Effectiveness of Sulfidic Materials on the N, P, K, Mg and S Nutrient Uptake by Rice Plants Grown in Sulfur Deficient Soil under Field Experiment

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Abstract: The experiment was conducted to evaluate the effectiveness of sulfidic materials (SM) and Gypsum (G) application at the rates of 0, 20, 30, 40, 50 and 60 kg S ha^{-1} on the N, P, K, Mg and S nutrient in rice (*Oryza sativa* L., var. BR11: Mukta) grown in sulfur deficient soil were evaluated under field experiment. The contents of N, P, K, Mg and S nutrient in rice shoots at different growth stages of rice were increased by the application of SM and G fertilizer. But the increments were surprisingly high in case of SM compared to G application. In addition, the applied SM increased the average organic matter and available sulfur contents in the soils by 72 % and 229 % increased over control (IOC), respectively, while these increments were 58 % and 196 % IOC for gypsum treatments, indicating that the SM have potential and effective impacts than that of gypsum not only as a source of fertilizer but also to enrich the fertility and productivity status of soil. Moreover, the SM treatment was found to be maintained the high nutrient status in the soil till the final harvest at maturity of rice, reflecting a good indication for its long term use. It is noted that the use of SM did not show any adverse effect on the plant and soil in this study. [New York Science Journal. 2009;2(4):33-41]. (ISSN: 1554-0200).

Key words: sulfur deficient soil, effectiveness of sulfidic materials, gypsum, N, P, K, Mg and S nutrient, rice, field

1. Introduction

Sulfur is the tenth most abundant element in the universe (Stevenson, 1986; Stevenson and Cole, 1999) and ranks thirteenth in abundance in the Earth's crust (Trudinger, 1975). It is one of the major essential nutrients required by all human beings, animals and plants. Agricultural crops require S in amounts similar to phosphorus P, and S is as important as nitrogen (N) in plant growth and in the formation of crop yield and quality (Morris, 2007). In today's agriculture with the emphasis on higher crop yields, there is an increased need for calcium, magnesium and sulfur. To produce at optimum yields, all crops must have an adequate supply of all of the 16 essential plant nutrients. If one or more is lacking in the soil, crop yields will be reduced even though an adequate amount of the other 13 elements are available. This is somewhat analogous to the fact that a wooden bucket will hold no more water than its shortest stave. Crop yields may be limited by the element that is in shortest supply.

Sulfur deficiency has become widespread over the past several decades in most of the agricultural areas of the world, becoming a limiting factor to higher yields and fertilizer efficiency. Maintenance of field S fertility is often overlooked, and S deficiency symptoms in crops are sometimes confused with P or N deficiencies or Al toxicity. Since concentrated fertilizers with a low S content are now widely used, S deficiency problems appear more often (Hitsuda, et. al., 2005). According to estimates of The Sulphur Institute (TSI) based on crop demand, fertilizer efficiency and current inputs, the current S deficit is about 9.6 million tonnes annually. With increased food production raising S requirements and assuming slower expansion rates for S application, this S deficit is projected to grow to 11.9 million tonnes by 2015 (Ming Xian FAN and Donald L MESSICK, 2007) In Asia: In the late 1990s and early 2000s, intensified agricultural production, pressured by the backdrop of food self-sufficiency goals and limited land resources in the globe's two most populous nations, China and India, has created the S nutrient imbalance. This imbalance is expected to grow due to the widespread gap between available production and supply, and crop requirements. Asia's annual S fertilizer deficit is projected to increase from over 5 million tonnes currently to 6.4 million tonnes by 2013, with over 70 % represented by China and India (Morris, 2007). It is noted that about 7 M ha (about 52 %) of agricultural lands are reported to consists of sulfur deficient soils in the northern region of Bangladesh (SRDI, 1999). The current intensive use of agricultural land for crop production has extended the sulfur deficient areas to about 80 % in the Northern region of Bangladesh (Khan, et al., 2007). Poor crop production as a result of acute sulfur deficiency has frequently been reported by many scientists in different regions of India (Tiwari, et al., 1985) and Bangladesh (Khan, 2000). The current use of gypsum, ammonium sulfate, zinc sulfate, etc. as sulfur fertilizers to the soils can instantly supply the sulfur to crops but the fertilization has to be done for each crop in every year, which was even unable to give satisfactory yield of crop and it is not a good practice for the soils as well as environments. Therefore, a suitable and sustainable source of sulfur is indispensable.

Highest levels of S are found in wetlands, mainly in soils containing acid-sulfate materials, and in alkaline, gypsiferous soils in arid and semiarid regions (Ribeiro, et. al., 2001). The utilize of sulfidic materials (SM) or layers obtaining from acid sulfate soils (ASSs) as sulfur fertilizer for crop production is very scanty. Khan, et al., (2002) reported that the high organic matter (2-9 %) total sulfur (3-7 %) and micronutrients in ASSs or SM deserve attention to use these soil materials for the reclamation of alkaline, calcareous or sulfur deficient soils and also for the amendment for ASSs themselves by the removal of SM from the soil. Khan, et al. (1994) also reported that the ASSs contained high Mg (1.3 to 2.6 c mol kg^{-1}) and Al (1 to 2 c mol kg^{-1}). But the use of high Al contained ASSs or SM did not notice any harmful effects when applied in the soils having pH > 4.5 (Khan, et al., 2002). The present studied SM in an ASS layer, which occupies 0.7 M ha land area in Bangladesh, had low pH (< 3), high sulfate and organic matter (Khan, et al., 2006)

The elimination of SM from the ASSs is not only reclaimed the ASSs for a long time but its use in sulfur deficient or non-fertile soils at the rate of about 300 to 1500 kg ha^{-1} may improve the fertility and productivity of the soils. Khan, et al. (2007) reported that the application of SM at the rate of 75 kg S ha^{-1} for sulfur deficient soils had no negative effect on soil pH, nutrient status in the soils and Sunflower production under pot experiment. They suggested that the application of SM was not only effective as sulfur fertilizer but also enriched the organic matter in the soils. Moreover, many studies have been conducted on the mineralization of elements such as N, P, and K from animal manures in various climates and soil conditions (Ebeling, et al., 2003; Egrinya-Eneji, et al., 2003; Eghball, et al., 2002; Schmitt, et al., 2001). However, there are relatively few that focus on nutrients such as Ca and S (Egrinya-Eneji, et al., 2003). Against this background, the present study was considered to evaluate the impacts of SM or ASSs compared with gypsum as sulfur fertilizer in relation to rice production in sulfur deficient soil under field experiment.

2. Materials and Methods

2.1 Soil collection and analyses

The SM (Cheringa acid sulfate soil) used for this study was obtained from the surface soil (depth of 0-15 cm) at Dulahazara in the Cox' Bazar district (Latitude 1206.2 rad or 21°3' N, Longitude 5220.0 rad or 91°6' E) in Bangladesh. Soils were collected from each replicated pots using Cork borer (2 cm diameter), then air-dried and screened by 1 mm sieve. The soils were oven dried at 105°C before analysis. The particle size distribution of the initial soil was determined by the pipette method (Day, 1965) with 1 M CH_3COONH_4 (pH 5.0) and with 30 % H_2O_2 to remove free salts and organic matter. Soil pH was measured by the soil-water ratio 1:2.5 and for the oven dried soil 0.02M $CaCl_2$ (1:2.5) suspension (Jackson 1973) using a Corning pH meter Model-7. For saturation extract of soils, the electrical conductivity (soil solution has extracted from saturated soil paste through vacuum pump: Richards, 1954), water soluble Na and K (Gallenkamp flame photometry using 589 and 766 nm filters, respectively: Black 1965), Ca^{2+} and Mg^{2+} (Pye UniCam-SP 9 atomic absorption spectrometry: Hesse, 1971) were determined. Organic matter content was determined (Nelson and Somners, 1982) by wet combustion with $K_2Cr_2O_7$. Available N (1.3M KCl extraction, Jackson, 1973), available P (0.002 N H_2SO_4, pH 3 extraction, Olsen, et al., 1954) and available S ($BaCl_2$ turbidity, Sakai, 1978) were determined. Cation exchange capacity was determined by saturation with 1 M CH_3COONH_4 (pH 7.0), ethanol washing, NH_4^+ displacement with acidified 10 % NaCl, and subsequent analyses by steam (Kjeldhal method) distillation (Chapman, 1965). Exchangeable Na^+, K^+, Ca^{2+} and Mg^{2+} were extracted with 1 M CH_3COONH_4 (pH 7.0) and determined by flame photometry (Na^+, K^+) and atomic absorption spectrometry (Ca^{2+}, Mg^{2+}). Total sulfur was obtained by digestion with a mixture of concentrated HCl/HNO_3 (1:3) and determined by turbidity method (Sakai, 1978).

2.3 Field experiment

The field experiment was conducted at Tongi, Gazipur district, Bangladesh during the period for June to October, 2000 to evaluate the impacts of SM compared with G as a source of sulfur fertilizer in relation to rice (*Oryza sativa* L., var. BR11: Mukta) production grown in sulfur deficient soil. The experimental treatments on the basis of furrow slice of the studied soils were: Control, 0 (no application of SM and G); SM_{20}, SM_{30}, SM_{40}, $SM_{50,}$ SM_{60} (SM 20, 30, 40, 50, 60 kg S ha^{-1}) and G_{20}, G_{30}, G_{40}, $G_{50,}$ G_{60} (G 20, 30, 40, 50, 60 kg S ha^{-1}). Each treatment was replicated thrice. Thirty three plots were selected as per experimental design (2 fertilizers X 6 doses = 12-1 = 11 X 3 = 33) having each plot size of 2 square meter (2 X 1 meter).

The soil in each plot was fertilized with N, P and K at the rates of 80, 40 and 60 kg ha^{-1} as urea, triple super phosphate (TSP) and murate of potash (MP), respectively. The full dose of TSP and MP and half of urea were mixed with the soil during plot preparation. The remaining urea was applied in equal splits, one at the active tillering stage of rice and the other at the panicle initiation stage. As per treatments, the soils in the plot were also subjected to the application of SM and G at the rates of 0, 20, 30, 40, 50 and 60 kg S ha^{-1} during plot preparation. Both the SM and G were dried, milled and sieved (1 mm sieve). Thirty five days old healthy and uniform seedlings were transplanted at the rate of five plants per hill and 60 hills per plot (row to row and hill to hill distance were 15 cm). The soils in the plots were irrigated by river water whenever necessary to maintain the soil under moist to wet conditions required for the production of rice. Seedlings were collected by the courtesy of Bangladesh Rich Research Institute (BRRI), Gazipur, Bangladesh.

2.4 Plant collection and analysis

At different stages of growth of rice shoot, the nutrients content were determined at 30 (20-40 early tillering stage = ETS), 60 (41-70 maximum tillering stage = MTS) and 110 (harvesting at maturity) days after transplanting (DT). The N contents were analyzed by the H_2SO_4 digestion through the micro-Kjeldhal method (Jackson, 1973) and P contents by spectrometry (Jackson, 1973); K content by Gallenkamp flame photometry (Black, 1965); S contents by turbidometry (Jackson, 1973) and Mg contents by atomic absorption spectrometry (Hesse, 1971) in HNO_3-$HClO_4$ acid (2:1) digest. The level of significance of the different treatments was determined at different stages of growth using Duncan's New Multiple Range Test (DMRT) and least significance different (LSD) techniques (Zaman, et al., 1982).

3. Results and Discussion

3.1 Sulfidic Materials (SM)

The SM was collected from the surface (depth: 0-15 cm) of an acid sulfate soil (Typic Sulfic Halaquept, detailed: Khan, et al., 2006) showed a silty clay loam texture with pH values of 3.3 (0.02 M $CaCl_2$) and 3.8 (field), indicating that the SM had probably accumulated a large amount of pyrite which had produced H_2SO_4 in the laboratory by oxidation. The EC, available and total sulfur and organic matter content in the SM were very high (Table 1). The content of Ca in SM was low compared with the Mg content, which might be due to occasional flooding with sea water rich in Mg. The Na content was also high due to the flooding with high saline water. The SM was in fact a fertile but unproductive soil due to its high acidity, salinity and imbalance of nutrients.

3.2 Conditions of initial and post harvested soils

The studied soil had silty clay loam textures, initial pH values of 5.0 to 5.3 as determined by the different conditions. These sulfur deficient soil was subjected to the application of SM and G in relation to rice production. The pH values at different conditions of the average soil data of all the treatments at post harvesting were found to be decreased by 0.1 to 0.3 pH units compared with the initial soil, indicating that the application of acidic SM on these soils had negligible influences on the pH of the soils. On the other hand, the SM strikingly increased the initial low content of organic matter, N, P, K, Ca, Mg, available and total sulfur in the soil by 2 to 233 % compared with the initial soils (Table 1), which was due to the high nutrient status of the applied SM though there might be a little contribution from the plant roots. The base saturation of the initial soil was 85 % which was increased to 89 % at the final harvesting of rice, (Table 1). These increases of base saturation were attributed to the high content of basic cations in the applied SM. The EC values of the soils were found to be increased from 1.0 to 2.1 dS m^{-1}, which are attributed to the higher EC values of the SM used. However, these increased levels of EC values might not have remarkable influence on the production of rice.

3.3 Sulfur and organic matters in the soils

The available S contents of the soil was found to be increased by the application of SM and G but the effects were more pronounced in case of SM and the increments were significantly ($p \leq 0.05$) stronger with the passes of time (Table 2 and Figure 1). Apart from fertilizer rates, the applied SM and G increased the available S contents by 295 and 218 %, respectively at post harvesting of rice at maturity (Table 2). This might be due to the contents of other essential nutrients especially N in SM (Table 1), which enhanced sulfur uptake by the rice compared with the G treated plots. On the other hand, S content was found to be increased by the treatments but decreased in few cases by the passes of time was attributed to the uptake of rice plant (Table 2).

The content of organic matter in the soil throughout the experimental period was found to be improved a little by the different rates of gypsum fertilization, whereas almost all the doses of SM significantly increased the organic matter status in the soils and the increments were more striking with the higher doses of SM (Table 2). The application of SM increased the average organic matter in the soil by 72 % IOC at post harvesting of rice at maturity, while these increments were 58 % for G treatments. These increments in organic matter status in the soil were attributed to the high content of organic matter in the applied SM and the little enrichment of organic matter by the G treatments were attributed to the contribution of cultivation processes. Shamim, et al. (2008) also found the same findings and reported that the application of SM at the rate of 160 kg S ha^{-1} for sulfur deficient soils had no negative effect on nutrient status in the soils and rice production under pot experiment.

3.4 Nutrition of rice

At different growth stages of rice, the contents of N, P, K, Mg and S in rice shoot were increased by the SM and G application. The increments were more striking in case of SM compared to G application (Table 3). The lowest contents of these nutrients were observed for the control treatments in the soil. The average S contents in plant tissue of all the SM treatments at the final harvesting (110 DT) of rice were increased by 156 % compared with the control treatments. But these increments of S by the average of all G treatments were 133 % for the rice plants grown in sulfur deficient soils. It is mentioned that sulfur concentration in rice shoots decreases over time. These findings suggest that the impacts of SM as S-fertilizer were much higher than G and would also be effective for the subsequent crops as indicated by the high contents of nutrient in rice plants at final harvesting (110 DT) stages. The use of SM from ASSs not only recover S deficiency of rice plants but also enhanced the growth of rice and improved the fertility status of the studied soils compared to gypsum. Moreover, the removal of SM from ASSs may lead the reclamation of acute problem of the ASSs. Khan, et al., (2002, 2007) reported that the nutrient uptake by tomato, onion and sunflower were strikingly increased by the application of SM compared to G and $MgSO_4$.

Table 1. Some selected properties of initial soils (depth 0-15 cm, oven dry basis), sulfidic materials and the average soils of all the treatments at post harvesting of rice used during field experiment.

Soil properties	Studied soil			Sulfidic Materials (‡ASSs)
	Before use	After use	% †IOC	
Textural class	Silty clay loam			Silty clay loam
Soil pH (Field)	5.3	5.2	-	3.8
Soil pH (Soil: Water=1: 2.5)	5.2	4.9	-	3.6
Soil pH ($CaCl_2$=1.2.5)	5.0	4.7	-	3.3
E C (1: 5 dS m^{-1})	1.0	2.1	110.0	19.0
Organic matter (g kg^{-1})	7.0	9.2	31.4	40.0
Extractable N (m M kg^{-1})	0.2	0.25	25.0	3.6

Available P (m M kg^{-1})	0.5	0.51	2.0	0.1
CEC (c mol kg^{-1})	16.1	17.8	10.6	17.2
Base saturation (%)	84.6	89.2	5.4	21.1
Exchangeable cations (c mol kg^{-1})				
Sodium	0.37	0.65	75.7	2.13
Potassium	0.07	0.14	100.0	0.24
Calcium	6.45	6.62	2.6	0.31
Magnesium	3.61	3.99	10.5	0.95
Water soluble ions (c mol kg^{-1})				
Sodium	0.12	0.21	75.0	4.8
Potassium	0.24	0.32	33.3	0.3
Calcium	3.8	3.94	3.7	0.3
Magnesium	2.64	3.6	36.4	3.3
Available sulfur	0.03	0.1	233	35.1
Total sulfur	1.56	2.87	84.0	165.6

†IOC = Increased over control, ‡ASS = Acid sulfate soil

Table 2 Contents of sulfur and organic matter of the soils at different growth stages of rice as influenced by the application of sulfidic material (SM: kg S ha^{-1}) and gypsum (G: kg S ha^{-1}) in the sulfur deficient soil.

Treatment	**Available sulfur (m M kg^{-1})**			**Total sulfur (m M kg^{-1})**			**Organic matter (g kg^{-1})**		
denotation	30 DT†	60 DT	110 DT	30 DT	60 DT	110 DT	30 DT	60 DT	110 DT
Studied soil: Silty clay loam, pH 5.2, Organic matter=7.0 g kg^{-1}, Total S=15.6 and available-S=0.30 m M kg^{-1}									
Control	0.32d	0.28e	0.26d	15.9d	15.4d	13e	7.1c	6.6b	6.1d
SM_{20}	0.38c	0.61c	0.74b	18d	15.7d	13.2e	7.3b	6.6b	6.9c
SM_{30}	0.46b	0.68b	0.79b	24.3c	22.1c	19.4d	7.4b	7.1b	8.1b
SM_{40}	0.59a	0.72b	0.81a	32.1b	28.2b	25.3b	7.8a	7.3a	8.3b
SM_{50}	0.62a	0.81a	0.87a	38.5a	35.1a	32.1a	8.1a	7.8a	9.2a
SM_{60}	0.65a	0.86a	0.9a	40a	36.3a	32.2a	8.4a	8.1a	9.4a
G_{20}	0.34c	0.56d	0.63c	17.4d	14.5d	12.8e	6.3c	6.4b	6.8c
G_{30}	0.4c	0.59c	0.67c	21.2c	16.6d	13.5e	6.9b	6.5b	7.3c
G_{40}	0.52b	0.65c	0.71b	23.5c	19.2c	15.6e	7.3b	6.7b	7.6b
G_{50}	0.59a	0.74b	0.78b	32.3b	28.6b	24.1c	7.6a	7.2b	8.1b
G_{60}	0.61a	0.78a	0.83a	36.2a	31.4b	27.8b	8a	7.8a	8.8a
LSD at 5%	0.06	0.08	0.09	3.8	3.5	3.0	0.8	0.75	0.9
SM-IOC (%)	110.94	228.57	295.19	140.41	123.05	135.00	37.32	39.77	71.72
G-IOC (%)	92.19	196.43	218.08	105.35	79.06	80.38	27.11	31.06	58.20

†DT = days after transplanting, ‡In a column, means followed by a common letter are not significantly different at 5% level by LSD. IOC = Increased over control.

Table 3 Effect of sulfidic materials (SM) and Gypsum (G) on the nutrients contents (g kg^{-1}) at different stages of growth of rice shoot in the sulfur deficient soil.

Treatment	Nitrogen		Phosphorus		Potassium		Magnesium		Sulfur	
denotation	60 DT†	110 DT	60 DT	110 DT	60 DT	110 DT	60 DT	110 DT	60 DT	110 DT
	(‡MTS)	(¶Maturity)	(MTS)	(Maturity)	(MTS)	(Maturity)	(MTS)	(Maturity)	(MTS)	(Maturity)
Control	20.2	7.8d	1.1	0.9e	22.3	15.5c	5.2	2.8c	1.9	1.3d
SM_{20}	20.7	9.2c	1.5	1.2d	26.2	16.4b	5.5	3.1b	2.6	1.8c
SM_{30}	21.5	9.9b	1.9	1.4c	26.7	16.7b	6.1	3.2b	3.1	1.9c
SM_{40}	22.3	11.4a	2.2	1.8b	27.4	17.5b	6.9	3.4b	3.7	2.5b
SM_{50}	23.6	11.8a	2.5	2.1a	29.6	18.8a	7.3	3.8a	4.2	3.4a
SM_{60}	24.2	12.5a	2.6	2.3a	30.1	19.7a	7.7	4.1a	4.4	3.7a
G_{20}	20.3	8.6c	1.2	1.1d	25.8	15.8b	5.3	3c	2.1	1.5c
G_{30}	20.6	9.1c	1.5	1.3c	26.4	15.9b	5.6	3.1b	2.3	1.8c
G_{40}	21.5	9.7c	1.8	1.5c	26.9	16.7b	6.2	3.2b	2.8	2.6b
G_{50}	21.9	10.4b	2.2	1.8b	28.1	17.5b	6.7	3.2b	3.5	2.9b
G_{60}	22.8	11b	2.3	2b	29.3	18.6a	7.1	3.5b	4.1	3.3a
LSD at 5%		1.2		0.2		1.8		0.38		0.36
SM-IOC (%)	38.99	75.64	143.18	144.44	56.95	43.71	61.06	57.14	136.84	155.77
G-IOC (%)	32.55	56.41	104.55	113.89	53.03	36.29	48.56	42.86	94.74	132.69

†DT=days after transplantation of rice, ‡MTS=maximum tillering stage of rice, ¶Maturity=maturity stage of rice, In a column, means followed by a common letter are not significantly different at 5% level by LSD. IOC=Increased over control.

4. Conclusion

In rice shoots, the content of N, P, K, Mg and S at different growth stages was increased by the application of sulfidic materials (SM) and gypsum (G). But the increments were surprisingly high in case of SM compared to G fertilizer. The use of SM and G increased the available S by 295 and 218 % increased over control (IOC) at post harvesting of rice at maturity, suggesting that the SM compared with G as a source of S-fertilizer was potential and effective for the recovery of S deficiency as well as fertility status of the soils. In addition, the improved knowledge of the available and total sulfur in the soil and plant over time can help or lead to a more rational use of fertilizers. The high organic matter (40.0 g kg^{-1}), available-S (35.1 c mol kg^{-1}) and total S (165.6 c mol kg^{-1}) and other nutrient contents, specially micro-nutrient of the SM deserve attention to use these soil materials for the reclamation of poor soils like saline, alkaline, calcareous, sulfur deficient soils, etc. But further field research is essential to find out the optimum doses of SM for different soils under variable conditions.

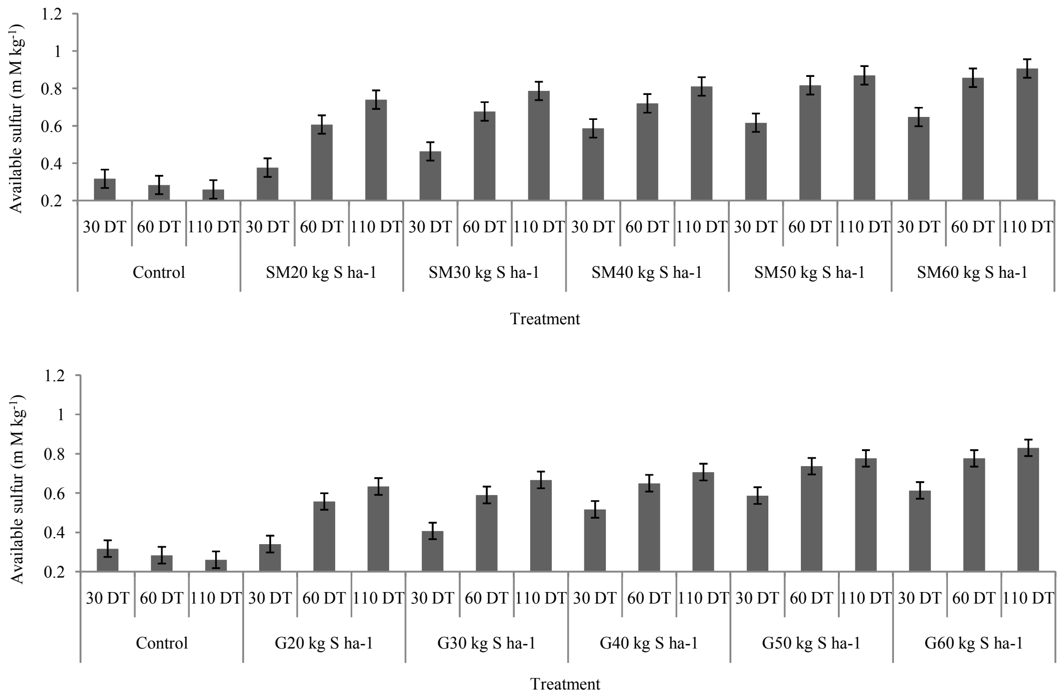

Figure 1. Effect of sulfidic material (SM) and gypsum (G) on the available sulfur at different growth stages of rice in the sulfur deficient soil. Vertical bars indicate ± standard errors of means.

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