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Extractability of different extractants and availability of sulphur in long-term rice growing alluvial soils of West Bengal

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Abstract

The present study was conducted during the year 2017-2018 with the objectives to assess the sulphur status in soils, delineate GPS-GIS based soil fertility map and to know the suitability of extractants for sulphur in one of the most intensively long-term rice growing regions of West Bengal, India. In-situ samples of soil and rice plants were collected by GPS based Grid sampling approach. The 0.15 % $CaCl_2$-extractable sulphur in soils ranged from 2.57 – 38.62 mg kg^{-1}, while sulphur content in grain and straw of rice ranged from 1198.87–1922.57 and 1802.22–3200.00 mg kg^{-1}, respectively. Soils are deficient in available sulphur. Among the four extractants used ($CaCl_2$, AB-DTPA, Mehlich-3 and Modified Morgan), Mehlich-3 extracted the highest amount of S ranging from 9.68-375.06 mg kg^{-1}. Regression analysis between extractable concentration in soil and plant parts revealed that Mehlich-3 was the most suitable extractant for sulphur for this type of soil.

Keywords: AB-DTPA, mehlich-3, alluvial soil, sulphur, $CaCl_2$, suitable extractant, rice

Introduction

Sulphur (S) is one of the essential secondary macronutrient elements required for optimum growth, metabolism and development of all plants and is rightly called as the fourth major plant nutrient (Rathore *et al*., 2015) [19]. Sulphur is best known for its role in the synthesis of proteins, oils, vitamins and flavoured compounds in plants. It is a constituent of three amino acids viz. Methionine (21% S), Cysteine (26% S) and Cystine (27% S), which are the building blocks of protein. Sulphur deficiencies in India are widespread. Intensification of agriculture with high yielding varieties and multiple cropping coupled with the use of high analysis sulphur free fertilizers along with the restricted or no use of organic manures have accrued in depletion of the soil sulphur reserve (Sahrawat *et al*., 2009) [22]. Apart from that, progressively higher removal of sulphur owing to high production level led to appearance of sulphur deficiency (Tandon, 2011) [25]. In soils, S mostly remains in organic combination, constituting more than 95% (Wang *et al*., 2006) [28] of total sulphur. Sulphate-S is the form plants prefer to uptake, which availability depends upon the mineralization of organic S in soils. Although, mineralization of organic S is solely a microbes mediated process, the availability of sulphate is controlled by pH, organic carbon and clay content of soils through some adsorption-desorption mechanism. Soils low in pH and high clay content bind the sulphate-S on the edge of colloidal matrix and plants find it difficult to uptake the same from the exchange sites (Padhan *et al*., 2016) [15]. On an average, 41 per cent of Indian soils are deficient in S and it is widespread in coarse textured alluvial, red and lateritic, leached acidic and hill soils and black clayey soils (Patel *et al*., 2018) [17]. The deficiency of sulphur is emerging fast in areas where continuously sulphur free fertilizers like DAP, urea etc are being used. In West Bengal, six districts viz. Birbhum, Burdwan, Murshidabad, Midnapore, Nadia and 24 Parganas have been reported to be sulphur deficient (Ghosh *et al*., 2012) [7]. Being a staple food grain of South-East Asia, rice is being grown intensively with high analysis fertilizers with very less external supplement of sulphur and micronutrients during the last few decades in this region. Besides, poor recycling of rice residue because of its demand for fuel and forage, further deterioted soil nutrients status of rice soils (Chandel *et al*., 2003) [2]. It is gradually making the major rice growing alluvial soils sulphur and micronutrient deficient. Again, the content of mineral sulphur forms in soil is decreasing rapidly in the last three decades (Balík *et al*., 2009; Scherer,

2009) [1, 23]. Therefore, mineral sulphur deficiency starts to be an actual problem in many locations (Lehmann *et al*., 2008; Kulhánek *et al*., 2016) [12, 11]. Because of these facts, relatively new methods have been developed and further improved for extracting bio-available and other soil sulphur forms (Morche, 2008; Förster *et al*., 2012) [14, 6]. It has been reported that anions, such as acetate and nitrate, are capable to extract S from the soils. The ability for replacing SO_4^{2-} tends to be low as compared to the phosphate (PO_4^{3-}) anion (Chang and Thomas, 1963) [3]. Though a number of extractants are there to extract phytoavailable forms of this element, the most commonly used extractant is 0.15 % $CaCl_2$. But, in order to get a rapid, reproducible, inexpensive, non-toxic extraction procedure which will be adaptable to soils and extract the labile forms of nutrient, choice of a suitable extractant is of utmost importance. Most of the studies on suitability of extractant for rapid determination of sulphur have focussed mainly on the pot experiment under controlled climatic conditions (Huda *et al*., 2004) [8]. In-situ collection of soil and plant samples from the same field and then screening suitable extractant in terms of determining extractable amounts in soil in relation to their plant uptake is very rare in scientific literature.

Having considered the above backgrounds, the present study has been undertaken to study the distribution of extractable or plant available sulphur in alluvial soils where rice is continuously being grown for the last few decades in relation to soil properties as well as to screen out a suitable extractant for rapid determination of plant available sulphur in such soils.

Materials and methods

Study area and sampling

Site description

For this study, representative samples of alluvial soils (both old and new) were collected from the East Midnapore district of West Bengal, India (Fig 1). The district is situated at the southern part of West Bengal with geographical area of 4736 sq km and located between 21º38' N and 22º30' N latitudes and between 87º27' E and 88º11' E longitudes. Soils of this district are intensively cultivated where generally rice based cropping system is practiced by the farmers' since centuries.

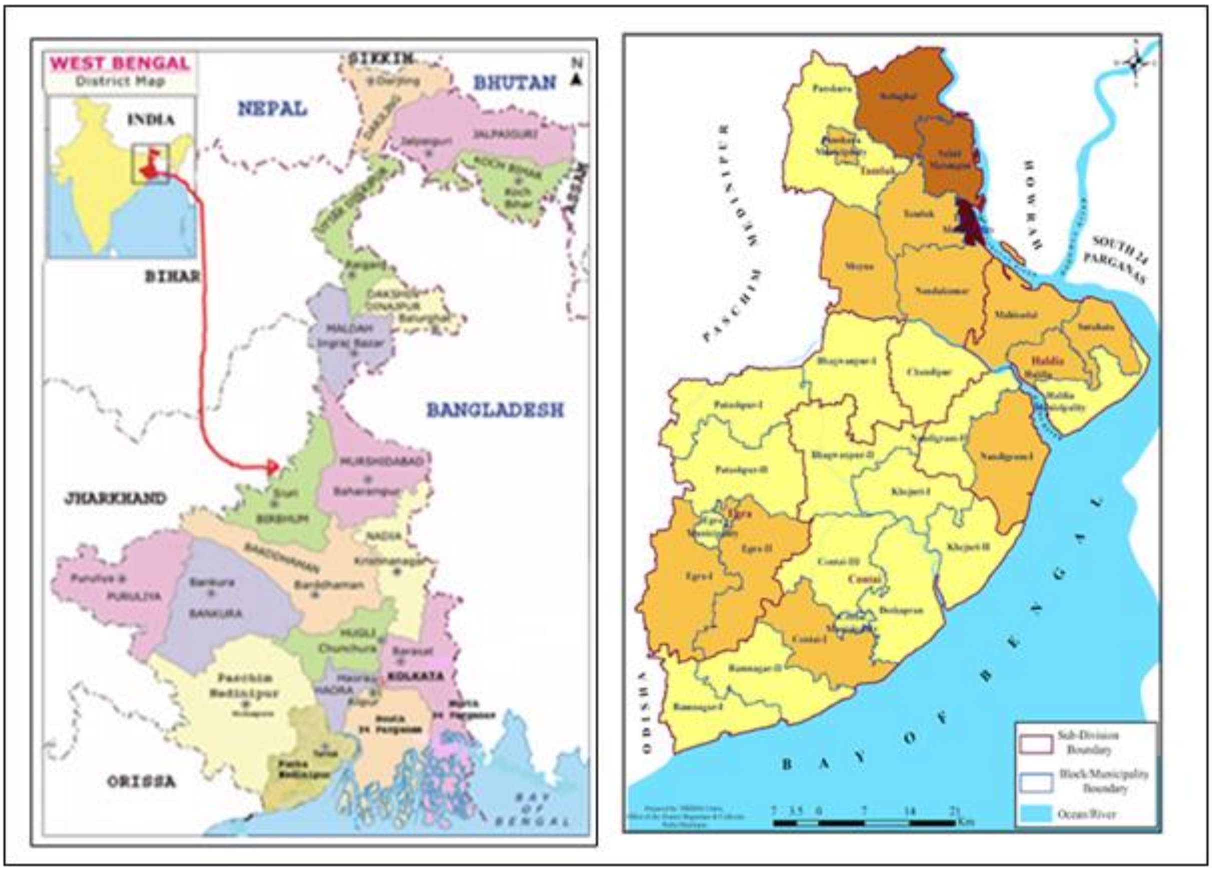

Fig 1: Map indicating the geographical location of East Midnapur district of W. Bengal, India.

Sample collection, processing and storage

Soil samples

Soil samples were collected from 0-15 cm layer of the experimental field after harvesting of rice crop. Grid based soil sampling was carried out at 5 x 5 km grid using hand held GPS (Garmin GPS 12). Total 250 soil samples were collected from the whole district. Composite samples were air dried, ground with wooden mortar and passed through 2 mm sieve and was stored in a refrigerator after packing in polyethylene packets for further analysis.

Plant samples

Total 42 plant samples were collected from the farmers' field just after harvesting of rice crop (last week of October, 2017). After collection, they were air-dried and then straw and grain were separated. These samples were first washed with running tap water to remove all visible soil particles followed by 0.1 M HCl and finally with double distilled water. After that, the samples were dried in a hot air oven at 60±5°C for 48 hr till the constant weight was achieved. After drying, the samples were ground to fine powder by using stainless steel grinder for further analysis.

Analytical procedure

Soil analysis

Soil samples were analysed for pH in soil suspension (Page *et al*., 1982) [16], oxidizable organic carbon (Walkley and Black, 1934) [27]. Available sulphur in the soil samples was determined by following the method outlined by Chesnin and Yien (1950) which involved extraction of soil with 0.15% $CaCl_2$ solution in 1:5 ratio (soil: extractant)and shaking for 30 minutes. Aliquot thus collected after filtering the soil samples through Whatman no. 42 filter paper used for development of turbidity in presence of sodium acetate - acetic acid buffer and stabilizing agent gum acacia. The intensity of prepared sample was measured in Turbidity meter 135. The concentration of sulphur in the soil samples was calculated from a standard curve and multiplied by the dilution factor. To assess the most suitable extractant for available sulphur, four different extractants were used namely, $CaCl_2$ (Chesnin and Yien, 1950) [5], AB-DTPA (Soltanpour and Schwab, 1977) [24] (ammonium bicarbonate-DTPA), Modified Morgan (Wolf, 1982) [29] or Wolf-Morgan and Mehlich-3 (Mehlich, 1984) [13] (Table 1).

Table 1: Summary of methodology through extractants

Extractants used	Extractant composition	Soil: extractant	Soil weight in g	Extractant volume in ml	Time of shaking in hr	Reported element in extraction
1. Mehlich-3 (Mehlich, 1984)	a mixture of 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3 and 0.001 M EDTA, pH 2.5	1: 10	2.5	25	5	S
2. AB-DTPA (Soltanpour & Schwab, 1977)	a mixture of M NH_4HCO_3 and 0.5 M DTPA, pH 7.6	1: 2	10	20	15	S
3. Modified Morgan (Wolf, 1982)	a mixture of 0.073M CH_3COONa, 0.52N CH_3COOH and 0.001M DTPA, pH 4.8	1: 5	5	25	15	S

Plant analysis

Plant sulphur was determined by precipitation of sulphate from the digest as barium sulphate with addition of $BaCl_2$ salt (turbidimetric method) in acidic medium. The plant sample was digested with di-acid mixture as outlined by Tandon (1993) [26]. One gram of plant sample was digested with 10ml of di-acid mixture (HNO_3 and $HClO_4$ in a ratio of 9:4) on a sand bath. The content was heated vigorously until the production of red NO_2 fumes ceased. The completion of digestion was confirmed when the liquid became colourless. After cooling, 20ml of double distilled water was added. Then it was filtered through Whatman no.42 filter paper into a 50ml volumetric flask and final volume was made with double distilled water. Sulphur in the plant sample was determined using Turbidity meter 135 exactly in the same manner as described for available S in the soil.

Preparation of thematic maps

The data used for preparation of GIS based map was Satellite Data of Landsat TM (Path-138, 139; Row-44; Year-1990). The Software used for this purpose is ArcGIS 9.3, Erdas Imagine 9.2, Microsoft Office 2007. The sample points have been used to locate on the district map of East Midnapore. These points have been interpolated for sulphur through ArcGIS software. The Inverse Distance Weighted (IDW) method has been used for interpolation. After that, the district map of East Midnapore has been extracted from the India as shape file. This shape file has been used to extract the interpolated sulphur maps. For East Midnapore, False Colour Composite (FCC) satellite image, firstly East Midnapore shape file has been used to extract district then the sample points have been overlaid upon it. This process is followed for generating the map.

Statistical analysis

Statistical analysis was performed by DOS-based SPSS version 20.0. Simple correlation coefficients and regression equations were also developed to evaluate relationships between the response variables using the same statistical package.

Results and Discussion

Physico-chemical properties of soil

The results showed that the soils varied widely in their pH values ranging from 4.82 to 7.2 with a mean value of 5.81 (Table 2).The results, therefore, suggests that soils were moderately acidic to neutral in reaction.

The soils of this region were found to have low to medium organic carbon content (0.15%-0.89%) with a mean value of 0.52% (Table 2). Results also showed that its content was negatively correlated with the pH of soil (Table 4). The negative correlation of OC with pH value might be related with the greater activities of microorganisms particularly soil bacteria at higher pH (not >8) (Rousk *et al*., 2009) [21].

Table 2: Status of soil pH and organic carbon in the studied soil samples

No. of Samples	Soil pH		Soil Organic Carbon	
	Range (%)	Mean ± SD	Range (%)	Mean ± SD
250	4.82- 7.20	5.81 ± 0.62	0.15-0.89	0.59± 0.15

Available status of sulphur and their relationship with physico-chemical properties of soil

The available sulphur content of this region (Table 3) varied from 2.57 to 38.62 mg kg^{-1} with an overall mean of 13.32 mg kg^{-1}. On the basis of available status of S in the soils (Fig-2), no samples were found to be high in available S content (>40 mg kg^{-1}) whereas, 25 samples were under medium (20-40 mg kg^{-1}), 151 were under low (10-20 mg kg^{-1}) and 74 were under deficient category (<10mg kg^{-1}). The calculated Nutrient Index Value of S was also very low (1.14). So, this study revealed that the rice growing soils of East Midnapore district were deficient in Sulphur (S). It is shown in Fig.-3. Similar findings were also reported by Jaggi and Sharma (2000) [9] in acid soils of Manipur. Rao and Sharma (1997) [18] found that on an average 8.1-11.0 mg kg^{-1} S extracted by 0.15 % $CaCl_2$ in some soils of Indian Western Himalaya. The available sulphur content in soil showed a significant and negetive correlation with pH and a significant and positive correlation with organic carbon.

From the results (Table-4) it was seen that S content in the rice straw ranged from 1802.22 to 3200 mg kg^{-1} or, 0.18 to 0.32 % with the mean value of 2549.17 mg kg^{-1} or, 0.25 %.

The results revealed that S content in straw was higher than the grain and its content is also higher than the critical value of S in plant. The results also showed that S content in the rice grain of samples ranged from 1198.87-1922.57 mg kg^{-1}or, 0.12 to 0.19 % with the mean value of 1432.48 mg kg^{-1} or, 0.143 % (Table- 4). The results also revealed that S content in grain is deficient as per the critical value of S in plant.

Table 3: Summary of the status of available S in studied soil samples

Block	Number of samples	Range (mg kg^{-1})	Mean	SD
Tamluk	11	5.94-11.79	8.8	2.25
Sahid Matangini	11	1.02-8.91	5.34	2.3
Panshkura	11	4.65-15.52	8.08	3.87
Kolaghat	11	2.92-10.86	7.6	2.54
Chandipur	11	2.83-28.48	11.47	7.82
Bhagawanpur 1	11	1.78-8.41	5.81	1.81
Potashpur	11	2.4-18	8.23	5.25
Bhagawanpur 2	11	2.48-5.8	4.32	1.19
Contai 1	11	2.57-14.56	9.14	4.35
Contai 2	12	6.83-20.6	13.45	4.51
Ramnagar 2	10	4.62-19.83	9.79	5.07
Ramnagar 1	11	1.26-10.5	6.81	2.37
Potashpur 2	11	4.52-10.25	6.72	1.94
Deshopran	11	4.71-16.28	8.89	4.46
Egra 1	12	4.67-15.98	8.12	4.13
Egra 2	11	3.21-13.69	7.47	3.35
Nandakumar	11	3.52-13.12	8.31	2.65
Sutahata	11	3.11-13.48	9.04	3.54
Nandigram 1	11	5.29-10.26	7.29	1.79
Haldia	11	3.43-19.64	10.43	4.53
Mahisadal	10	4.89-19.48	8.13	4.34
Khejuri 2	9	4.52-21.88	10.23	6.81
Khejuri 1	10	5.94-11.63	8.51	2.14
Total	250	2.57-38.62	13.32	6.98

Table 4: Concentration of Sulphur in the Straw and Grain of Rice Plant

Elements	Range	Mean	Standard Deviation
Straw-S (mg kg^{-1})	1802.22 - 3200.00	2549.17	478.71
Grain-S (mg kg^{-1})	1198.87 - 1922.57	1432.48	226.59

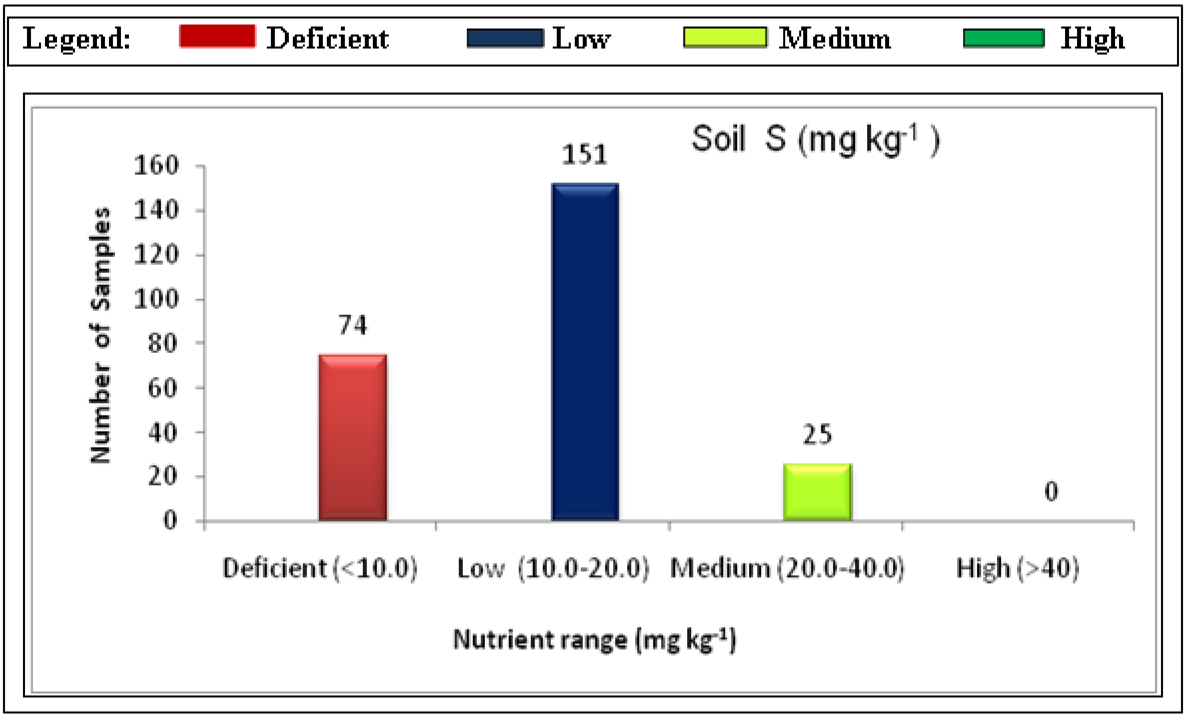

Fig 2: Graphical representation of available status of $CaCl_2$ extractable S in some rice growing soils of East Midnapore district, West Bengal.

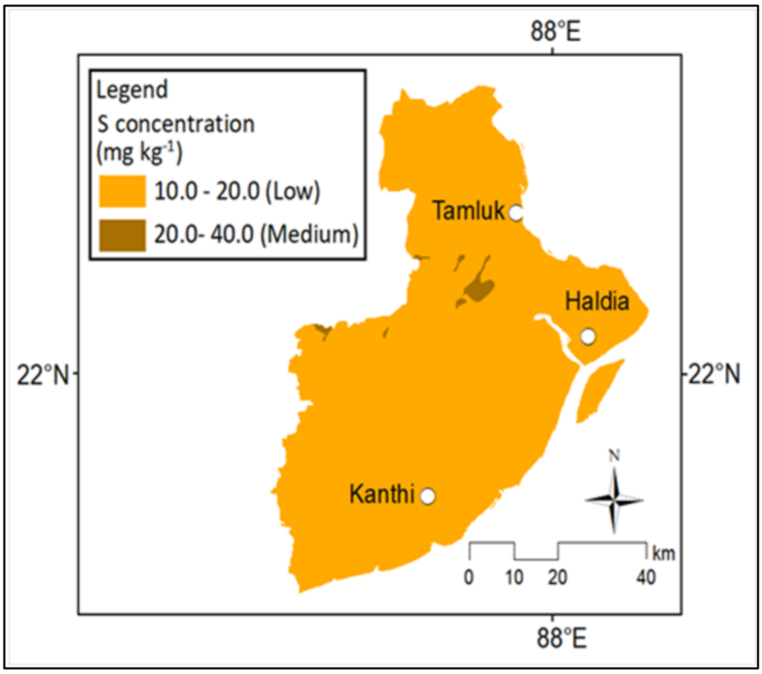

Fig 3: Sulphur Status of East Midnapore District. This map shows that maxium part of East Midnapore district recorded under low range of sulphur.

Dynamics within different forms of extractable Sulphur

All forms of extractable S were highly and significantly correlated with each other indicating that although the ability of sulphur extraction is different for these extractants, their trends of S displacement from soil into solution is similar (Fig.-4). The best correlation (r=0.862**) was found between $CaCl_2$- S and AB-DTPA-S followed by the correlation between $CaCl_2$-S and Modified Morgan-S (r= 0.780**) and $CaCl_2$-S and Mehlich-3 (r= 0.724**). Similar findings were also reported by Rao and Sharma (1997) [18].

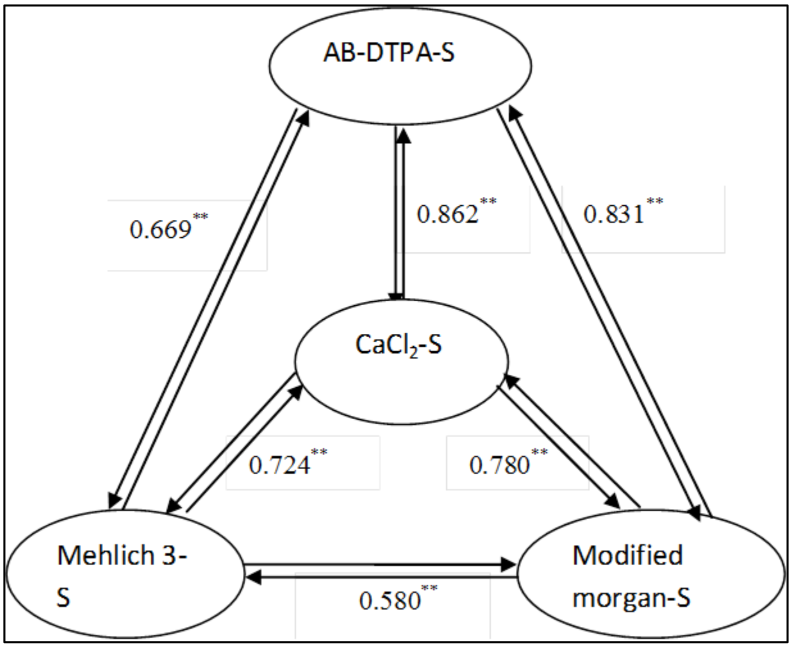

Fig 4: Suitability of different extractants of S.

Suitability of extractants for determination of Sulphur

The Mehlich-3 solution extracted maximum amount of S from soil in comparison to other extractants. The order of correlation between soil and plant concentration of S was $CaCl_2$ <AB-DTPA < Modified Morgan < Mehlich-3 (Table-5). Similar findings were reported by Rao and Sharma (1997) [18].

However, regression analysis revealed that there was greater relationship of straw and grains with the soil available S extracted by Mehlich-3 extractant (Fig.5). Sulphur extracted by Mehlich 3, Modified Morgan and AB-DTPA in different soils ranged from 9.68-375.06, 9.66-465.57 and 6.26-18.39 mg kg^{-1} respectively (Table-6). The differential magnitude of extractability of available S by these extractants could be explained based on their chemical composition and replacing power of SO_4^{2-} and the fraction that tend to remove from the soils (Kanwar and Mudahar, 1986) [10].

According to Reisenauer (1967) [20], the adsorbed SO_4^{2-} is in kinetic equilibrium with SO_4^{2-} in solution and it may be replaced by another anion of greater co-ordinating ability according to the series hydroxyl> phosphate>sulphate= acetate>nitrate=chloride (Chao and Thomas, 1963) [4]. In case of Mehlich-3, the anions, acetate and nitrate are present in the reagent, which could be participating in the extraction of the water-soluble S fraction and in the replacement of adsorbed SO_4^{2-}. In case of Wolf - Morgan and $CaCl_2$, the presence of acetate anion and chloride anions respectively led to the similar consequences.

Table 5: Correlation coefficients (r) between soil extracted S and plant S content

	Correlations			
	CaCl2-S	AB-DTPA-S	Mehlich-3-S	Modified Morgan-S
Straw S	0.689**	0.792**	0.738**	0.808**
Grain S	0.764**	0.772**	0.885**	0.768**
** - p<0.01.				

Table 6: Summary of the available status of Sulphur extracted by different extractants

Elements		CaCl₂	AB-DTPA	Mehlich-3	Modified Morgan
S	Range	6.09-31.68	6.26-18.39	9.68-375.06	9.66-465.57
	Mean	12.05	11.32	39.02	132.84
	SD	4.96	2.90	26.57	111.09

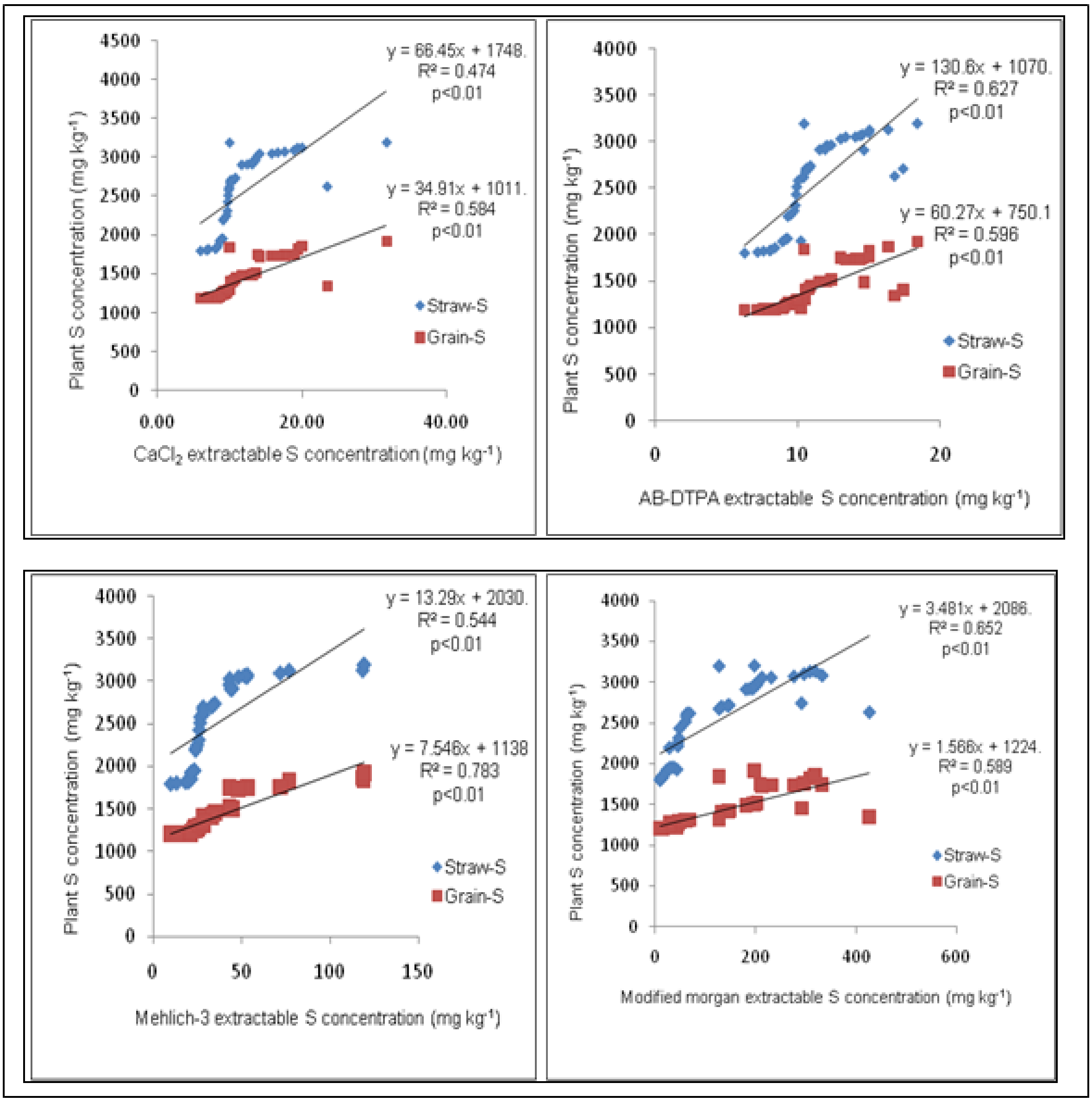

Fig 5: Relationship between available soil S and its content in both rice grain and straw.

Conclusions

This study concludes that long-term rice growing alluvial soils of the region are low in plant available sulphur content. Hence, it can be suggested that including sulphur containing fertilizers in the normal fertilizer schedule is necessary for sustaining the rice yield. This study also confirmed that all forms of the extractable sulphur as extracted by different extractants in the soils were highly and significantly correlated with each other indicating that the extractants could extract sulphur from more or less similar pools from soil. Among the extractants, Mehlich 3 extracted highest amount of sulphur. Regression analysis between extractable concentration of the elements in soil and plant parts revealed that Mehlich 3 was the most suitable extractant for rapid determination of available sulphur for this type of soil. This study, therefore, would provide valuable information for future Researchers and field extension workers working in such areas for determination as well as to optimise sulphur application for quality production and also maintaining sulphur status in deficient soils through external sources.

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