 cm) for this variable (Figure 3).
Figure 1. Shoot K accumulation of maize plants grown in the Typic Quartzipsamment (a) and in the Rhodic Hapludox (b), depending on the rates and sources of K. **—Significant at the $p < 0.01$ level. Bars represent the standard error of the mean.

Table 12. Effect of treatments on plant height, shoot dry matter, stem diameter, and leaf chlorophyll index (LCI), 45 days after the emergence of maize plants grown in the Typic Quartzipsamment (TQ) and in the Rhodic Hapludox (RH), depending on the application of K sources and rates.

| Treatments          | Plant Height | Shoot Dry Matter | Stem Diameter | LCI   |
|---------------------|--------------|------------------|---------------|-------|
|                     | TQ           | RH               | TQ            | RH    | TQ         | RH     | TQ           | RH     |
| Source (F)          | cm           | g per plant      | mm            |       |            |        |               |        |
| Nepheline syenite   | 87.7 c       | 119.3 b          | 17.4 c        | 25.8 b | 9.8 b      | 11.7 b | 27.4 a        | 38.2 ab |
| Phonolite           | 95.3 b       | 121.0 b          | 20.7 b        | 27.1 b | 10.4 b     | 11.7 b | 26.6 a        | 39.2 ab |
| KCl                 | 115.0 a      | 135.2 a          | 37.1 a        | 37.0 a | 12.7 a     | 14.2 a | 20.4 b        | 37.3 b |
| F-test              | 61.08 **     | 26.44 **         | 181.50 **     | 77.75 ** | 27.80 **   | 63.95 ** | 38.82 **     | 7.07 ** |
| F-test (F) × (DK)   | 5.52 **      | 1.74 NS          | 9.41 **       | 4.51 ** | 2.36 *     | 3.31 ** | 2.37 *        | 2.24 * |
| Overall average     | 99.3         | 125.2            | 25.1          | 30.0       | 11.0       | 12.5    | 24.8          | 38.3    |
| CV (%)              | 8.8          | 6.6              | 15.2          | 11.3       | 12.9       | 7.1     | 12.2          | 5.5     |

**, *, and NS—Significant at 1 and 5% probability and not significant, respectively. Averages followed by the same letter do not differ by Tukey’s test at 5% probability.
**Figure 2.** Plant height and comparative growth 45 days after the emergence of maize grown in the Typic Quartzipsamment with increasing rates of K via nepheline syenite (a,b), phonolite (c,d), and potassium chloride (e,f). **—Significant at the p < 0.01 level. Bars represent the standard error of the mean.**

**Figure 3.** Cont.
Maize showed significant differences in plant growth (comparison must be intended among the plot of the same K source) and biomass production of shoot as a function of K applied soil rates. These reflect differences in SDM yield (Figures 2 and 3).

Regarding K sources, application of KCl provided greater SDM with no differences in both soils (Table 12). The rates of K from the sources of KCl, nepheline syenite, and phonolite contributed to an increase in the production of SDM; however, no differences were found between nepheline syenite (25.8 g per plant) and phonolite (27.1 g per plant) in the production of SDM from plants grown in RH. However, plants grown on TQ soil that received phonolite (20.7 g per plant) resulted in greater SDM compared to nepheline syenite (17.4 g per plant) (Table 12). In evaluating the effect of the nepheline syenite and phonolite rates, it was found that SDM linearly increased (nepheline syenite: $y = 10.59 + 0.045x$; $R^2 = 0.94$ and phonolite: $y = 12.31 + 0.056x; p > 0.01; R^2 = 0.94$) in TQ. We also verified that nepheline syenite rates provided a positive increment in SDM of the plant grown (nepheline syenite: $y = 24.00 + 0.012x; p > 0.05; R^2 = 0.81$) in RH and a quadratic adjustment (phonolite: $y = 22.99 + 0.055x - 0.0001x^2; p > 0.05; R^2 = 0.57$) as a function of the phonolite rates applied in RH with an estimated K rate of 275.0 mg kg$^{-1}$, providing the highest value (30.5 g per plant of SDM). The K rates in the form of KCl increased SDM production with application of an estimated optimal rates of 268.6 mg kg$^{-1}$ in TQ.
(KCl: $y = 16.0 + 0.274x - 0.0002x^2; p > 0.01; R^2 = 0.81$) and $284.5 \text{ mg kg}^{-1}$ in RH (KCl: $y = 25.46 + 0.143x - 0.0002x^2; p > 0.01; R^2 = 0.81$).

In general, it was noted that SDM was higher in RH soil with application of KCl. Our results are similar to those obtained by Castro et al. [12] for sunflower where differences may have been related to greater water and nutrient retention capacity of RH, thereby strengthening root volume and shoot growth. The stem diameter increased with KCl application in both soils, being $12.7 \text{ mm}$ in TQ and $14.2 \text{ mm}$ in the RH. The application of nepheline syenite and phonolite provided similar values for stem diameter, ranging from $9.8$ to $10.4 \text{ mm}$ in TQ and $11.7 \text{ mm}$ in RH. The K rates linearly increased (nepheline syenite: $y = 8.91 + 0.006x; p > 0.01; R^2 = 0.76$ and phonolite: $y = 8.84 + 0.010x; p > 0.01; R^2 = 0.86$) stem diameter in TQ soil and with no effect in RH soil. Conversely, there was a quadratic adjustment (KCl: $y = 8.37 + 0.056x - 0.0001x^2; p > 0.01; R^2 = 0.99$) as a function of the KCl rates applied in TQ with an estimated K rate of $276.4 \text{ mg kg}^{-1}$, providing the highest value ($16.2 \text{ mm}$) and a linear adjustment (KCl: $y = 12.87 + 0.009x; p > 0.01; R^2 = 0.75$) for RH. In relation to LCI, higher values were observed with the application of less soluble sources (Table 12). There were similarities in the values obtained from K sources, which may be directly related to the higher N concentrations obtained in these plants (Table 12).

The agronomic efficiency index (AEI) of nepheline syenite and phonolite were lower than for KCl (Figure 4). The AEI varied from 10 to 50% with the increasing K rates of nepheline syenite and from 16 to 64% with application of phonolite in TQ soil (Figure 4a). In RH, the AEI ranged from 7 to 27% and 18 to 44% with application of nepheline syenite and phonolite rates, respectively (Figure 4b). The AEI of nepheline syenite and phonolite were similar to those obtained by Santos [3] for millet with remineralizer application. These results indicated technical feasibility for the use of alternative K sources, mainly in the highest applied rates. In addition, these materials have a relatively slow dissolution when compared to conventional fertilizers, indicating a residual effect to maintain K availability, especially in low CEC soils. The fact that these materials do not promote a saline effect is another very favorable aspect for the use of these sources when compared to KCl, not to mention the lesser external dependence they have on fertilizers.

![Figure 4](image-url)  
Figure 4. Agronomic efficiency index (AEI) of K sources tested in the Typic Quartzipsamment (a) and Rhodic Hapludox (b).

4. Conclusions

The application of K rates through nepheline syenite, phonolite and KCl sources did not influence soil pH. The application of nepheline syenite and phonolite had a similar effect on soil chemical attributes (OM, pH, SB, CEC, and BS) as well as on the concentrations of K, Ca, Mg, and S, in both soils. Conversely, these sources differed from KCl for soil pH, Al, BS, K, Ca, and S in Typic Quartzipsamment and for pH, H+Al, BS, K, Ca, and
S in Rhodic Hapludox. KCl provided higher K concentrations in both soils compared to nepheline syenite and phonolite. Macronutrient concentrations in maize shoots were similar for less soluble K sources (nepheline syenite and phonolite). The plants grown on the soil fertilized with KCl were shown to have higher K concentrations in both soils. All three K sources (nepheline syenite, phonolite, and KCl) increased K accumulation in maize plants. However, we noted that KCl was responsible for a significant increase in K accumulation. Different rates of nepheline syenite, phonolite, and KCl did not influence leaf chlorophyll index, but plant height, stem diameter, and shoot dry matter increased in both soils. There was similar behavior between nepheline syenite and phonolite sources in relation to AEI. Nepheline syenite and phonolite sources reach 50% and 64% relative to KCl AEI, respectively, at the highest rates in sandy texture soil. Nepheline syenite and phonolite sources also reached 27% and 29% relative to KCl AEI, respectively, at the highest rates in medium texture soil. These results indicate the efficiency of nepheline syenite and phonolite as alternative K sources for maize.

Author Contributions: Conceptualization, T.A.R.N., B.G.M., M.C.M.T.F., A.J., L.G.F.L., N.C.M. and A.M.; methodology, T.A.R.N., B.G.M., M.C.M.T.F., L.G.F.L., É.d.S.M., and A.J.; software, G.F.C. and B.G.M.; validation, É.d.S.M., N.C.M., A.D.J. and G.F.C.; formal analysis, T.A.R.N. and B.G.M.; investigation, T.A.R.N. and B.G.M.; resources, T.A.R.N.; data curation, T.A.R.N., B.G.M. and A.D.J.; writing—original draft preparation, T.A.R.N., B.G.M., A.J. and A.M.; writing—review and editing, T.A.R.N., C.H.A.-J., A.D.J., L.G.F.L., G.F.C.; É.d.S.M., and A.M.; visualization, M.C.M.T.F., L.G.F.L. and A.D.J.; supervision, T.A.R.N.; project administration, T.A.R.N.; funding acquisition, T.A.R.N. and N.C.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financed by the Fundação de Ensino, Pesquisa e Extensão de Ilha Solteira, project No. 2.007/2018 (2018–2019). The research was co-financed by the Mineragro Pesquisa e Desenvolvimento LTDA. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES/AUXPE award number 88881.593505/2020-01).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Acknowledgments: The GENAFERT (Grupo de Estudo em Nutrição, Adubação e Fertilidade do Solo) for technical support. The Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES) for the master’s scholarship granted to the second author. The World Academy of Sciences (TWAS) and the National Council for Scientific and Technological Development (CNPq) for the third author’s scholarship (CNPq/TWAS grant # 166331/2018-0). The CNPq for the Research Grant to the seventh author (grant # 312728/2017-4).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study, the collection, analyses or interpretation of data, the writing of the manuscript or the decision to publish the results.

References
1. Malavolta, E. *Mineral Plant Nutrition Manual*, 1st ed.; Agronômica Ceres: São Paulo, Brazil, 2006; p. 638.
2. Nascimento, C.O. Evaluation of Biodegradable Polymer Coatings in KCl Granules Obtained through Fluidized Bed. Master’s Thesis, Federal University of Bahia, Salvador, Brazil, 2014.
3. Santos, D.S. Rochagem as an Alternative to Supply Potassium to Crops. Master’s Thesis, Federal University of Uberlândia, Uberlândia, Brazil, 2013.
4. AMA BRASIL. Brazilian Fertilizer Mixers Association. *Production and Import of Fertilizers*. Available online: http://amabrasil.agr.br/web/portfolio-item/producao-e-importacao-de-fertilizantes/ (accessed on 3 June 2020).
5. Di Loreto y Sampaio, M.; Melo, T.R.; Moreira, A. Potassium and spontaneous clay dispersion in two soils of Paraná State. *Agrotrópica* 2019, 31, 205–212.
6. Cantarella, H. Fertilization with nitrogen, potassium and sulfur. *Fertilization and Liming Recommendations for the State of São Paulo*, 2nd ed.; van Raij, B., Cantarella, H., Quaggio, J.A., Furlani, A.M.C., Eds.; Campinas Agronomic Institute: Campinas, Brazil, 1997; Volume 1, pp. 22–27.
7. Sangoi, L.; Ernani, P.R.; Blanchet, P.; Vargas, V.P.; Picoli, G.J. Effect of rates of potassium chloride on the germination and initial growth of maize, in soils with contrasting textures. Rev. Bras. Milho Sorgo 2009, 8, 187–197. [CrossRef]
8. National Fertilizer Diffusion Association—ANDA. Macro Indicators. Available online: http://www.anda.org.br/estatisticas/ (accessed on 24 May 2019).
9. Ministry of Industry, Foreign Trade and Services (MDIC). Comex Vis: Visualizations of Foreign Trade. Available online: http://www.mdic.gov.br/comercio-exterior/estatisticas-de-comercio-exterior/comex-vis/frame-ppi (accessed on 25 May 2020).
10. Resende, A.V.; Martins, E.S.; Oliveira, C.G.; Sena, M.C.; Machado, C.T.T.; Kimpapa, J.D.; Oliveira Filho, E.C. Supply of potassium and research on the use of “in natura” rocks in Brazilian agriculture. Spat. Geogr. 2006, 9, 19–42.
11. Almeida, G.R. Petrographic analysis, geophysical and geobotanical prospecting: Agroecological potential in the central portion of the state of Tocantins. In Congresso Brasileiro de Rochagem, Proceedings of the III Brazilian Congress of Rochagem, Pelotas, Brazil, 8–11 November 2016; Bamberg, A.L., Silveira, C.A.P., Martins, E.S., Bergmann, M., Martinazzo, R., Theodor, S.H., Eds.; Triunfal Gráfica e Editora: Assis, Brazil, 2017; Volume 3, pp. 129–133.
12. Castro, C.; Oliveira, F.A.; Moreira, A.; Salinet, L.H.; Veronesi, C.O. Brazilian rocks as an alternative source of potassium for sunflower cultivation. Spat. Geogr. 2006, 9, 179–193.
13. Melamed, R.; Gaspar, J.C.; Miekeley, N. Rock powder as alternative fertilizers for sustainable production systems in tropical soils. In Fertilizers: Agribusiness and Sustainability, 1st ed.; Loureiro, F.E.L., Melamed, R., Figueiredo Neto, J., Eds.; CETEM/MCT: Rio de Janeiro, Brazil, 2009; Volume 1, pp. 385–395.
14. Moreira, A.; Castro, C.; Oliveira, F.A.; Salinet, L.H.; Sfredo, G.J. Residual effect of Brazilian rocks as soil acidity fertilizers and correctives. Spat. Geogr. 2006, 9, 163–177.
15. Cola, G.P.A.; Simão, J.B.P. Rochagem as an alternative form of potassium supplementation in agroecological agriculture. Rev. Verde Agroecol. Desenvolv. Sustent. 2012, 7, 1–8. Available online: https://dialnet.unirioja.es/descarga/articulo/7422237.pdf (accessed on 25 May 2020).
16. Alvarez, V.H.; Novais, R.F.; Barros, N.F.; Cantarutti, R.B.; Lopes, A.S. Interpretation of the results of soil analysis. In Recommendations for the Use of Correctives and Fertilizers in Minas Gerais, 5th ed.; Ribeiro, A.C., Guimarães, P.T.G., Alvarez, V.H., Eds.; UFV: Viçosa, Brazil, 1999; Volume 1, pp. 25–32.
17. Moreira, A.; Fageria, N.K.; Souza, G.B.; Freitas, A.R. Production, nutritional status and chemical properties of soils with addition of cattle manure, reactive natural phosphate and biotite schist in Massaii cultivated. Rev. Bras. Zootec. 2010, 39, 1883–1888. [CrossRef]
18. Faquín, V. Effect of the Heat Treatment of Nepheline Syenite Added with Dolomitic Limestone, on the Availability of Potassium to Maize (Zea mays L.), in a Greenhouse. Master’s Thesis, School of Agriculture “Luiz de Queiroz”, Piracicaba, Brazil, 1982.
19. Siqueira, J.O.; Guedes, G.A.A.; Ribeiro, M.A.V. Potassium availability of the Poços de Caldas nepheline syenite, evaluated in successive crops with maize. Pesq. Agropec. Bras. 1985, 20, 299–307.
20. Martins, C.C. Potassium: Alternative Sources, Heat Treatments and Availability for Maize Plants (Zea mays L.). Master’s Thesis, Center for Agricultural Sciences—Federal University of Espírito Santos, Espírito Santo, Brazil, 2014.
21. Alovissi, A.M.T.; Alovissi, A.A.; Hartmann, C.F.; Tokura, L.K.; Silva, R.S. Attributes of soil fertility and productivity of maize and soybeans influenced by rock formation. Acta Igazuzu 2017, 6, 55–68.
22. Coelho, A.M.; França, G.E. Be the Doctor of Your Maize, 2nd ed.; Potafos: Piracicaba, Brazil, 1995; pp. 1–9.
23. USDA. Soil Survey Staff. Keys to Soil Taxonomy, 12th ed.; Natural Resources Conservation Service: Washington, DC, USA, 2014. Available online: https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/survey/class/taxonomy/?cid=nrcs142p2_053580 (accessed on 21 October 2020).
24. van Raij, B.; Cantarella, H. Maize. Fertilization and Liming Recommendations for the State of São Paulo, 2nd ed.; van Raij, B., Cantarella, H., Quaggio, J.A., Furlani, A.M.C., Eds.; Campinas Agronomic Institute: Campinas, Brazil, 1997; Volume 1, pp. 56–59.
25. Malavolta, E. Elements of Mineral Nutrition of Plants, 1st ed.; Editora Agronômica Ceres: São Paulo, Brazil, 1980; p. 251.
26. van Raij, B.; Andrade, J.C.; Cantarell, H.; Quaggio, J.A. Chemical Analysis to Assess Fertility in Tropical Soils, 1st ed.; Campinas Agronomic Institute: Campinas, Brazil, 2001; p. 285.
27. Teixeira, P.C.; Donagemma, G.K.; Fontana, A.; Teixeira, W.G. Manual de Métodos de Análise de Solo, 3rd ed.; Embrapa Informação Tecnológica: Brasília, Brazil, 2017; 573.
28. Malavolta, E.; Vitti, G.C.; Oliveira, S.A. Evolution of the Nutritional Status of Plants: Principles and Applications, 2nd ed.; Potafo: Piracicaba, Brazil, 1997; p. 319.
29. Goedert, W.; Souza, D.M.G.; Rein, T.A. Methodological Principles for Agronomic Evaluation of Phosphorus Sources, 1st ed.; Embrapa: Planaltina, Brazil, 1986; p. 23.
30. R Core Team. R: A Language and Environment for Statistical Computing; R Foundation for Statistical Computing: Vienna, Austria, 2013; Available online: http://www.r-project.org/index.html (accessed on 18 May 2020).
31. Raij, B. Soil Fertility and Nutrient Management, 1st ed.; International Plant Nutrition Institute (IPNI): Piracicaba, Brazil, 2011; p. 420.
32. Echart, C.L.; Cavalli-Molina, S. Phytotoxicity of aluminum: Effects, tolerance mechanism and its genetic control. Cienc. Rural 2001, 31, 531–541. [CrossRef]
33. van Raij, B.; Cantarella, H.; Quaggio, J.A.; Furlani, A.M.C. (Eds.) 4. Interpretation of soil analysis results. In Fertilization and Liming Recommendations for the State of São Paulo, 2nd ed.; Campinas Agronomic Institute: Campinas, Brazil, 1997; Volume 1, pp. 8–13.
34. Sato, S.; Comerford, N.B. Influence of soil pH on inorganic phosphorus sorption and desorption in a humid Brazilian Ultisol. *Rev. Bras. Ciência Solo* 2005, 29, 685–694. [CrossRef]

35. Fia, R.; Matos, A.T.; Aguirre, C.I. Productivity and concentration of nutrients and heavy metals in maize fertilized with increasing rates of chilled sewage sludge. *Eng. Agric.* 2006, 14, 39–50.