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Effect of Elemental Sulphur on Calcium Uptake and Translocation in Maize Grown in a High pH soil of Malaysia

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ABSTRACT

Introduction: Acidification of high pH soils by elemental sulphur application is introduced for increasing plant nutrient availability and improving plant performance. The present study was aimed to elucidate the effect of elemental sulphur timing and application rates on soil Ca release, Ca concentration in maize and its relationship with maize yield.
Materials and Methods: Bintang Series soil was treated with four rates of elemental sulphur (0, 0.5, 1.0, and 2.0 g S kg^{-1} soil) and incubated for 0, 20, and 40 days before maize plantation. The experiment was laid out in randomized complete block design (RCBD) with factorial arrangement and carried out in University Putra Malaysia. Soil samples were provided before and after the maize plantation and were extracted for nutrient analysis. The nutrients in the solution were determined by an inductively coupled plasma spectrometer.
Results and Discussion: The results exhibited that application of elemental sulphur significantly decreased soil pH and it increased soil Ca, Mn and Zn availability for plants. In addition, the results showed that soil acidification by elemental sulphur decreased Ca concentration in maize root, stem and leaves and it is due to the antagonistic effects of Mn and Zn on Ca uptake by maize.
Conclusion: Overall, the maximum maize performance was obtained at Ca concentration of 0.75, 1 and 1.4 percent in maize leaves, stem and roots, respectively.

Introduction

Plant production is greatly affected by the availability of plant nutrients in soil (Ye et al., 2011) and it is influenced by soil characteristics, especially soil pH (Chien et al., Lindsay, 1979; Shenker and Chen, 2005; Wang et al., 2006). For instance, the poor performance of crops in high pH soils is attributed to the limited availability of plant nutrients in soil. Acidification and fertilization are common practices in high pH soils to enhance nutrient availability and improve plant performance. Elemental Sulphur, as a soil amendment, is of special interest to increase soil nutrient solubility since it possesses the slow release acidifying characteristic and is readily available (Chien et al., 2011). In spite of the advantages of elemental Sulphur as a soil acidulate, there is contrasting reports on the effect of elemental Sulphur on soil pH and nutrient availability (Klikocka, 2011; Safaa et al., 2013; Skwierawska et al., 2012a). While the effectiveness of elemental Sulphur application on nutrient solubility was not observed in some soils (De la Fuente et al., 2008; Sameni and Kasraian, 2004; Shenker and Chen, 2005; Skwierawska et al., 2012b), the positive effect of elemental Sulphur on soil nutrient solubility is reported by others (Cui et al., 2004). Therefore, it is necessary to find the optimum Sulphur rate to obtain optimum pH for each specific soil in which nutrient solubility has increased; concurrently extreme soil acidification and its consequences such as nutrient toxicity for plants were avoided.

As an essential nutrient, Ca plays a key role in plants and is indispensable in a number of metabolic pathways. It regulates plant growth and development, participate in cell wall and cell membrane, as well as root and stem elongation. Being in large amounts in apoplast, it also maintains cell tissue viability. Despite the invaluable role of Ca in plants, it was recently found that there are some intrinsic proteins that can restore the Ca actions and the Ca requirements for efficient functioning, especially that of photosynthesis which is very minimal. Ca interaction with other nutrients is well documented (Merino-Gergichevich et al., 2010).

From an environmental point of view, the increased availability of nutrients intensifies the risk of nutrient leach out and transport (Faltmarsch et al., 2008). They reported the elevated concentrations of Zn and Al in cow milks, metal imbalances in crops and actual threat on human health, due to the chronic exposure to high concentration of metals, as negative effects of acid Sulphate soils. Furthermore, numerous cases of mass fish kills were reported as the significant effect of acid soils on biodiversity and community structure of aquatic ecosystems. In a review of environmental adverse impacts of soil acidification, Lockwood et al., (2004) reported the production of 90 kg/ha bicarbonate salts in the streams draining the landscape.

Located in Perlis, Malaysia, Bintang Series Soil has developed on limestone materials and is characterized by the pH value of 7.3 and is known as a high pH soil (Karimizarchi et al., 2016). The available concentration of nutrients in this soil is far below the recommended adequate range (Karimizarchi et al., 2014a), and necessitated specific fertilizer management practices to maintain plant nutrients at concentrations sufficient for optimal plant growth. While the application of elemental Sulphur for optimum plant performance was recommended by Karimizarchi et al., (2014a), the role of elemental Sulphur on the mobility of Ca in Bintang Series soil and its availability to plants need to be elucidated. Therefore, the objective of this study was to elucidate the effect of soil acidification due to elemental Sulphur application on soil Ca release in Bintang Series soil and Ca uptake by maize.

Materials and Methods

To evaluate the effect of soil acidification on soil Ca solubility and uptake by maize, the Bintang Series soil was treated by four rates of elemental Sulphur, 0, 0.5, 1 and 2 g S kg^{-1} soil (Karimizarchi et al., 2014b), and incubation for 0, 20 and 40 days (Karimizarchi et al., 2014b) before maize planting in plastic pots (30 cm diameter and 50 cm height). The maize plants were grown for 45 days under greenhouse conditions of University Putra Malaysia (The glasshouse conditions were as that of tropical conditions of Malaysia, the minimum temperature is 23 and the maximum one is 32 centigrade. The mean annual precipitation is around 2.5 m.). Soil samples were retrieved at planting and harvesting stages and subjected to nutrient analysis.

Site description and Soil characterization

Soil samples (Table 1) were collected from the A horizon (0-20 cm) of Bintang Series soil located in Perlis, Malaysia (6° 31′ 01.61″ N and 100° 10′ 12.43″ E). The area, Bukit Bintang, is affected by limestone parent materials and is under natural vegetation (Karimizarchi et al., 2014b). Soil samples were air dried and grounded (< 2 mm) before use. Soil electrical conductivity and pH were measured in a soil water suspension (10 g soil to 25 ml deionized water) 24 hours after shaking for 30 min on a reciprocal shaker. Total carbon, nitrogen and Sulphur were determined by CHNS LECO analyzer. Soil mechanical analysis was done using pipette method (Gee et al., 1986), and texture class was determined by United States Department of Agriculture (USDA) soil textural triangle.

Plant growth and management

Sweet maize (*Zea mays* L.) seeds, Masmadu, were provided by Malaysian Agricultural and Development Research Institute (MARDI, 2008; Mohammadi et al., 2020). Seeds were germinated in laboratory conditions and transplanted into 30 cm (diameter) by 50 cm (height) plastic pots after 24 hours. Each pot contained 10 kg soil and received three plants which were thinned to one within one week. Seedlings were grown for 45 days in greenhouse conditions located in University Putra Malaysia (UPM). Plants were irrigated daily to maintain 90 percent soil field capacity moisture content by a gravimetric method. All plants were supplied with fertilizers based on MARDI recommendation; 120 kg N /ha in the form of urea, 60 kg P_2O_5 in the form of triple superphosphate and kg K_2O in the form of muriate of potash (Karimizarchi et al., 2014a).

Soil and plant nutrient extraction and determination

As buffered extractants may hinder the effect of S on soil nutrient solubility, the mobile fraction of soil nutrients were extracted by water (Hlavay et al., 2004; Jones, 2001;Ye et al., 2011) as follows: 10 g air dried soil was shaken for 1 hour with 50 g distilled water. It was centrifuged for 15 minutes at 3000 rpm and filtered. Plant leave, shoot and root tissues were separately washed in deionized water then dried at 65 ℃ and weighed. After grounding, weighed plant tissues were turned into ash in a muffle furnace at 480 ℃ for about 10 h and dissolved in diluted acid mixture (Jones, 2001). Ca, Mn and Zn concentrations were determined by ICP-OES (Perkin Elmer, Optima 8300). Soil acidity was measured in a soil water suspension (10 g soil to 25 ml deionized water) 24 h after shaking for 30 min on a reciprocal shaker. For Ca, 10 g air dried soil was shaken for 1 hour with 50 g distilled water. It was centrifuged for 15 minutes at 3000 rpm and filtered. The extracted nutrients including Ca were determined by ICP-OES (Jones, 2001).

Statistical analysis

To model the relationship between plant and soil properties, the data were subjected to different regression models at the probability level of 0.05 with the help of SigmaPlot software. The data on soil nutrient content were analyzed using SAS commands through split plot experimental design. The data on maize performance was analyzed using SAS commands through randomized complete block design (RCBD) with factorial arrangement and four replications. ANOVA analysis and Duncan’s test at α = 0.05 were employed to determine the significance differences among the mean treatments.

Table 1. Some physicochemical properties of Bintang Series soil (n=3)

Soil property	Unit	Value or concentration	Soil property	Unit	Value or Concentration
pH (H_2O)	-	7.30 ± 0.1	Sand (%)	%	9.0 ± 0.19
$CaCO_3$	%	Tr	Silt (%)	%	66.40 ± 0.37
Total C	%	1.75 ± 0.05	Clay (%)	%	24.6 ± 0.32
Total N	%	0.12 ± 0.01	Texture	-	Silt loam
Total S	%	0.004 ± 0.01	FC	%	20.00 ± 0.84
C/N	-	16.58 ± 1.2	Ex. Ca	$cmol_+ kg^{-1}$ soil	5.75 ± 0.13
C/S	-	437.50 ± 1.26	Ex. Mg	$cmol_+ kg^{-1}$ soil	0.583 ± 0.02
CEC	$cmol_+ kg^{-1}$ soil	11.50 ± 0.35	Ex. K	$cmol_+ kg^{-1}$ soil	0.06±0.01
BS	%	56.0 ± 2.0			

BS; Base Saturation, FC: Field Capacity, Ex.: Exchangeable.

Results and Discussion

Soil acidity

The relationship between S rate and soil pH change is of special interest and needs to be studied for each specific soil. The effectiveness of elemental Sulphur on Bintang Series soil acidification was demonstrated by the result of the experiment. As Figure 1 depicts the role of elemental Sulphur rate on Bintang Series soil acidity, Sulphur application significantly decreased the soil pH and with each unit increase in S rate, the soil pH decreases by around 1.52 units, pH = 6.94-1.52 S and $R^2 = 0.98^{**}$ .The results agree well with Owen et al. (1999) findings. They modeled the relationship between elemental Sulphur application rate and soil pH under laboratory and field conditions. They found that application of 4 tons of S per hectare linearly decreased soil pH from 7 to 4.8. While they reported a slight decrease in soil pH by application of 8 tons of S, compared to S rate of 4 t ha^{-1}, it reached to the minimum of 4.2 at S rate of 12 t ha^{-1}. They found that the relationship between S rate and soil pH was fitted best by an exponential model. Similar results were reported by Chambers et al., (1996). As a result of Bintang Series soil acidification, the release of soil nutrients might be affected. Therefore, the correlation between soil nutrient availability and soil pH needs to be studied.

Soil acidity and nutrient release

The data showed a strong and significant correlation of -0.98 between soil pH and soil Ca concentrations (Table 2). Such a finding indicates the significance of soil pH in soil Ca release. As the correlation is negative, it signifies that with a decrease of the soil pH the soil Ca release was increased. This is in line with the general opinion of the positive effect of soil acidification on the soil nutrient solubility (Bolan et al., 2003; Lindsay, 1979; Pendias, 2001; Wang et al., 2006). Therefore it is expected that Ca uptake by plants would be increased due to soil acidification. In addition, there is a strong and significant correlation between soil pH and soil Mn and Zn with the Pearson correlation coefficients of -0.86 and 0.78 (Table 2). Indicating that the soil Mn and Zn concentration increase with the soil pH reduction (Karimizarchi and Aminuddin, 2015); this may result in the interactive effects of these nutrients with Ca uptake by plants or vice versa.

To better understand the pattern of Ca release due to the elemental Sulphur management, the soil Ca concentration as a function of Sulphur application rate and timing in Bintang Series soil was elucidated (Table 3).

Elemental Sulphur application rate and soil Ca release

Extractable Ca was greatly affected by Sulphur application rate and maize growth stage (Table 3). Averaged across Sulphur timing, addition of elemental Sulphur increased the soluble Ca concentration in soil solution at planting from the background of 191.12 to 523.97, 690.07 and 838.23 mg kg^{-1} for second, third, and fourth Sulphur application rates, respectively. In other words, application of 0.5, 1 and 2 g S kg^{-1} soil increased the available Ca by 2.74, 3.61, and 4.38 times compared to the untreated soil at planning. The changes in soil Ca concentration under the conditions of the experiment can be explained by the role of elemental Sulphur on soil acidity changes. This is strongly supported by the relationship between Ca concentration and soil pH (Figure 2). As it can be seen form the graph, with a decrease of the soil pH the Ca concentration was linearly increased; each unit decrease in the soil pH resulted in 540.12 mg kg^{-1} increase in the Ca content. The results are in line with the Khan and Mazid (2011). They showed that the acidity produced on oxidation of elemental Sulphur in soil increased the solubility of nutrients (Khan and Mazid, 2011). The soluble Ca may be provided from the exchangeable form of Ca (Owen et al., 1999) or from the increased weathering rate of minerals at acidic conditions (Bolan et al., 2003; Lambers et al., 2008; Viani et al., 2014). Owen et al. (1999) showed that while elemental Sulphur decreased the soil pH, exchangeable Ca, Mg, K and extractable P decreased, and it depends on the time after S addition. The finding, however, is not in line with Wang et al. (2006). They found that with the acidification of soils with elemental Sulphur soil, Ca extracted by 0.1 M Sr $(NO_3)_2$ was decreased. It seems that soil leaching after soil pH adjustment is the main reason for soil Ca reduction at treated soils.

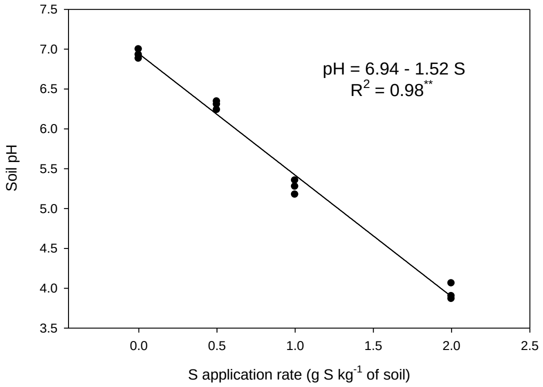

Figure 1. Soil pH changes in response to elemental Sulphur application rate

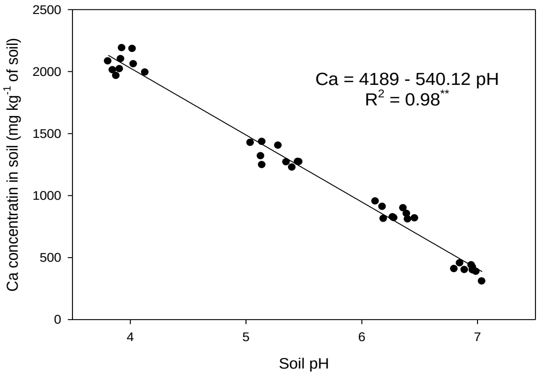

Figure 2. Relationship between soil pH and extractable Ca concentration (mg kg^{-1}) in Bintang Series soil

Table 2. Pearson correlation coefficients between soil pH and some nutrients concentration at harvest (n=72)

Soil factors	Mn	Zn	pH	Ca
Mn	1.00			
Zn	0.78**	1.00		
pH	-0.86**	-0.78**	1.00	
Ca	0.83**	0.81**	-0.98**	1.00

Values of r followed by ** are significant at α= 0.01.

Table 3. Soil total water soluble Ca changes in response to elemental sulphur timing (0, 20 and 40 days application before planting) and application rates (g S kg^{-1} soil) at planting and at harvest

Sulphur rate	Soil Ca (mg kg $^{-1}$ soil)							
	At planting			Mean	At harvest			Mean
	0	20	40		0	20	40	
0	126.05^{Ab}	215.7^{Da}	231.61^{Da}	191.12^{Db}	362.61^{Da}	422.55^{Da}	414.28^{Da}	399.82^{Da}
0.5	131.73^{Ac}	684.16^{Cb}	792.00^{Ca}	523.97^{Cb}	849.66^{Ca}	856.66^{Ca}	855.66^{Ca}	854^{Ca}
1	125.26^{Ac}	880.93^{Bb}	1064.00^{Ba}	690.07^{Bb}	1262.00^{Ba}	1353^{Ba}	1336.67^{Ba}	1317.22^{Ba}
2	133.5^{Ac}	1034.29^{Ab}	1346.87^{Aa}	838.23^{Ab}	2099.5^{Aa}	2021.49^{Aa}	2077.11^{Aa}	2066.04^{Aa}

Means within column followed by the same capital letter and means within rows followed by the same small letter are not significant at the 0.05 level, according to DMRT test at 5% level.

Interestingly, soil extractable Ca for un-amended soil significantly increased. For instance, at 0 application rate of S, incubation of soil for 40 days significantly increased soil Ca from background of 126.05 to 231.61 mg kg^{-1} and from 362.62 to 414.28 mg kg^{-1}, at planting and harvest, respectively. This increase in Ca content in un-amended soil can be partly related to the Ca content in irrigation water, 17.68 ppm.

As the application of elemental Sulphur significantly increased the available Ca in Bintang Series soil, the expectation was that Ca concentration in plants grown in Sulphur treated soil would be increased. Therefore, the Ca uptake by maize was elucidated.

Ca concentration in maize

Despite the significant increase in extractable soil Ca due to the application of elemental Sulphur (Table 3), the Ca concentration in plant parts including leaves, stem and roots decreased linearly (Figure 3). As it can be clearly seen, the maximum Ca concentration, being 0.85, 1.11 and 1.97 percent for leaves, stem and root respectively, was found in untreated plants and the figures were decreased to 0.57, 0.62 and 0.5 percent at the highest S rate. As the availability of Ca in soil was increased by the addition of elemental Sulphur (Table 3); this decrease in Ca content in plant parts cannot be attributed to the soil Ca availability. However, it may be related to the lower ability of plant in Ca uptake and the antagonistic effects of other nutrients such as Mn and Zn with Ca uptake.

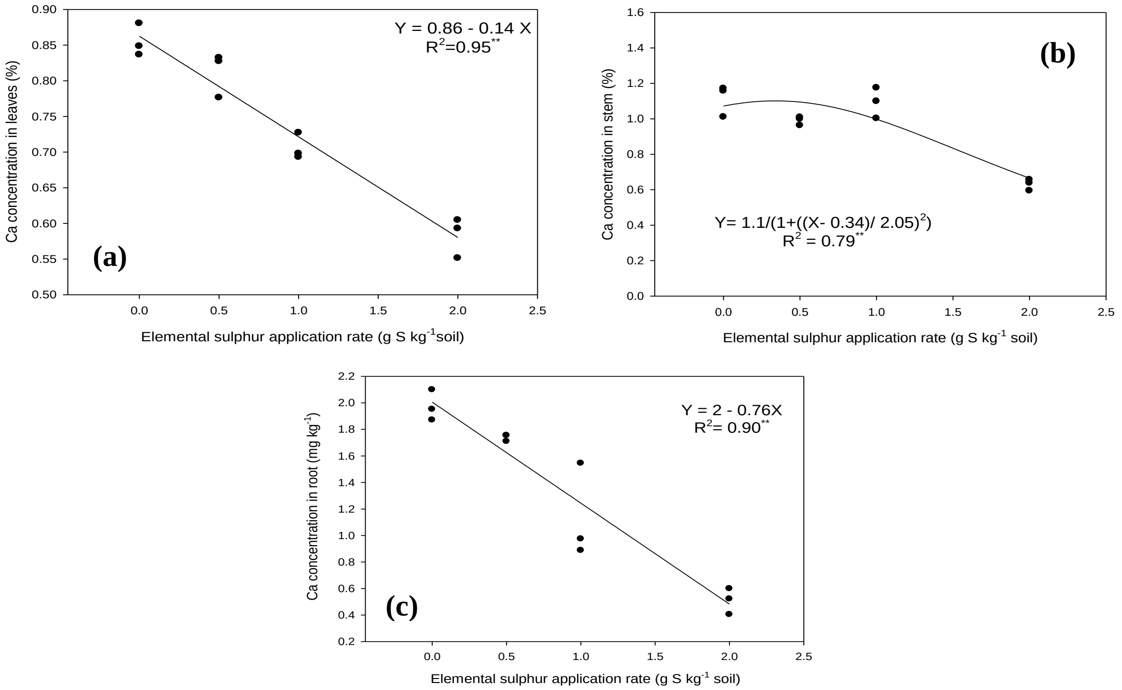

Figure 3. Effect of elemental sulphur on the Ca concentration in maize leaves (a), stem (b) and root (c)

Mn interaction with Ca

Nutrient interaction in plants is one of the most important factors affecting crop yields. It can be neutral, positive or negative. Nutrient interaction can be quantified in terms of plant growth and nutrient concentrations in plant tissue. Plant, soil and climatic factors can contribute to interaction (Fageria, 2002). Therefore, the interaction between Ca and other nutrients in conditions of the study was elucidated to explain the decrease in leaves, stem and root Ca due to soil acidification through elemental Sulphur application. The results of the experiment demonstrated the antagonistic effect of Mn on Ca concentration in maize leaves, stem and roots (Fig. 4). For instance, with the increasing Mn concentration in maize leaves the Ca concentration decreased linearly (Figure 4a). The same trend was found for maize stem and roots (Figure 4b and 4c). This strong and significant correlation between Mn and Ca concentrations in maize leaves, stem and roots supports the theory of the antagonistic effects of Mn on Ca uptake by maize. The antagonistic effects of these elements can be explained by the similarity of these elements in terms of their ionic radius, charge and coordination chemistry (Dou et al., 2009). The results agree well with previous studies in terms of the effect of Mn on the accumulation and concentration of Ca in maize and other plants (Dou et al., 2009; Fageria, 2002). The decreasing trend in maize Ca content and the concurrent upward trend in Mn due to the elemental S addition were reported by Kayser (2000). The Mn-induced Ca deficiency in plants was also released by Marschner and Marschner (2012). While the decrease in Mn, Fe and Zn concentration at root surface occurs with liming acid soils, the competition of ions for the site of absorption and transport may be common for ions with similar charges, size, electronic configuration and coordination. This kind of interaction occurs both within plant tissue and on the root surface (Fageria, 2002). Since the soil Ca concentration was increased with an increasing rate of Sulphur, it can be concluded that the antagonistic effect of Mn and Ca is responsible for this observation. In addition, although the retardation of the bioavailability of Ca in an acidic condition due to high concentration of Al was previously reported (Bolan et al., 2003; Meriño-Gergichevich et al., 2010), we did not find any relationship between Al and Ca content in maize. The data showed that Mn and Zn are the main reasons for the lower concentration of Ca in maize plant grown in acidified Bintang Series soil (Figure 4 and Figure 5).

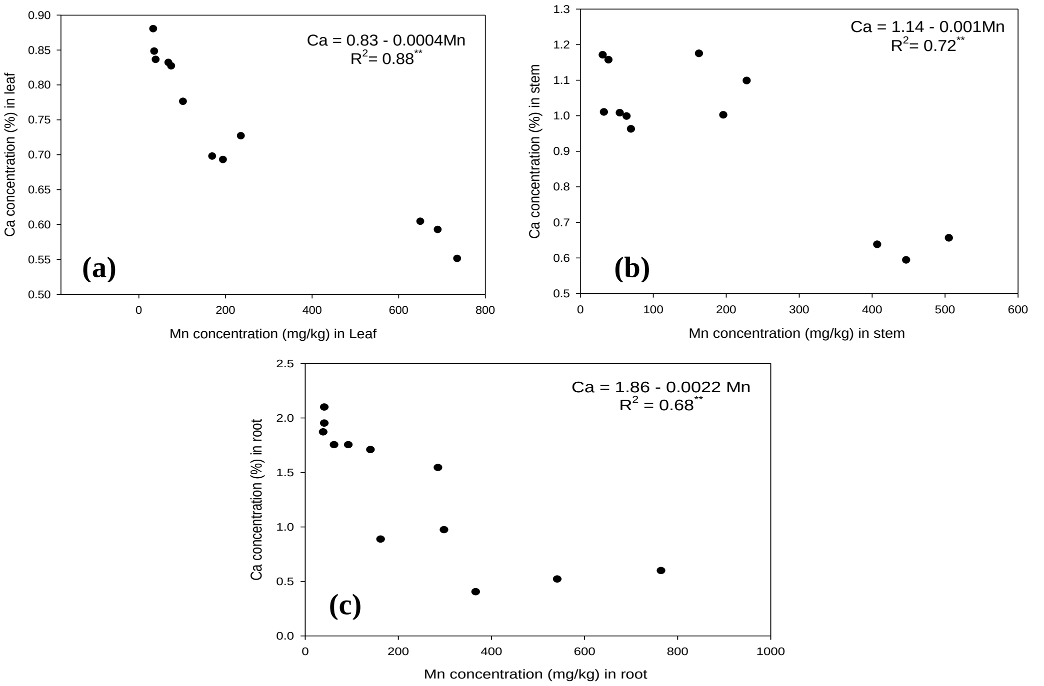

Figure 4. Antagonistic effects of Mn on Ca concentration in maize leaves (a), stem (b) and root (c)

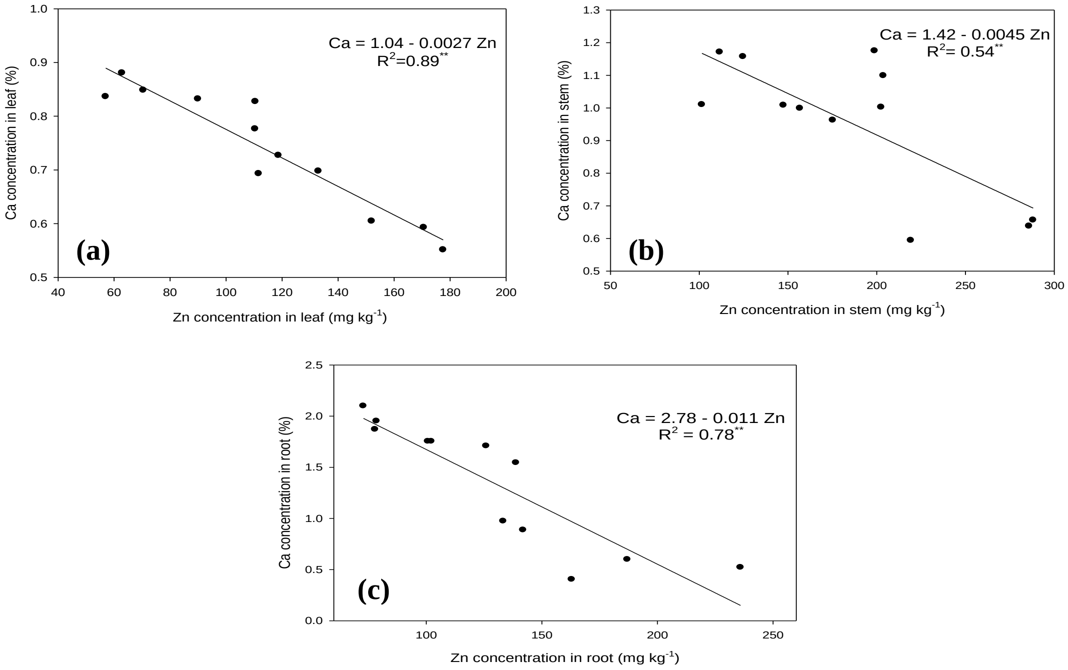

Figure 5. Antagonistic effects of Zn on Ca concentration in maize leaves (a), stem (b) and root (c)

Zn interaction with Ca

Likewise Mn, a linear decreasing trend between Ca and Zn concentration in maize leaves, stem and roots was found (Figure 5). This linear reduction in Ca content due to higher Zn content, with the strong and significant correlations of 0.89, 0.54, and 0.78 for maize leaves, stem and root respectively, supports the antagonist effects of Zn and Ca in the maize under the conditions of the experiment. This observation agrees well with previous studies with regard to the role of Zn on the uptake of Ca in upland rice under glasshouse conditions. As stated by Fageria (2002) uptake of N, Ca, and Cu in upland rice was decreased by zinc treatment. The competition of Ca and Zn, with similar charges, for site of absorption and transport may be involved for the antagonistic interactions between these two elements (Fageria, 2002; Jashni ea al., 2017).

Maize performance and its relation with Ca content

To elucidate the role of Ca in maize performance, the leaves, stem and root dry matter were correlated with Ca concentration. There is a strong and significant relationship, quadratic regression model; $Y = 188.46 + 558.75X - 370.56X^2$, $R^2 = 0.83^{**}$, between Ca concentration in leaves and leave dry weight (Figure 6). According to this model, the maximum performance of maize, 22.18 g pot^{-1}, was obtained at Ca content of 0.75 percent in leave (Figure 6). Comparing this value with the recommended adequate range of Ca, 0.25 to 0.8 percent in maize (Barker & Pilbeam, 2007; Campbell, 2000), reveals that this is within the sufficiency range of Ca normally found for maize. In addition, it can be concluded that the Ca was not the limiting factor for maize growth under conditions of the experiment. The conclusion was more supported by the literature review (Bennet et al., 1986; Meriño-Gergichevich et al., 2010). As an essential nutrient that plays an invaluable role in plants, it was recently found that (Merino-Gergichevich et al., 2010) there are some intrinsic proteins that can restore the Ca actions and the Ca requirement for efficient functioning, especially that of photosynthesis is very minimal. Additionally, Bennet et al. (1986) demonstrated that the major requirement for Ca and K in plants involves charge neutralization.

Calcium as an immobile nutrient in Maize

The Ca concentration in maize leaves under the conditions of the experiment was low compared to root and stem (Figure 5). This reflects the poor ability of maize to translocate Ca from roots and stem to leaves. The leaf calcium content in maize plants received 0, 0.5, 1 and 2 g S kg^{-1} soil, was 0.85, 0.81, 0.7 and 0.58 percent, respectively. This indicates that as elemental Sulphur application rate increased, the leaf Ca content decreased. The ratio of Ca concentration in leaves to stem (translocation factor) for all the treatments under conditions of the experiment was less than one (Table 4). The translocation factor (TF) for maize plants received 0, 0.5, 1 and 2 g S kg^{-1} soil was 0.76, 0.82, 0.64, and 0.92, respectively. The Ca content of maize leaves and stem under the conditions of their study were on average 0.73 and 0.95 g kg^{-1} dry weight, respectively. As transfer factors integrates a number of soil chemical, biological, and physical factors, as well as plant physiological processes and human agricultural practices, the high variability of this macroscopic parameter becomes obvious (Ehlken and Kirchner, 2002).

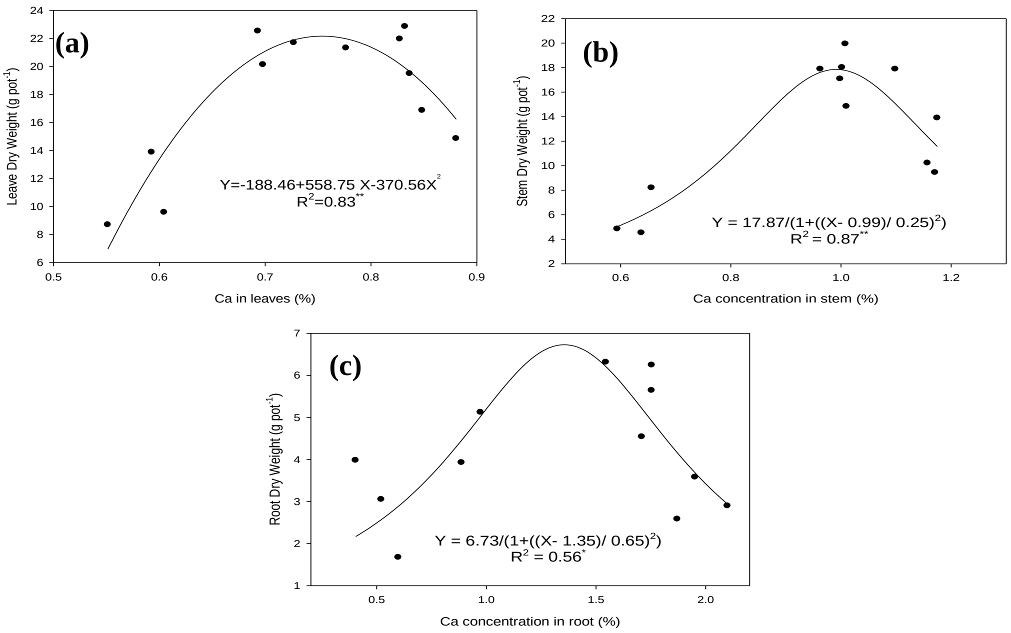

Figure 6. Maize leaves (a), stem (b) and root (c) dry weight (Y) as a function of Ca concentration in plant (X)

Table 4. Calcium transfer factor in different parts of maize plant treated with different rates of elemental S

Sulphur rate (g kg^{-1} soil)	Leaves/root	Leaves/stem	Stem/root
0	0.43	0.76	0.56
0.5	0.46	0.82	0.56
1.0	0.62	0.64	0.96
2.0	1.14	0.92	1.23

Conclusion

From this research we found that the application of elemental Sulphur increases the soil acidity, and subsequently stimulates the Ca, Mn and Zn release in soil. However, the Ca concentration in maize was not followed by Ca concentration in soil. Furthermore, the results showed that the interactions of Mn and Zn with Ca were responsible for the decreasing trend in maize Ca concentration in response to elemental Sulphur application rate in Bintang Series soil.

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