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Distribution and management of total and available sulfur under Durian orchard soils in the Eastern Thailand

Jaisue, N., Tawinteung, N.*, Worphet, A. and Khurnpoon, L.

Department of Plant Production Technology, Faculty of Agriculture Technology, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand.

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Abstract Sulfur is necessary plant nutrient but is rarely determined on a routine basis because of interpretive and analytical problems resulted in the lack of consistent identification of S sufficiency or deficiency in soils. Sulfur status of durian orchard soils in the Eastern Thailand was evaluated for plant availability. The result indicated that total S ranged from 315 to 1340 mg/kg (average 813 mg/kg) which 93-99% was in organic form and relatively the same comparison between topsoil and subsoil. Total S was significantly correlated with C (r = 0.41**), N (r = 0.36**), pH (r = -0.52**) and SOM (r = 0.51**). The C:S and N:S ratios varied from 7.8-54.8 and 0.74-4.67 respectively, indicating the dominance of the mineralization process toward sulfur nutrition. C:N:S was 20:2:1 due to heavy S fertilizer application. Extractable S (available S) was varied from high to very high ranged depending on soil standard, of which about 75% of soil samples were classified to be no response to S application. Out of the average available S of 24.2 mg/kg the topsoil (28.2 mg/kg) was higher than subsoil (25.6 mg/kg). Available S showed very closely correlation to total S (r = 0.72**), C (r = 0.61**), N (r = 0.57**), pH (r = -0.29**) and SOM (r = 0.61**). Stepwise multiple regression showed that approximately 73.0% variation in the extractable or available S could be explained in terms of several soil parameters.

Keywords: *Durio zibethinus* Murr., Plant-available sulfur, Soil and plant analysis

Introduction

Sulfur (S) is an essential element for plants growth, being a component of plant-proteins and having an important role in the synthesis of chlorophyll. It has particularly of onion-like odor, espiacially, on durian pulp which is contributed to by volatile sulfur compounds such as thiols and disulfide (Haruenkit *et al.*, 2007). S content on durian fruit (petiole, skin, aril, seed) was 0.10% lead to removes large amounts of S, with an estimated removal of 1.0 g S/kg (dry weight basis) every year (Diczbalis and Westerhuis, 2005). Since, limited research has been conducted on soil testing tools for S management, the

***Corresponding Author:** Tawinteung, N.; **Email:** nukoon.ta@kmitl.ac.th

S fertilizer recommendations program was often not included in agricultural practice for durian production in Eastern Thailand. However, durian growers, mostly applied K as K_2SO_4 ranging from 1,000-3,000 g K_2O/tree/year (Poovarodom and Phanchidawan, 2006) indicated that S was also applied at the rate of 340-1,020 g/tree/year.

The S in the soil occurs in two basic forms, organic and inorganic inwhich S in the form of inorganic (SO_4^{-2}) is readily available to plants. But organic S which accounts for 95 % of all S in most soils has to mineralize before S is available to the plant that is indicated by the close relations between organic C, total N, total S, C:S N:S and soil pH (Freney, 1967; Beiderbeck, 1978; Tabatabai, 1996). Sulfate (SO_4) is soluble and is easily lost from soils by leaching especially on coarse-textured soil under high rainfall condition of the Eastern part of Thailand. Therefore, it was often not found in correlation to plant yield (Scott, 1981; Esmel *et al.*, 2010). The soil solution is resupplied with SO_4 through the mineralization of organic S compounds or desorption of SO_4 from clay and Fe and Al oxide surfaces. Since, adsorbed SO_4 resupplies solution S during the growing season therefore, the soil test method measures SO_4 in solution as well as readily exchangeable adsorbed SO_4 and readily mineralizable organic S across a wide range of soil types provide more effective. That is why the extraction with a weak acid, acidified NH_4OAc and $Ca(H_2PO_4)_2$ showed a good correlation to plant yield (Huda *et al.*, 2004; Bharathi and Sangeetha, 2008; Quirine *et al.*, 2011).

Accurate and rapid determination of S is important in soil and plant research program. Many methods have been proposed for the determination of available S in soils. In Thailand, the laboratory of Land Development Department (LDD) has recommended acidified NH_4OAc as extraction solution and used the turbidimetric method of determination of S in solution as followed Bardsley and Lancaster (1965). The results could be varied from soil to soil, however, and less reproducible because of interferences from colloidal organic matter, colored compounds, and coprecipitation with metal ions (Quirine *et al.*, 2011). Currently, the determination of total S in soil and plant samples can be accomplished using automated dry combustion instrument. The advantage of this technique is the relative simplicity of use, speed and convenience compared to other methods (Kowalenko, 2001). However, a measure of total S has not proven to be a satisfactory index for S management for agricultural practice (Bentley *et al.*, 1955; Williams and Steinbergs, 1959).

Lack of consistent identification of S sufficiency or deficiency by the current recommended methodology has encouraged durian growers to apply blanket applications of S-containing fertilizers whether the crops respond to the added S fertilizer or not. Furthermore, the determination of available S was always time-consuming, complicated and often do not reflect plant S requirement. The objectives of this study were to assess the S status of durian orchard soil in Eastern Thailand and obtain information required for evaluation of the sulfur fertilization of these soils and to predict available S on durian orchard soil and determine if a relationship could be established among total S, extractable S and plant tissue.

Materials and methods

Eighty soil samples were collected from 4 “Mon Thong” durian orchards located in Rayong, Chanthaburi and Trat provinces, Eastern Thailand. Ten composite samples of both top soil (0-20 cm) and sub soil (20-40 cm) were taken from five durian trees for each orchard. The samples were collected in 2 times, January 2019 and October 2020. These samples were air-dried, ground and passed through a 10-mesh (2.0 mm) sieve and their physico-chemical properties were determined following the standard method proceduced of Land Devlopment Department (2004). Extractable S was measured by extracting soil with 1 N NH_4OAc (pH 5), 1:10 of soil: solution, shaking for 30 minutes and amount of S measured by the turbidimetric procedure (Bardsley and Lancaster, 1965). Soil organic matter (SOM), total C, total N and total S analyses were performed on soil samples that has been ground to pass 100-mesh (0.15 mm) screen. SOM was determined by loss on ignition, LOI (Schulte and Hopkins 1996), total C, total N and total S by TruMac CNS-2000 (Leco) (Kowalenko, 2001). Organic S was calculated by total S minus by extractable S (Tabatabai and Bremner, 1972).

Durian leaf samples were collected simultaneously as soils sampling. Twenty leaves from the perimeter of each tree were collected to make a composite sample per tree according to standard method (Poovarodom *et al.*, 2002). The leaves were washed in tap water, soaked briefly in 0.1 M HCl, rinsed with distilled water three times and dry at 70°C. The dried leaves were ground to pass a 40-mesh screen (0.40 mm). A sub-sample of leaves was extracted by dry ashing at 550°C for 6 hrs, then P, K, Ca, Mg, Fe, Mn, Cu, Zn, B, Ni and Mo were analyzed by ICP-OES (Allen, 1971). C, N and S were determined by TruMac CNS-2000 (Leco) (Kowalenko, 2001) on leaf samples that has been ground to pass 100-mesh (0.15 mm) screen.

Standard analysis of variance and correlation were used with $p < 0.05$ accepted as being significant. Simple and stepwise multiple regression were employed to determine the relative contributions of various soil characteristics toward available S.

Results

Physico-chemical properties of soil

The soils were sandy loam to sandy clay loam (kaolinitic, isohyperthermic Typic Kandiudults) with clay content 16.5-37.3% (Table 1). Soil reactions were very strongly acidic (pH 4.78-4.99) except, on Chantaburi1 which found moderately acidic 5.58 and 5.54 for top soil and sub soil respectively. EC was low (11-71 μS/cm) thus, no effected of salinity. Soil organic matter of top soil (2.62-3.89%) was higher than that of sub soil (1.57-3.49%). It was found high range (3.49-3.89%) on Trat orchard soils and slightly high in the rest. Available P (Bray II) was extremely high (82.9-815 mg/kg) in all orchard soils. Exchangeable K, Ca and Mg were ranged from 85-164, 250-685 and 5.9-68.7 mg/kg respectively. The CEC was found low (5.11-8.99 cmol/kg) for all locations. Base saturation percentage was low to moderate (19.3-67.6%) Extractable (DTPA) Fe, Mn, Cu and Zn were average of 66.7, 17.4, 16.1 and 4.07 mg/kg respectively (data were not shown).

Table 1. Selected physico-chemical properties of soils

Locations (provinces)	**Soil[/1] series**	**depth** (cm)	**Clay** (%)	**Text-[/2] ure**	**pH** 1:1	**OM** (%)	**EC** μS/cm	**CEC** cmol/kg	**BS** %	**P[3/]**	**K**	**Ca**	**Mg**
										<----	mg/kg	---->	
Rayong	Te	0-20	19.3	SL	4.91	2.62	64.4	5.11	53.7	481	85.1	517	68.7
		20-40	26.0	SCL	4.99	2.15	43.4	7.41	38.1	298	87.6	553	67.7
Chanthaburi1	Pga	0-20	31.5	SCL	5.58	2.62	71.0	5.86	67.6	435	136	543	52.1
		20-40	37.3	SC	5.54	2.21	48.4	7.65	43.9	244	101	580	58.6
Chanthaburi2	Ba	0-20	34.8	SCL	4.99	3.64	24.2	8.13	58.4	815	104	647	57.8
		20-40	21.5	SCL	4.91	1.57	18.8	6.25	59.0	338	92.2	685	54.7
Trat	Kc	0-20	24.8	SCL	4.80	3.89	14.6	6.89	38.6	325	126	250	53.2
		20-40	16.5	SL	4.78	3.49	11.2	8.99	19.3	82.9	164	302	51.9

[1/] Te = Tha Sae, Pga = Phang-nga, Ba = Bang Nara, Kc = Khlong Chak, [2/] SL = Sandy loam, SCL = Sandy clay loam, SC = Sandy clay, [3/] P = available P (BrayII)

Total sulfur

The analyzed 80 soil samples of both top soil and sub soil, showed that total S varied from 315-1340 mg/kg, of which 93-99% were found in organic form (306-1299 mg/kg). It was found relatively the same in comparison between top soil and sub soil (Table 2). Total C and total N of top soil were higher than that of sub soil and the highest of both parameters were found on Trat orchard soils, which is similar as found on SOM. Total C and total N were ranged from 0.87-3.06 and 0.10-0.28% for top soil and 0.56-2.73 and 0.06-0.25%

for sub soil respectively. The ratios of C:S, N:S and C:N were ranged from 7.8-54.8, 0.74-4.67 and 6.97-11.7 respectively. The C:N:S ratio was found 20:2:1. Total S was significantly correlated with total C (r = 0.410**), N (r = 0.363**), OM (r = 0.512**) and soil pH (r = -0.517**) (Figure 1).

Table 2. Total sulfur, carbon, nitrogen and extractable sulfur in soils (n = 10)

Locations (provinces)	**depth** (cm)	**total S** (mg/kg)	**total C** (%)	**total N** (%)	**C:S** ratio	**N:S** ratio	**C:N** ratio	**C:N:S** ratio	**Ext. S** (mg/kg)	**Org. S**[1/] (mg/kg)
Rayong	0-20	977	1.62	0.159	16.9	1.66	10.2	20:2:1	26.5	950
	20-40	943	1.21	0.117	13.1	1.27	10.2	17:2:1	24.6	918
Chanthaburi1	0-20	729	2.03	0.203	28.7	2.91	9.90	23:2:1	26.9	702
	20-40	764	1.74	0.172	23.4	2.36	10.1	19:2:1	24.5	739
Chanthaburi2	0-20	694	1.25	0.135	18.5	1.99	9.22	28:3:1	20.4	674
	20-40	553	0.80	0.094	15.5	1.86	8.56	22:2:1	14.9	538
Trat	0-20	954	2.38	0.228	27.4	2.60	10.4	20:2:1	39.1	915
	20-40	1038	2.15	0.204	21.6	2.05	10.5	13:1:1	38.3	999

[1/]Org. S (organic S) = total S - extractable S (Tabatabai and Bremner, 1972)

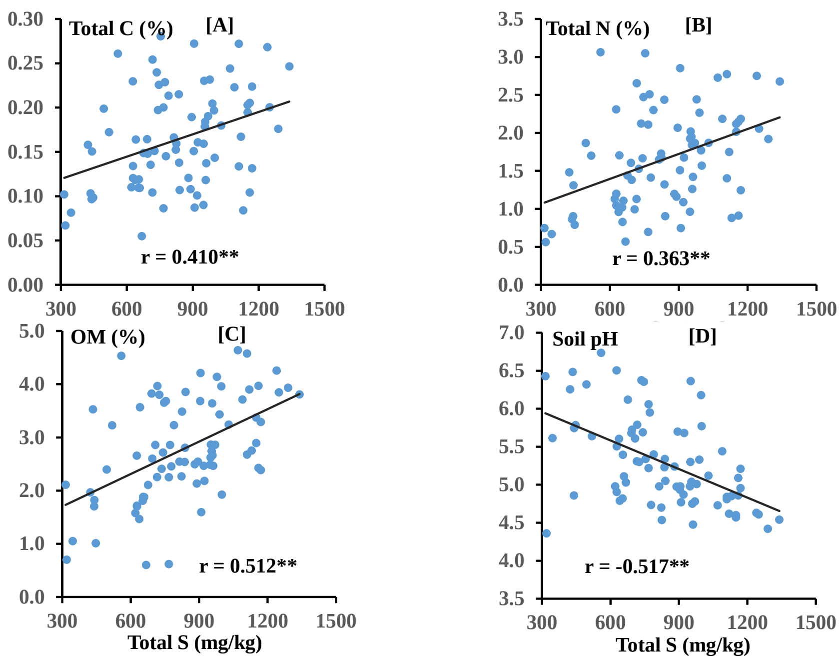

Figure 1. Relationship between total S to total C [A], total N [B], OM [C] and to soil pH [D] (n = 80)

Available sulfur

Available sulfur (extractable sulfur) was evaluated according to Land Development Department (2004). It was found that 77.5% of top soil and 67.5% of sub soil were varied from high (21-30 mg/kg) to very high (>30 mg/kg) availability and only 2.5% and 12.5% was found in low available sulfur level for top soil and sub soil respectively (Figure 2). In addition, it was significantly higher on top soil as compared to that of sub soil ($p < 0.05$), which is also similar on total C, N and OM (Table 3). Available sulfur was significantly correlated with several soil parameters. Slightly high correlation was found to total S (r = 0.715**), total C (r = 0.611**) and OM (r = 0.607**), moderate correlation was found to total N (r = 0.569**), C:N ratio (r = 0.486**) and slightly low correlation was found to soil pH (r = -0.293**).

Table 3. Selected of soil properties compared between top soil and sub soil by paired sample t-tests (n = 40)

Soil layers	total S (mg/kg)	total C (%)	total N (%)	C:S ratio	N:S ratio	C:N ratio	ext. S (mg/kg)	Org. S (mg/kg)	pH	EC µS/cm	OM (%)
Top soil	838	1.82	0.182	22.9	2.29	9.92	28.2	810	5.36	64.6	3.14
Sub soil	824	1.48	0.147	18.4	1.86	9.86	25.6	799	5.22	48.9	2.42
F-test	ns[1/]	**[2/]	**	**	**	ns	*[3/]	ns	*	**	**

[1/]ns = nonsignificant diffences, **[2/] and *[3/] significant diffences at p < 0.01 and < 0.05

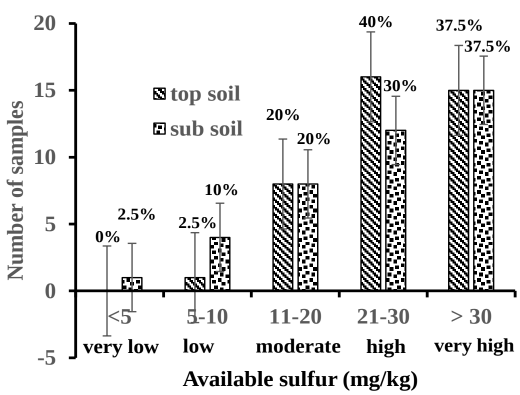

Figure 2. Distribution of soil samples in ranges of sulfur availability (n = 40)

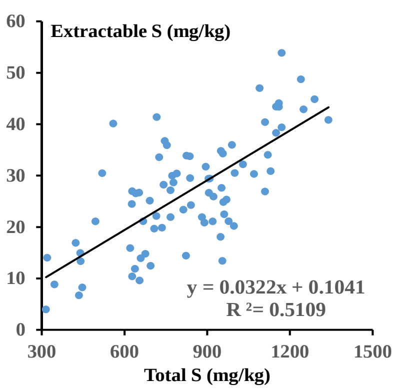

Figure 3. Regression of available S versus total S (n = 80)

Calibation of total sulfur to predicted plant response

In order to predict the responsibility of plant to total sulfur, the linear regression was established between available S and total S (Figure 3). The linear model was Y = 0.0322x+0.104 with R^2 = 0.5109 ($p < 0.01$). The interpretive ranges of total S were calculated according to the S suitability of Land Development Department (2004) as shown in Table 4. It was found that 85-90% of soil samples were high to very high of total S, which is classified as unlikely response and no response from S application.

Table 4. Interpretive ranges of total S for durian orchard soil, Eastern Thailand

Suitability of S	Total S (mg/kg)	Number of samples (%) (n=40)		Response to S application
		Top soil	Sub soil	
Very low	< 150	0	0	Very high response
Low	150 - 300	0	0	High response
Moderate	301 - 600	15.0	10.0	Moderately response
High	601 - 900	42.5	47.5	Unlikely response
Very high	> 900	42.5	42.5	No response

Estimate of available sulfur on durian orchard soils

Stepwise multiple regression and correlations were employed to determine the relative contributions of different soil parameters toward available S (Table 5). Soil characteristics, i.e., total S, C:S ratio, pH, C, C:N ratio, N:S ratio, N and EC were taken for study and the R^2 obtained indicated that approximately 73.0% variation is observed in available S of durian orchard soils.

Table 5. Multiple regression equation indicating the relationship between soil parameters and available S

	Multiple regression equation	R^2
Y_1 =	0.106+0.032 (total S)	0.551
Y_2 =	-16.214+0.039 (total S)+0.535 (C:S)	0.659
Y_3 =	-3.461+0.036 (total S)+0.603 (C:S)-2.341 (pH)	0.669
Y_4 =	-11.093+0.050 (total S)+1.125 (C:S)-2.827 (pH)-7.044 (C)	0.679
Y_5 =	-2.212+0.052 (total S)+1.201 (C:S)-3.382 (pH)-7.052 (C)-0.934 (C:N)	0.683
Y_6 =	38.007+0.049 (total S)+3.028 (C:S)-2.931 (pH)-6.380 (C)-4.794 (C:N)-19.604 (N:S)	0.706
Y_7=	33.34+0.048 (total S)+3.278 (C:S)-3.139 (pH)-14.408 (C)-4.164 (C:N)-22.127 (N:S)+82.503 (N)	0.707
Y_8=	19.732+0.060 (total S)+3.753 (C:S)-2.938 (pH)-27.402 (C)-3.537 (C:N)-23.740 (N:S)+168.143 (N) -0.042 (EC)	0.730

Leaf nutrient concentration

Nutrient concentrations of durian leaf tissue were significantly different when compared among 4 orchards except, K and S were relatively the same, while Ni and Mo were not detected (Table 6). However, mostly nutrients were varied in a range of critical value (Poovarodom *et al.*, 2002) including S content was in a range of critical value (0.23-0.25%) as prescribed by Diczbalis and Westerhuis (2005). There were no correlations between S concentration of leaf tissue and both of total and available S in soils (Figure 4).

Table 6. Nutrient concentration of durian leaf tissue of 4 orchards (n = 10)

Orchard (provinces)	**C**	**N**	**P**	**K**	**Ca**	**Mg**	**S**	**Fe**	**Mn**	**Cu**	**Zn**	**B**
	<------------------- (%) ---------------------->							<------------ (mg/kg) ------------>				
Rayong	$44.3^{b4/}$	2.3^{a}	0.26^{a}	1.6	3.5^{a}	0.61^{a}	0.25	120^{a}	103^{a}	24.3^{b}	16.3^{c}	92.5^{b}
Chanthaburi1	45.0^{ab}	2.3^{a}	0.22^{ab}	1.8	2.0^{c}	0.44^{b}	0.24	89.0^{ab}	53.2^{b}	41.8^{b}	25.4^{b}	94.4^{b}
Chanthaburi2	43.9^{b}	1.9^{b}	0.26^{a}	1.5	2.1^{bc}	0.57^{ab}	0.27	67.8^{b}	28.3^{c}	32.4^{b}	13.2^{c}	39.8^{b}
Trat	46.3^{a}	2.2^{a}	0.17^{b}	1.4	3.0^{ab}	0.69^{a}	0.25	133^{a}	65.2^{b}	163^{a}	36.0^{a}	165^{a}
F-test	**1/	**	**	ns3/	**	*2/	ns	*	**	**	*	*
CV %	3.43	8.64	26.9	18.6	35.7	29.7	14.1	52.5	40.08	145	37.4	76.4

**1/ and *2/ significant differenes at $p<0.01$ and $p<0.05$, 3/ns = nonsignificant differenes, 4/means followed by common letter are not significantly differently by Duncan's Multiple Rannge Test.

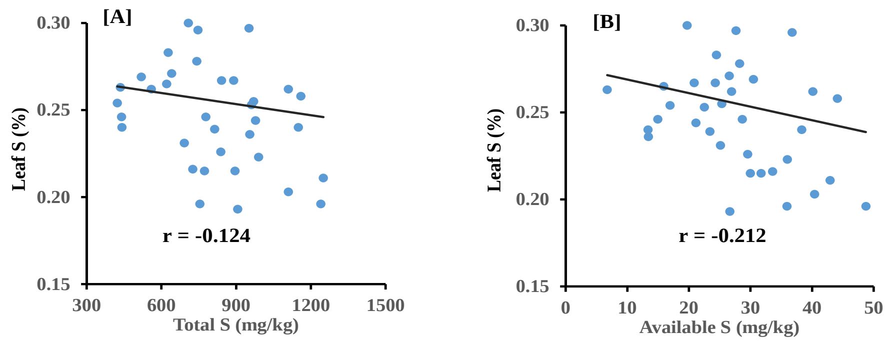

Figure 4. Relationship between total S with S in leaf [A] and available S with S in leaf [B] (n = 40)

Sulfur removal by durian fruit

The amount of sulfur removed by the harvested portion of the durian fruit (petiole, skin, aril, seed) was needed to develop nutrient balances. The purpose of this part was to provide an average value of S uptake by durian fruit, which can be used in nutrient management planning activities. Based on durian growers, an average yield/tree was 160 kg fresh weight (40 fruits/tree, 1 fruit = 4 kg). Mean fruit of sulfur was 0.10% (dry weight) and average fresh weight to dry weight was 4.69 (Diczbalis and Westerhuis, 2005), calculating S removal as follows:

$$\textbf{S removal (g/tree)} = \frac{\textbf{yield (kg/tree, fresh wt.) x 1000}}{\textbf{fresh wt. to dry wt.}} \times \frac{\textbf{S of durian fruit (\%, dry wt.)}}{\textbf{100}}$$

Therefore, S was removed by an average of 32.3 g/tree/year. The finding indicated that input S was higher than that of yield removal by about 10 to 30 folds as S was applied 340-1,020 g/tree/year in the composition of K_2SO_4 (Poovarodom and Phanchidawan, 2006).

Discussion

The characteristic of durian orchard soils revealed that the lighter texture of soil in these areas facilitates durian cultivation due to proper root penetration and good drainage condition. Very strongly acidic soil lead to affect the availability of both macro and micronutrients; however, it was slightly affected to available S in soil (McKenzie, 2003). The extremely high of available P to cause a decrease in the total uptake of Zn and Fe in plants (Loneragan, 1951) but, it was not found antagonism among these 3 elements on durian leaf tissue due to foliar application of micronutrients. Sulfur in soils was mostly found in organic forms (96-97%). Landon (1991) indicated that in humid climate S in aerobic soil normally occurs in organic forms. This has been suggested from the close relationship between total S and total C, total S and total N, total S and OM. Tabatabai (2005) reported that agricultural soils, have a mean of C:N:S ratio about 130:10:1.3 but approximately 20:2:1 was found in durian orchard soils indicated that S fertilizer was heavily applied. In addition, the negative correlation between total S and soil pH was found. This is likely due to the adsorption of SO_4^{2-} is favored by strong acid which may lead to decreased leaching loss (Tisdale *et al.,* 1993).

Mineralization of organic S produces inorganic S (available S) which is microbiological in nature, any variable that affects microbial growth should affect S mineralization. Therefore, temperature, moisture, pH, and the availability of nutrients are the most important (Tabatabai, 2005). The S mineralization is closely to C and N levels in the soil (Williams, 1967). Sulfur will become or remain immobilized if either the C:S or N:S ratios are too large (Tisdale and Nelson, 1975) and conditions conducive to S mineralization often lead to N mineralization (Williams, 1967). The N:S ratio in many soils is in the range of 8-12:1 (Anderson, 1975). The C:S ratios have been reported in the range from about 57-141:1 (Anderson, 1975; Tabatabai and Bremner, 1972). Freney (1967) proposed that C:S ratio < 200 results in a net release of plant available mineral sulfur and a ratio > 400 results in a net immobilization. Hadas *et al.* (2004) reported that soil with C:N < 20 results in net N mineralization. The ratios of C:S, N:C and C:N of the durian orchard soil were ranged from 13.1-28.7, 1.27-1.9 and 8.6-10.5 indicating that mineralization process towards S nutrition.

Measurements of available S seldom give a reliable estimate of S levels in soils, since the ion is often readily removed by dissolution, and measurement is greatly dependent on the conditions of soil sample and only very approximate limits can there be given (Landon, 1991). Several soil parameters offer a good correlation to available S. Therefore, the estimation of the optimum parameters would be practical and offer an alternative approach for S management in agricultural soils. Seal *et al.* (2005) showed that 94.5% variation in the Morgant's solution extracted S may be explained by pH, clay, organic S, CEC, BS, total S and C:S ratio. On durian orchard soils, approximately 73.0% variation in available S was explained by total S, C:S ratio, pH, C, C:N ratio, N:S ratio, N and EC. In addition, the calibration of total S to predicted durian response to S applied was assessed, the result showed a similar trend to the interpretive ranges for total S in pastoral soils as given by Hill Laboratories (2001) which, 300-400 mg/kg was interpreted as high response whereas, 900-1000 mg/kg was interpreted as no response by the plant. Malkerns Research station (1959) reported that total S, of 200 mg/kg was likely termed deficient.

Available S of all durian orchard soils was varied from high to very high on both top soil and sub soil. Approximately 78% of top soil and 68% of sub soil were classified as unlikely response and no response by plant respectively. This may be the main reason that no relationship between S in soil and S in plant tissue was found. McGrath *et al.* (2014) stated that there is a critical concentration of each essential element, within plant tissue above which added nutrients will not increase plant performance but may or may not increase tissue concentrations of that nutrient. Esmel *et al.* (2010) pointed that the S fertilizer recommendations were not soil test based and relied upon leaf analysis results due to which no reliable correlation has been found between extractable S and plant yield. Durian growers, mostly applied K as K_2SO_4 ranges from 1,000-3,000 g K_2O/tree/year (Poovarodom and Phanchidawan, 2006). Meanwhile, S was also applied of 340-1,020 g/tree/year resulted of input S was higher than that of yield removal about 10 to 30 folds. Poovarodom and Phanchidawan (2006) suggested that KCl could be used as an effective replacement for K_2SO_4 in durian orchard soils because it is twice as cheap, although Cl was increased in leaf but it did not increase in durian fruit.

In conclusion, durian orchard soils were very strongly acidic, however it was slightly affected to available S in soil. Total S was varied in range, from 553-1038 mg/kg, of which 96-97% were organic S. The C:S ratio was 13.1-28.7 indicating the mineralization process towards S nutrition. The heavy S fertilizer has been practiced as C:N:S ratio was found at 20:2:1, whereas agricultural soils were normally found at 130:10:1. Available S has a high corelation to total S and varied from high to very high on both top soil and sub soil. The relative contribution of various soil characteristics toward available S revealed that several soil parameters could be explained 73.0% variation in available S. Durian growers have applied 340-1,020 g/tree/year as a composition of K_2SO_4. This result suggested that KCl should be used as an effective replacement for K_2SO_4. Soil and plant analysis can assist in managing crop nutrient requirements in order to maintain both K and S.

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