Residual effects of calcium amendments on oil palm growth and soil properties

S H Husain1, A Mohammed1*, H Y Ch'ng1 and S I Khalivulla2
1 Faculty of Agro-Based Industry, Universiti Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia
2 Department of Pharmaceutical Chemistry, UCSI University, 56000 Kuala Lumpur, Malaysia

*E-mail: aurifullah@umk.edu.my

Abstract. Residual liming is one of the measures of the efficacy of liming materials. Ca2+-amendments such as calcium hydroxide (Ca(OH)2), calcium oxide (CaO) and calcium carbonate (CaCO3) in soils may contribute to plant growth response in plant height and total dry matter yield of oil palm seedlings. The increasing of other essential elements such as nitrogen (N), phosphorus (P) and ions of potassium (K+) also play a great role in the plant growth and crop yield, conversely, the soil pH and ions of aluminium (Al3+) will inhibit the plant growth and crop yield. This main aim this experiment is to determine the residual liming effect of Ca2+-amendments to highly acidic soils collected from Jeram and Bungor series, Malaysia, which also contains 2 times of Al3+. The highly acidic soils of previously planted with oil palm seedlings initially incubated with selected Ca2+-amendments along with Mg2+-amendments such as, dolomite (CaMg.CO3) for 360 days and, kept for additional 180 days before planting for a total of 540 days in a greenhouse environment. In this experiment, the soil chemical analysis, plant growth response, and the possible mechanisms responsible for the Ca2+-amendment liming effects were measured. The results of the soil chemical analysis showed that Ca2+-amendment residues potentially reduced the soil acidity than Mg2+-amendments. Ca(OH)2 was the most prominent Ca2+-amendment to increase soil-water pH, soil solution pH, and concentrations of soluble Ca2+ and K+. While, concentration of soil solution and exchangeable Al were effectively reduced 540 days after the application of Ca-amendments. The dry shoot weight of the oil palm seedlings improved about 1.67 g/pot and 16.87 g/pot in control and Ca2+-amendment treatments, respectively. In this study, it has showed that the root dry weight of oil palm seedlings increased from 0.18 g/pot to 4.49 g/pot in pot and Ca2+-amended soil, respectively. Increased plant height and total dry matter yield of oil palm seedlings grown on the Ca-amended soils may be attributed to increased soil pH which resulted in lowered concentration and activity of soluble Al, and increased concentrations of soil solution Ca and K which were released of Ca. This finding concluded that the possible mechanisms of Ca2+-amendments from residual liming might be: a) complexation interaction between Al3+ and Ca2+; (b) capacity of Ca-amendments to increase the concentration of Ca to maintain soil desired pH; (c) alleviation effect of Ca-amendments to reduce Al toxicity concentration in the soil. Last but not least, this finding showed that dry matter yield and plant height positively associated with the presence of Al3+ in both soil conditions.
1. Introduction
Calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) are important elements in the soil for the healthy growth of plants. At high concentration of Aluminium (Al\(^{3+}\)) and also, due to high acidic nature (low pH) the Ca\(^{2+}\) and Mg\(^{2+}\) ions get replace with hydrogen ions in humid tropics results in leaching of the soil which leads to restricted crop growth. High rainfall and intense rates of naturally acidic soils cause Ca\(^{2+}\) deficiencies [1]. Current practices such as using fertilizer together with liming materials (CaO) burdens to the farmers due to its high-cost and transportation charges. In addition, excessive liming practices also negatively affect the growth of plants and soil properties such as the tendency of trees deficient to nitrogen (N), phosphorus (P) and manganese (Mn\(^{2+}\)) [2, 3]. The application of lime can increase plant growth by increasing the soil pH [3,4], reducing Al\(^{3+}\) toxicity [5, 6] and also provides basic cation for plant intake [6].

All of the other liming products used in the industry are Ca\(^{2+}\)-based, which decreases the amount of Al\(^{3+}\) exchangeable. It is impossible to discerning the practical benefit of reducing the concentration of Al\(^{3+}\) due to enhanced Ca\(^{2+}\) nutrition [7, 8]. However, most research on plant-nutrient-soil interactions and mitigating the toxicity of Al\(^{3+}\) in plants exposed to acidic soil through additional Ca\(^{2+}\) amendments have proved successful and productive in alleviating Al\(^{3+}\) toxicity in highly acidic soil [9]. Increasing the Ca\(^{2+}\) uptake by the plant [10-14], alleviating highly acid soil [10], and mitigating Al\(^{3+}\) to precipitate into Al(OH)\(_3\) [11, 12] was the proven approach.

Common Calcium-amendments which effectively used as multiple functional solutions in acid soil are calcium oxide (CaO), calcium hydroxide (Ca(OH)\(_2\)), and calcium carbonate (CaCO\(_3\)) [13-17]. Applying these Ca\(^{2+}\)-amendments significantly affects Ca\(^{2+}\) efficacy in mitigating Al\(^{3+}\) toxicity [17]. Integrating soils containing Ca\(^{2+}\) by liming methods would reduce soil acidity, which significantly increases the plant development [18-20]. This practice offers many advantages such as low-cost option, low environmental impact, high nutrient supply, requiring the unique capacity to sustain agricultural productivity and increases the nutrients.

Although several studies have demonstrated the positive effect of Ca\(^{2+}\)-amendments in detoxifying Al\(^{3+}\) and improving plant growth [21-25], the information is scarce on residual liming effect of Ca\(^{2+}\)-amendments application to strongly acid soils. In view of the above, this study was conducted to achieve the following objectives: (a) to assess the persistence of the "liming effect" of Ca\(^{2+}\)-amendments applied to Al\(^{3+}\)-toxic soils; (b) identify the potential mechanisms responsible for the liming effect of Ca\(^{2+}\)-amendments by chemical analyses.

2. Materials and Methods

2.1. Soil series used and Ca\(^{2+}\)-amendments properties
The residual liming effect treatment took two strongly acid Ultisols Bungor Series (Typic Paleudult) and Jeram Series (Typic Hapludult) samples from Kota Bahroe Estate Gopeng Perak, Malaysia which initially incubated with different kinds of Ca\(^{2+}\)-amendments (CaO, Ca(OH)\(_2\), and CaCO\(_3\)) for 360 days and another 180 days planted with oil palm seedlings. This study let the soils dry and undisturbed under greenhouse conditions for another 360 days without further treatment. After 360 days of the untreated incubation period, the oil palm seedlings were planted for 42 days on both soils replicated 3 times and experimental designed with randomized complete block design. This study selected the utmost dolomite dosage (unamended soil was 2 times of Al\(^{3+}\) exchangeable). No fertilizer was applied to the soils except for phosphorus (P) fertilizer in the form of potassium dihydrogen phosphate (KH\(_2\)PO\(_4\)) with 100 mg P/Kg for Jeram soil and 150 mg P/Kg for Bungor soil. During harvesting, measurement such as plant height was measured and then, the plant component (shoot and roots) collected and separated, washed carefully to remove dirt.

2.2. Chemical analysis
Dry matter yield (DMY) of plant shoot and roots were dried in the oven for two days at 70°C. Dry plant components were ground in a 40-mesh sieve for 3-4 hours at 500°C for leaf lab testing.
Mg\(^{2+}\), Ca\(^{2+}\), K\(^{+}\), Mn\(^{2+}\), Na\(^{+}\), Zn\(^{2+}\), and Fe\(^{2+/3+}\) were analyzed by spectrophotometry from the ashed sample solution. Cumulative tissue nitrogen was calculated using the micro-Kjeldahl process and, the concentration of P in plant components were calculated from the ashed sample using the sulfo-molybdate ascorbic method and the results were tabulated in Table 1.

2.2.1. Analysis and evaluation of soil

50 g of soil was placed into funnel with a filter paper of Whatman no. 42 and 500g of soil to centrifuge for half-an-hour. The soil extracted solution was analysed for the soil pH to prevent losses of CO\(_2\). The removed soil solution was placed in a refrigerator at 4°C to analyse other nutrients. Soil solutions used to analyse parameters, pH and total soluble Al\(^{3+}\) were used through the centrifugation process [23].

2.2.2. Soil extraction and chemical analyses

Soil P is measured by collecting 20 mL of 0.5 M NaHC03 solution from 1.0 g of air-dried soil. The mixture was put in a centrifuge tube and shaken for 30 minutes before centrifuging for 10 minutes at 10,000 rpm. The molybdate-ascorbic acid process is then used to determine the amount of phosphorus in the supernatant. For plant tissue, high-performance liquid mass spectroscopy (HPLC) was performed to analyse soil solutions SO\(_4^{2-}\) and NO\(_3^-\). In a 50-mL centrifuge tube, four-gram of air-dried soil solution was diluted in 20 mL of 1 M of ammonium acetate (CH\(_3\)COONH\(_4^+\)). The mixer of soil solution placed in the shaker for half-an-hour and centrifuged for 10 min at 10,000 rpm. The solution was filtered in 50-mL volumetric flasks via a filter paper. The filtration process was repeated, and the samples were then analysed utilizing flame atomic absorption spectrometry for the evaluation of metallic cations.

2.2.3. Aluminium analysis

The analysis of exchangeable Al\(^{3+}\) was performed by mixing 5 g of soil with 30 mL of 1M KCl solution. The mixture was shaken for 30 mins followed by centrifugation for 10 mins at 10,000 rpm. The filtration process was repeated for 3 times and the compounds derived from the centrifuge tube were combined, and the KCl formulation was formed at a maximum volume of 100 mL.

2.3. Statistical analysis

The collected data were analyzed using Analysis of variance (ANOVA). The variations between Bungor and Jeram soil treatments and, the plant component (shoot and roots) were also analysed with the Waller-Duncan K-ratio T-test at a 5 percent significance level.

3. Results and Discussion

3.1. Soil chemical analysis before Ca\(^{2+}\)-amendments treatment

The results of the oil palm seedlings before planting (Table 1) and 540 days after the application of Mg\(^{2+}\) and Ca\(^{2+}\)-amendments for different soil analysis are tabulated in Table 2 and Table 3. Soil pH has indeed increased substantially, from 4.66 to 6.45, which Ca(OH)\(_2\) and CaO, which are much greater than CaMg.CO\(_3\) given the positive impact of Ca\(^{2+}\)-amendments. Even though the CaCO\(_3\) treated soils' pH values dropped below 5.0, they were still higher than those of the control treatment. The EC of soil solution of the modified Ca\(^{2+}\)-treated soil was also substantially higher than that of the control soil, and the increased values were also observed in modified Mg\(^{2+}\)-treated soil. The concentration of Ca\(^{2+}\)-amends treated soil was dramatically increased in soil solution. The K\(^{+}\) concentration significantly greater in CaCO\(_3\)-amends soil in Bungor soil than Jeram soil.
Table 1. Soil chemistry of untreated soils.

| Properties            | Bungor series | Jeram series |
|-----------------------|---------------|--------------|
| **Soil Texture**      |               |              |
| Clay                  | 36.70         | 49.28        |
| Silt                  | 35.50         | 23.03        |
| Sand                  | 27.73         | 27.61        |
| **Soil Texture Class (USDA)** | Clay loam     | Clay         |
| **Chemical Properties**         |               |              |
| Soil pH (1:2; soil: H₂O) | 4.25          | 4.03         |
| Soil pH (1:2; soil: 0.03 M KCl) | 3.04          | 3.59         |
| Soil solution EC (dS m⁻¹) | 0.70          | 0.80         |
| Organic C (%)         | 0.79          | 0.29         |
| Exchangeable cations (CH₃COONH₄⁺) |           |              |
| Ca²⁺ (µg/g)           | 13.00         | 154.00       |
| Mg²⁺ (µg/g)           | 25.00         | 103.00       |
| K⁺ (µg/g)             | 59.00         | 102.00       |
| Na⁺ (µg/g)            | 5.00          | 10.00        |
| Soil solution Al³⁺ (µM)| 108.00        | 244.00       |
| N (%)                 | 0.14          | 0.17         |
| P (%)                 | 5.60          | 3.20         |

Table 2. Soil chemical properties of Bungor Series soil after 540 for Ca²⁺-amendments application.

| Treatment        | Soil pH⁺ (1:2; soil: H₂O) | Soil solution EC (dS m⁻¹) | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | K⁺ (mg/L) | Mn²⁺ (mg/L) | Al³⁺ (KCl) (µM) |
|------------------|---------------------------|---------------------------|-------------|-------------|-----------|-------------|----------------|
| Control          | 4.66d¹                    | 1.05e                     | 33.82e      | 17.40e      | 66.18d    | 11.08a      | 55.71a         |
| CaMg.CO₃         | 4.63de                    | 1.59d                     | 72.05d      | 39.08a      | 172.50b   | 5.69c       | 4.25c          |
| CaO              | 6.31b                     | 1.89c                     | 105.33b     | 29.75d      | 55.73e    | 2.25d       | 2.20d          |
| Ca(OH)₂          | 6.45a                     | 2.40a                     | 200.10a     | 33.30c      | 157.78c   | 1.23e       | 3.89e          |
| CaCO₃            | 4.88e                     | 2.22b                     | 92.10c      | 37.48b      | 228.33a   | 10.34b      | 10.23b         |

¹ 1 soil: 2 H₂O ratio
² Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.
Table 3. Soil chemical properties of Jeram Series soil after 540 for Ca-amendments application.

| Treatment     | Jeram series |
|---------------|--------------|
|               | Soil pH (1:2; soil: H₂O) | Soil solution EC (dS m⁻¹) | Ca²⁺ (mg/L) | Mg²⁺ (mg/L) | K⁺ (mg/L) | Mn²⁺ (mg/L) | Al³⁺ (KCl) (μM) |
| Control       | 4.48d        | 1.95e          | 33.37e       | 18.74d       | 63.20d     | 9.00c       | 57.81a       |
| CaMg.CO₃      | 4.45e        | 2.49d          | 37.60d       | 40.42a       | 169.52b    | 31.48b      | 6.35c        |
| CaO           | 6.13b        | 2.79c          | 104.88b      | 11.09e       | 52.75e     | 0.31e       | 4.30e        |
| Ca(OH)₂       | 6.27a        | 3.30a          | 199.65a      | 34.64c       | 154.80c    | 4.60d       | 5.99d        |
| CaCO₃         | 4.70c        | 3.12b          | 38.82b       | 225.35a      | 66.75a     | 12.33b      |

Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.

3.2. Plant growth response to the residual accumulation

Ca²⁺-amendment oil palm seedlings showed that the plants were taller or identical to those in the control treatments (Error! Reference source not found. and Table 5). Plant height also increased substantially with Ca²⁺ and Mg²⁺-modifications. Oil palm seedlings obtained by Ca(OH)₂ and CaO were considerably higher than any of those received by CaMg.CO₃. The improvement in root dry matter yield in response to Ca²⁺-amendments or Mg²⁺-modifications significantly affected. Mg²⁺-amendments and Ca²⁺-amendments raised the dry root weight about 19-fold and 10-fold for oil palm seedlings, respectively. The different Ca²⁺-amendments also greatly increased the root dry weights of the oil palm seedlings across the corresponding controls treatment. The control oil palm seedlings produced minimal development, apart from initial acquisition before transplantation, as evidenced by their very low yields. Statistical results reveal that the Ca²⁺-amendments and Mg²⁺-amendments substantially improved the shoot and dry root weights. Comparably, the dry shoot weight of the oil palm seedlings improved about 1.67 g/pot and 16.87 g/pot in control and Ca²⁺-amendment treatments, respectively. Dry weight of roots increased significantly from liming application. In this study, it has showed that the root dry weight of oil palm seedlings increased from 0.18 g/pot to 4.49 g/pot in pot and Ca²⁺-amended soil, respectively. Excluding for the CaCO₃ treatment, there were no difference in the dry weights between Ca²⁺-modified soils than from those in the Mg²⁺-modification treatment. In contrast, seedlings treated with Ca(OH)₂ showed the maximum dry weights yield.

Table 4. Effects of liming to the oil palm seedlings response after 540 days of incubation.

| Treatment     | Bungor series |
|---------------|---------------|
|               | Shoot dry matter yield (g/pot) | Root dry matter yield (g/pot) | Plant height (cm) |
| Control       | 1.67*e        | 0.18de         | 38.77e         |
| CaMg.CO₃      | 14.95d        | 3.48b          | 161.00a        |
| CaO           | 16.11b        | 0.24d          | 40.40d         |
| Ca(OH)₂       | 16.87a        | 3.57c          | 141.90b        |
| CaCO₃         | 15.62c        | 4.49a          | 117.00c        |

Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.
Table 5. Effects of liming to the oil palm seedlings response after 540 days of incubation.

| Treatment     | Jeram series |                |                |                |
|---------------|--------------|----------------|----------------|----------------|
|               | Shoot dry matter yield (g/pot) | Root dry matter yield (g/pot) | Plant height (cm) |
| Control       | 4.88*e       | 0.30d          | 57.00e         |
| CaMg.CO$_3$   | 11.85c       | 0.46bc         | 149.70d        |
| CaO           | 5.39d        | 0.47b          | 68.60d         |
| Ca(OH)$_2$    | 14.26ab      | 3.14a          | 168.40b        |
| CaCO$_3$      | 14.91a       | 0.41c          | 186.40a        |

a Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.

3.3. Chemical composition of plants

Table 6 shows the effects of different Ca$^{2+}$-amendments on the root and shoot of oil palm seedlings and the effects of changes in N, P, K$^+$, Ca$^{2+}$, Mg$^{2+}$, Fe$_{2/3}^{3+}$ and Zn$^{2+}$ Bungor and Jeram series. Ca$^{2+}$-amendments in Jeram soil greatly increased the amount of N in oil palm seedlings. N concentrations in oil palm seedlings shoot in the Ca$^{2+}$-amended treated soil was two times greater (28.3 to 28.5 g/kg) than plants in untreated soil. N in plant tissue varied between 18.6 to 28.5 g/kg in Ca$^{2+}$-modified soil compared to 16.7 g/kg in Mg$^{2+}$-amendments application.

P levels in shoot were increased significantly both by the Ca$^{2+}$-modifications and the Mg$^{2+}$-modifications relative to the control treatment. However, P concentrations were highest in CaCO$_3$, because, high amount of Ca$^{2+}$ enables P to release into the soil which becomes available to the plants. Ca$^{2+}$ oil palm seedlings application resulted from expressively greater K$^+$ concentration when comparing with Mg$^{2+}$-amendments treated plants and the control. Having applied lime Ca$^{2+}$-amendments substantially resulted in the accumulation of K$^+$ in the shoots, from 9.6 to 17.8 g/kg than the lower concentration in the control seedlings level (10.0 g/kg). Ca(OH)$_2$ and CaO represented 14.5% and 19.6% off Ca$^{2+}$, both and 40 to 50% of Ca$^{2+}$ in these materials were extracted upon 168 days of incubation.

Shoot Ca$^{2+}$ concentrations in these oil palm seedling treatments were also higher than those in Mg$^{2+}$-amendments lime treatment. With Mg$^{2+}$ and Ca$^{2+}$ lime amendments, shoot Ca$^{2+}$ increased, particularly in oil palm seedlings amended with Ca(OH)$_2$ and CaO. In the oil palm shoot seedlings Mg$^{2+}$-amendments concentration is better than the Ca$^{2+}$-lime amendments. In the CaMg.CO$_3$ supplemented oil palm and the control oil palm seedlings have the same concentration 9.8 g Mg$^{2+}$/kg). Iron would not be a restricting element throughout all treatments because the amount of Fe$_{2/3}^{3+}$ was between 50-150 mg/kg, which was considered adequate by oil palm [21]. In oil palm seedlings, the maximum Fe$_{2/3}^{3+}$ shoot of 181 mg/kg was from lime-treated. Oil palm seedlings varied between 113 to 140 mg Fe$_{2/3}^{3+}$/kg among the treatments. Shoot Fe$_{2/3}^{3+}$ was affected by liming in oil palm seedlings and was greatly improved with Ca-amendments.

In the Mg$^{2+}$-amendments lime treatment, the lowest shoot Zn$^{2+}$ was when the highest concentrations were from plants receiving Ca(OH)$_2$. The oil palm seedlings treated with Ca$^{2+}$ and Mg$^{2+}$-amendment lime had Zn$^{2+}$ concentrations in plant tissue substantially lesser than control treatments. In oil palm seedlings, no specific pattern was detected for Zn$^{2+}$. The highest control was Shoot Zn$^{2+}$ in oil palm seedlings.
Table 6. Effects of Ca\(^{2+}\)-amendments residual on plant chemical composition after 540 days of incubation.

| Treatment       | Bungor Series |             |             |             |             |             |              |
|-----------------|---------------|-------------|-------------|-------------|-------------|-------------|---------------|
|                 | N (g/Kg)      | P (g/Kg)    | K\(^+\) (g/Kg) | Ca\(^{2+}\) (g/Kg) | Mg\(^{2+}\) (g/Kg) | Fe\(^{2+/3+}\) (mg/Kg) | Zn\(^{2+}\) (mg/Kg) |
| Control         | 16.7e\(^a\)   | 1.0d        | 10.0c       | 5.2e        | 9.8bc       | 66.6c       | 222.4a        |
| CaMg.CO\(_3\)  | 18.6d         | 1.9bc       | 9.6d        | 6.2d        | 9.8bc       | 65.3d       | 223.1ab       |
| CaO             | 28.3ab        | 2.0b        | 17.8d       | 13.0a       | 9.9b        | 62.9e       | 66.4e         |
| Ca(OH)\(_2\)   | 28.5a         | 1.9bc       | 17.8d       | 8.1bc       | 8.5d        | 86.8b       | 155.3c        |
| CaCO\(_3\)     | 25.0c         | 5.7a        | 16.5b       | 8.4b        | 10.2a       | 155.8a      | 128.7d        |

| Treatment       | Jeram Series |             |             |             |             |              |               |
|-----------------|--------------|-------------|-------------|-------------|-------------|---------------|
|                 | N (g/Kg)      | P (g/Kg)    | K\(^+\) (g/Kg) | Ca\(^{2+}\) (g/Kg) | Mg\(^{2+}\) (g/Kg) | Fe\(^{2+/3+}\) (mg/Kg) | Zn\(^{2+}\) (mg/Kg) |
| Control         | 20.1e\(^a\)  | 1.5e        | 13.6b       | 2.8e        | 1.4e        | 116.1de      | 132.7c        |
| CaMg.CO\(_3\)  | 21.7c         | 21.8d       | 1.8d        | 15.0d       | 2.6d        | 117.7d       | 136.6b        |
| CaO             | 31.2b         | 29.3c       | 7.0a        | 19.1c       | 23.5a       | 186.8a       | 53.3e         |
| Ca(OH)\(_2\)   | 34.3a         | 47.6a       | 2.3e        | 22.2b       | 19.7b       | 130.4b       | 127.5d        |
| CaCO\(_3\)     | 24.1cd        | 44.9b       | 1.8d        | 26.5a       | 16.2c       | 127.5c       | 168.5a        |

\(^a\) Waller-Duncan K-ratios-tests at the T-test of 5% level of significance

3.4. Dry matter shoot and Al\(^{3+}\) and Mn\(^{2+}\) concentration in shoot

Figures 1 and 2 displayed the interactions between dry shoot weight with Al\(^{3+}\) and Mn\(^{2+}\) concentration in shoot. Figure 2 showed a reduction of Al\(^{3+}\) concentration in the shoots which gradually increase the shoot dry matter significantly. Hence, it can be observed that application of liming can led to a reduction of Al\(^{3+}\) concentration in oil palm seedlings where Al\(^{3+}\) concentration in shoots was associated with a sharp decrease in shoot dry weight showed in Figure 1.

Concentration of Zn\(^{2+}\) in plants treated with Ca\(^{2+}\) and Mg\(^{2+}\) treated soil greatly reduced compared to CaCO\(_3\) treatments. In contrast, the Al\(^{3+}\) concentration significantly highest in shoot in control treatment. Concentration of Mn\(^{2+}\) in shoot (6.25, 0.88, 1.29, 1.58 and 1.23 mg/kg) showed a reverse association with shoot dry weight (0.72, 3.92, 4.90, 4.36, and 2.12 g/pot), respectively, at 5% level of significance. Application of Ca amendments particularly Ca(OH)\(_2\) and CaO reduced Mn\(^{2+}\) uptake effectively by plants compared to the CaCO\(_3\) and CaMg.CO\(_3\).
Figure 1. Shoot dry matter yield of oil palm seedlings as affected by plant tissue aluminium (Al$^{3+}$).

Figure 2. Effect of Ca$^{2+}$-amendments on shoot dry matter yield of oil palm and Mn$^{2+}$ concentration.

3.5. Soil pH and exchangeable Ca$^{2+}$ after harvest

Soil pH and Al$^{3+}$ exchangeable were observed after harvest by comparing the residual liming effects of Ca$^{2+}$-amendments with conventional liming treatment (Table 7). CaCO$_3$ also greatly increased the pH.
of the soil over controls. These pH rises led to a dramatic reduction in the exchangeable Al$^{3+}$, which was almost zero. Ca(OH)$_2$ and Ca$^{2+}$ increased the pH of soil by almost two units from 4.05 in Bungor soil and 4.06 in Jeram soil to more than 6.0, or 540 days after application.

**Table 7.** Effects of liming sources on the exchangeable Al concentrations and soil pH of Bungor and Jeram soil series after harvest.

| Treatment       | Bungor Series |          | Jeram Series |          |
|-----------------|---------------|----------|--------------|----------|
|                 | pH            | Exchangeable Al$^{3+}$ (cmol, kg$^{-1}$) | pH            | Exchangeable Al$^{3+}$ (cmol, kg$^{-1}$) |
| Control         | 4.05e         | 3.71e    | 4.06e        | 5.35a    |
| CaMg.CO$_3$     | 4.89cd        | 0.20c    | 4.81c        | 0.70b    |
| CaO             | 6.47b         | 0.07a    | 6.40b        | 0.04d    |
| Ca(OH)$_2$      | 6.57a         | 0.12b    | 6.84a        | 0.02e    |
| CaCO$_3$        | 4.90e         | 0.29d    | 4.61d        | 0.67c    |

*Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.*

3.6. Relationship between plant dry matter yield and pH, Al$^{3+}$ and Mn$^{2+}$ in soil solution

Two crucial elements that could affect the soil acidity intensity was the presence of high concentration of soluble Mn$^{2+}$ and Al$^{3+}$. The effects of Ca$^{2+}$ amended soils to the Mn$^{2+}$ concentration and total soluble Al$^{3+}$ both in shoot and root dry matter yield was shown in Table 8.

The negative effects of greater content of Mn$^{2+}$ and total soluble Al$^{3+}$ was exhibited in both plant components. The oil palm seedlings produced only 1.23 g of dry shoot dry matter in control soil. These result is confirmed by the finding of Ismail et al. [21] who reported that the concentration of total soluble Al$^{3+}$ at 30 μM is the threshold level for maize that grown in Ultisols and Oxisols soils in Malaysia. Application of both liming sources could reduce Al$^{3+}$ concentration about 4.5 μM in the Bungor soil. This is due to the positive effects of lime application in reducing the total soluble Al$^{3+}$ concentration in both soils which directly affect the yield of shoot dry weight. Plant dry weight has been increased 9 times greater than the control soil. For CaO application, it can be observed the reducing of soluble Al$^{3+}$ concentrations from 13.3 to 4.5 μM and 14.81 to 6.1 both in Bungor soil and Jeram soil, respectively. Ca(OH)$_2$ was more effective than CaCO$_3$ in reducing Al$^{3+}$ concentration in soil solution when total soluble Al$^{3+}$ concentration ranged from 25 μM and 19.5 μM in the Jeram and Bungor soil, respectively. Concentrations of Mn$^{2+}$ concentrations decreased with both liming sources except for CaCO$_3$ applications which increase the Mn$^{2+}$ release into the soil solution, particularly in the Jeram soil.
Table 8. Effects of liming sources on the dry matter yield of shoots and roots and concentrations of soluble Al$^{3+}$ and Mn$^{2+}$

| Treatment | Bungor Series | Jeram Series | Soil pH | Soluble Al$^{3+}$ (μm) | Soluble Mn$^{2+}$ (mg/L) |
|-----------|---------------|--------------|---------|------------------------|--------------------------|
|           | SDW (g)       | RDW (g)      |         |                        |                          |
| Control   | 1.67e         | 0.18e        | 4.30e   | 48.57a                 | 14.08a                   |
| CaMg.CO$_3$ | 14.95d       | 3.84b        | 4.72d   | 13.15b                 | 6.71c                    |
| CaO       | 16.11b        | 0.24d        | 6.39b   | 4.68d                  | 1.41d                    |
| Ca(OH)$_2$ | 16.87a       | 3.57c        | 6.51a   | 4.40e                  | 1.07e                    |
| CaCO$_3$  | 15.62c        | 4.49a        | 4.86c   | 12.50c                 | 10.55b                   |

| Treatment | SDW (g)       | RDW (g)      | Soil pH | Soluble Al$^{3+}$ (μm) | Soluble Mn$^{2+}$ (mg/L) |
|-----------|---------------|--------------|---------|------------------------|--------------------------|
| Control   | 4.88e         | 0.30e        | 4.25e   | 88.20a                 | 9.50c                    |
| CaMg.CO$_3$ | 11.85c       | 0.46bc       | 4.77c   | 11.25c                 | 34.70b                   |
| CaO       | 5.39d         | 0.47b        | 6.50a   | 6.18d                  | 7.43d                    |
| Ca(OH)$_2$ | 14.26b       | 3.14a        | 6.49ab  | 2.43e                  | 0.50e                    |
| CaCO$_3$  | 14.91a        | 0.41d        | 4.60d   | 14.18b                 | 55.73a                   |

*Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.

3.7. The concentration of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ in soil solution

Many acid soil types would have low levels of nutrients needed to survive. Concentrations of soil solution Ca$^{2+}$, Mg$^{2+}$ and K$^+$ were lowest in control soils (Table 9 and Table 10). Ca(OH)$_2$ treated soils had a substantially higher concentrations of these nutrients than Mg$^{2+}$-calmed soils. Liming increased in soluble Ca$^{2+}$ but had little effect on soluble Mg$^{2+}$, K$^+$ and Na$^+$. Ca$^{2+}$-amendments and Mg$^{2+}$-amendments greatly improved the soluble Ca$^{2+}$ and Mg$^{2+}$ of the controls. With the exception of CaCO$_3$ in both soils and CaO treatment in Jeram soil, Ca$^{2+}$-modifications had no major impact on Na$^+$ soil solution. Soil solution K$^+$ concentrations were also higher in Ca$^{2+}$-modified soils than in control soils and Mg$^{2+}$-treated soils with the exception of CaCO$_3$ modified Bungor soil. Thus, apart from their Al$^{3+}$-detoxifying effect (liming effect), Ca$^{2+}$-amendments can also supply essential cations that are often deficient in acid soils.

Table 9. Effects of liming sources on concentrations of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ in the soil solution during harvest.

| Treatment | Bungor Series | Jeram Series | Ca$^{2+}$ (mg/L) | Mg$^{2+}$ (mg/L) | K$^+$ (mg/L) | Na$^+$ (mg/L) |
|-----------|---------------|--------------|------------------|-----------------|--------------|---------------|
| Control   | 10.10e        | 31.00d       | 22.03de          | 145.25d         |              |               |
| CaMg.CO$_3$ | 48.33d       | 77.05c       | 62.15c           | 132.18e         |              |               |
| CaO       | 141.20b       | 3.58e        | 22.55d           | 125.93c         |              |               |
| Ca(OH)$_2$ | 261.45a      | 143.53a      | 75.13b           | 201.65b         |              |               |
| CaCO$_3$  | 70.33e        | 112.25b      | 141.80a          | 259.05a         |              |               |

*Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.
Table 10. Effects of liming sources on concentrations of Ca\(^{2+}\), Mg\(^{2+}\), K\(^{+}\) and Na\(^{+}\) in the soil solution during harvest.

| Treatment   | Jeram Series | Jeram Series |
|-------------|--------------|--------------|
|             | Ca\(^{2+}\) (mg/L) | Mg\(^{2+}\) (mg/L) | Ca\(^{2+}\) (mg/L) | Na\(^{+}\) (mg/L) |
| Control     | 15.58e\(^a\)    | 11.33d        | 22.40d           | 111.70cd         |
| CaMg.CO\(_3\) | 53.48d        | 97.50c        | 61.35c           | 122.65b          |
| CaO         | 98.05b         | 6.30e         | 22.45d           | 102.46e          |
| Ca(OH)\(_3\) | 190.85a       | 118.29a       | 74.65b           | 180.58a          |
| CaCO\(_3\)  | 58.70c         | 172.43b       | 142.03a          | 111.80c          |

\(^{a}\)Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.

3.8. Possible processes responsible for the liming effect of the Ca\(^{2+}\)-amendments

3.8.1. **Aluminum complexation by Ca\(^{2+}\)**.

Acid soils that are applied with Ca\(^{2+}\)-amendments detoxified Al\(^{3+}\) by interactions with Ca\(^{2+}\) with the increase of Ca\(^{2+}\) supply to be uptake by the plant [8-12], alleviating highly acidic soil [25] and mitigating Al\(^{3+}\) by inducing precipitation of Al\(^{3+}\) to Al(OH)\(_3\) [13-14]. Applying these Ca\(^{2+}\)-amendments significantly affects Ca\(^{2+}\) efficacy in mitigating Al\(^{3+}\) toxicity [17]. Additionally, healthier plant growth is reached with an increase of Ca\(^{2+}\) supply to the soil [20]. Table 11 relates the amount of Al\(^{3+}\) extracted by LaCl\(_3\) with that extracted with KCl. The difference in the amount of Al\(^{3+}\) extracted by the two solutions could be attributed mostly to Ca\(^{2+}\) (Table 11). It is believed that Ca\(^{2+}\) displaced the Al\(^{3+}\)-complexing sites [26-28] by electrostatic effects on the cell surface, most probably by blocking plasma membrane channels to the toxic cation [29]. Hence, from this study, it has been observed that Ca\(^{2+}\)-amended soils had significantly higher soil Al\(^{3+}\) levels when 0.33M LaCl\(_3\) was used as the extractant. It is generally considered that KCl removes mostly exchangeable Al\(^{3+}\) while LaCl\(_3\) or CuCl\(_2\) solutions remove Al\(^{3+}\).

Table 11. Soil Al\(^{3+}\) extracted by 1M KCl and 0.33 M LaCl\(_3\).

| Treatment   | Bungor Series | Jeram Series |
|-------------|---------------|--------------|
|             | 1M KCl | O.33M LaCl\(_3\) | 1M KCl | O.33M LaCl\(_3\) |
| Control     | 5.49a\(^a\) | 5.45a        | 3.75a  | 3.59a           |
| CaMg.CO\(_3\) | 0.71b        | 0.85c        | 0.19c  | 0.42b          |
| CaO         | 0.03de       | 0.14d        | 0.02d  | 0.18d          |
| Ca(OH)\(_3\) | 0.02d        | 0.03e        | 0.02d  | 0.04e          |
| CaCO\(_3\)  | 0.70bc       | 1.02b        | 0.22b  | 0.39bc         |

\(^{a}\)Means indicated by the same letter in the column and soil are not significant according to the Waller-Duncan K ratio of the T-test at the 5% level of significance.

3.8.2 **Ameliorative effect of Ca\(^{2+}\)**.

**Error! Reference source not found.** and **Error! Reference source not found.** demonstrate a significant, major correlation between the quantity of Ca\(^{2+}\) solutions used and the overall yield of dry matter in the root and shoot. Holland [25] reported increased productivity by ameliorating Al\(^{3+}\) toxicity.
and increasing plants' capacity to uptake and keep nutrients from the acidic soil. [30] have shown that even when Ca\(^{2+}\) inputs enhance the electrolyte strength, Al\(^{3+}\) ions' negative effects are inactivated. The stronger soil's ability to convert toxic Al\(^{3+}\) could partly be attributed to increased Ca levels in the soil. It improves soil conditions and promotes plant productivity by alleviating Ca\(^{2+}\) deficiency, decreasing Al\(^{3+}\) toxicity, and improving plant nutrient availability [31]. Calcium can change the concentration of exchangeable soil cations (Ca\(^{2+}\), Mg\(^{2+}\), and Al\(^{3+}\)) [32]. The strong effects of Ca\(^{2+}\) in soil could be shown in recent results from field studies on acidic soil suggested that liming increased K\(^{+}\) availability by competitive adsorption of Ca\(^{2+}\) and Mg\(^{2+}\) [33]. In comparing the effectiveness of Ca\(^{2+}\)-amendments, Li et al. [34] found that Ca(OH)\(_2\) appeared to be more effective for neutralizing acidity in field soils than in potting soils. Li et al [4] reported that CaCO\(_3\) did much better than CaMg.CO\(_3\) to contribute to raising the soil pH, largely because of its greater solubility. CaO seemed to be a better chemical liming solution for increasing pH in soil due to its higher neutralizing value [35]. Ca(OH)\(_2\) has more stable alkalinity in field environments.

### Figure 3.
The relationship between the yield of a oil palm seedling's dry matter and Ca\(^{2+}\) concentration in the Bungor series soil.

### Figure 4.
The relationship between the yield of a oil palm seedling's dry matter and Ca\(^{2+}\) concentration in the Jeram series soil.

3.8.3. Precipitation of Al\(^{3+}\) due to pH increase.

The reaction mixture acid was then diluted to the standard solution with such a consistent solution of NaOH. That liming capacity of Ca(OH)\(_2\) and CaO was stronger than CaMg.CO\(_3\) and CaCO\(_3\) (Figure 5). The liming similarity was calculated by interacting with 0.5M HCl for 30 minutes on each of the Ca\(^{2+}\)-amendments and using dolomite as a reference. This increase in soil pH in the prevalence may be linked to the Ca\(^{2+}\)-amendment liming effect. OH\(^{-}\) ions are formed by the dissolution of lime, which precipitates Al\(^{3+}\) as Al(OH)\(_3\), considered non or unavailable to crops. Ca\(^{2+}\)-amendments can partially explain their capacity to sustain soil pH above those of the untreated control to boost plant growth. Due to liming, good plant growth can be related to lower soluble and exchangeable Al\(^{3+}\) concentrations as soil increases [36].

Soil pH increases only after improvements to Ca\(^{2+}\) due to the H\(^{+}\) and Al\(^{3+}\) changes of Ca\(^{2+}\) via exchange sites to the solution [11, 33]. A recent study showed that Ca\(^{2+}\)-amendments have a more significant effect on improving the soil pH in crop production than conventional
liming practices [10]. The soil pH increases only after the initiation of improvements to Ca\(^{2+}\) due to the H\(^+\) and Al\(^{3+}\) changes of Ca\(^{2+}\) via exchange sites to the solution [34, 35]. Increased Al\(^{3+}\) of soil levels caused a reduction in leaf levels of Zn\(^{2+}\), Ca\(^{2+}\), Mg\(^{2+}\), or Mn\(^{2+}\).

4. Conclusion
Liming effects of the Ca\(^{2+}\)-amendments could explain the following mechanisms: a) Ca\(^{2+}\)-amendments detoxify Al\(^{3+}\) through complexation with soluble Ca\(^{2+}\) molecules; b) they supply Ca\(^{2+}\); c) they increase soil pH and precipitate Al\(^{3+}\). Ca\(^{2+}\)-amendments significantly increased concentrations of cations such as calcium, magnesium, potassium and sodium in the soil, which is helpful to plant growth that cultivated in acid soils. The shoot yields for the Ca\(^{2+}\)-amended soils were comparable to that of previously produced in the Mg\(^{2+}\)-limed soils. Ca\(^{2+}\)-treated were effective than untreated lime in increasing soil pH and decreasing the concentration Al\(^{3+}\) and concentration of soluble Mn\(^{2+}\). Crop response and soil chemical properties suggest that the Ca\(^{2+}\)-amendments residual liming effect lasted at least 540 days after their application.

References
[1] Zannah T I, Jusop S, Ishak C F and Roslan I 2016 FTIR and XRD analyses of highly weathered Ultisols and Oxisols in Peninsular Malaysia reducing soil acidity in Ultisols and Oxisols using red gypsum in combination with biochar Asian J. Agric. Food Sci. 4 1571-21
[2] Njoku B O, Enwezor W O and B I Onyenakwe 1987 Calcium deficiency identified as an important factor limiting maize growth in acid Ultisols of Eastern Nigeria Fertil. Res. 14, 2 113–23
[3] Horst M 1991 Mechanisms of adaptation of plants to acid soils Plant Soil. 134 1–20
[4] Jusop S, Ishak C F and Sharifuddin H A H 1992 Effects of limestone and gypsum application to a Malaysian Ultisol on soil solution composition and yields of maize and groundnut Plant
[5] Jusop S, Fauziah C I, Anda M, Kapok J and Shazana M A R S 2011 Using ground basalt and/or organic fertilizer to enhance productivity of acid soils in Malaysia for crop production *Malaysian J. Soil Sci.* **15** 127–46

[6] Brendan S and Roberts A 2000 Conyers Management of soil acidity in long-term pastures of south-eastern Australia: A review *Aus. J. of Exp. Agric.* **40** 1173–98

[7] Qiquan L, Shan L, Yi X, Bing Z, Changquan W, Bing L, Xuesong G, Yiding L, Genchuan B, Yongdong W and Dagang Y 2019 Soil acidification and its influencing factors in the purple hilly area of southwest China from 1981 to 2012 *Catena* **175** 278–85

[8] Arolu A, Jusop S, Ishak C F and Othman R 2020 Utilization of magnesium-rich synthetic gypsum as magnesium fertilizer for oil palm grown on acidic soil *PLoS One* **15** 1–17

[9] Yuan L, Cui S, Chang S X and Qingping Z 2019 Liming effects on soil pH and crop yield depend on lime material type, application method and rate, and crop species: A global meta-analysis *J. Soils Sediments* **19** 1393–406

[10] Keith W T G 2016 Soil acidification and the importance of liming agricultural soils with particular reference to the United Kingdom *Soil Use Mgt.* **32** 390–99

[11] Maria Luz M, B Schnettler and R Demanet 1999 Effect of liming and gypsum on soil chemistry, yield, and mineral composition of ryegrass grown in an acidic Andisol *Commun. Soil Sci. Plant Anal.* **30** 1251–66

[12] Maria Luz Mora, P Cartes, R Demanet, and I S Cornforth 2002 Effects of lime and gypsum on pasture growth and composition on an acid Andisol in Chile, South America *Commun. Soil Sci. Plant Anal.* **33** 2069–81

[13] Keith W T G 2015 Factors affecting soil pH and the use of different liming materials. Proceedings-International Fertiliser Society. 772 International Fertiliser Society

[14] Virginia I M, Fernando G, Carmen V and García-González M T 2004 Field application of industrial by-products as Al toxicity amendments: Chemical and mineralogical implications *Eur. J. Soil Sci.* **55** 681–92

[15] Chris G C, Garrido F, Illera V and García-González M T 2006 Transport of Cd, Cu and Pb in an acid soil amended with phosphogypsum, sugar foam and phosphoric rock *Appl. Geochemistry* **21** 1030–43

[16] Tadashi T, Yuya I, Fujita K and Nanzyo M 2006 Effect of liming on organically complexed aluminum of nonallophanic Andosols from northeastern Japan *Geoderma*. **130** 26–34

[17] Samuel L T and Nelson W L 1966 Soil fertility and fertilizers *Soil Sci.* **101** 346

[18] Md Atikur R, Sang Hoon L, Hee Chung J, Ahmad Humayan K, Chris Stephen J and Ki Won L 2018 Importance of mineral nutrition for mitigating aluminum toxicity in plants

[19] Meriño-Gergichevich C, Alberdi M, Ivanov G A and M Reyes-Díaz 2010 Al$^3+$-Ca$^{2+}$ interaction in plants growing in acid soils: Al-phytotoxicity response to calcareous amendments *J. Soil Sci. Plant Nutr.* **10** 217–43

[20] Fred A and P J Hathcock 1984 Aluminum toxicity and calcium deficiency in acid subsoil horizons of two coastal plains soil series *Soil Sci. Soc. Am. J.* **48** 1305–09

[21] Ismail H, Jusop S, and Omar S R S 1993 Alleviation of soil acidity in Ultisols and Oxisol for corn growth *Plant Soil* **151** 55–65

[22] Scott B J, Ridley A M and Conyers A M 2000 Management of soil acidity in long-term pastures of south-eastern Australia: A review *Aus. J. of Exp. Agric.* **40** 1173–98

[23] Smith C J, Goh K M, Bond W J and Freney J R 1995 Effects of organic and inorganic calcium compounds on soil-solution pH and aluminium concentration *Eur. J. Soil Sci.* **46** 53–63

[24] Kinraide T B 1998 Three mechanisms for the calcium alleviation of mineral toxicities *Plant Physiol.* **118** 513–20

[25] Holland J E, Bennett A E, Newton A C, White P J, McKenzie B M, George T S, Pakeman R J, Bailey J S, Fornara D A and Hayes R C 2018 Liming impacts on soils, crops and biodiversity in the UK: A review *Sci. of the Tot. Envi.* **610–611** 316–32
[26] Kinraide T B and Parker D R 1987 Cation amelioration of aluminum toxicity in wheat *Plant Physiol.* **83** 546–51

[27] Kunhikrishnan A, Thangarajan R, Bolan N S, Xu Y, Mandal S, Gleeson D B, B, Seshadri, Zaman M, Barton L, Tang C, Luo J, Dalal R, Ding W, Kirkham M B and Naidu R 2016 Functional relationships of soil acidification, liming, and greenhouse gas flux in *Adv. in Agronomy* **139** 1–71.

[28] Moore J D, Duchesne L, and Ouimet R 2008 Soil properties and maple-beech regeneration a decade after liming in a northern hardwood stand *For. Ecol. Manage.*, **255** 3460–68

[29] Schneider A, Augusto L, and Mollier A 2016 Assessing the plant minimal exchangeable potassium of a soil *J. Plant Nutr. Soil Sci.* **179** 584–90

[30] Thomas G W and Hargrove W L 2015 The chemistry of soil acidity, Soil acidity and liming **12** 3–56

[31] Hue N V and Amien I 1989 Aluminum detoxification with green manures *Commun. Soil Sci. Plant Anal.* **20**, 1499–11

[32] Noble A D, Sumner M E, and Alva A K 1988 The pH dependency of aluminum phytotoxicity alleviation by calcium sulfate *Soil Sci. Soc. Am. J.* 1398-02

[33] Mora M L, Schnettler B and Demanet R 1999 Effect of liming and gypsum on soil chemistry, yield, and mineral composition of ryegrass grown in an acidic Andisol *Commun. Soil Sci. Plant Anal.* **30** 1251–66

[34] Li G D, Conyers M K, Heylar K R, Lisle C J, Poile G J, and Cullis B R 2019 Long-term surface application of lime ameliorates subsurface soil acidity in the mixed farming zone of south-eastern Australia *Geoderma* **338** 236–46

[35] Alva A K, Kerven G L, Edwards D G and Asher C J 1991 Reduction in toxic aluminium to plants by sulfate complexation *Soil Sci.* **152** 351–59

[36] Siecińska J and Nosalewicz A 2016 Aluminium toxicity to plants as influenced by the properties of the root growth environment affected by other co-stressors: A Review. *Rev Environ Contam Toxicol.* **243** 1-26